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Fat bloom in chocolate and compound coatings

Although bloom in chocolates and compound coatings has been studied for many decades, the specific mechanisms of fat bloom still remain largely unknown. Furthermore, it is generally considered that the mechanisms for fat bloom formation in chocolate are different than those for compound coatings.

After a brief review of chocolates and compound coatings, we summarize past studies on fat bloom formation in both products. A comparison of the effects of various parameters on bloom formation, either as accelerators or inhibitors, provides insight into the similarities and differences in these phenomena.

Based on this analysis, a global view of the mechanisms of bloom formation in both chocolates and compound coatings is suggested.

Keywords: Bloom, chocolate, compound coatings, emulsifier, cocoa butter.

1 Introduction

The Olmec civilization (1500 BC) was the first to transform the cocoa bean into a form of chocolate. For a long time, the cocoa bean has been used as a foodstuff as well as currency. It also has had both religious and divine aspects. In the eighteen-century, the Europeans found it had some aphrodisiac properties [1]. Although chocolate is no longer reserved for the elite, from a scientific point of view, chocolate still retains some mysteries. For example, bloom in chocolate, perhaps a less poetic notion but just as much exciting, is still somewhat a mystery.

Fat bloom is directly related to the fat in chocolate products, either cocoa butter (CB) or vegetable oils. CB represents not less than 95% of chocolate fat. In the EU, addition of other vegetable fats above this level means the products are named compound coatings. Another type of bloom, sugar bloom, can also occur with humidity problems, but it will not be presented in this review.

A bloomed chocolate is characterized by the loss of the initial gloss of surface, giving rise to a more or less white aspect. Furthermore, the bloom can have different appearances, from a uniform dull gray to a marble aspect, as well as from small individual white points to large white spots on the chocolate. It can be due to many factors, including improper processing conditions, composition, and temperature. One of the problems in characterizing bloom problems is its plurality of shape and also of formation conditions. Moreover, differences between products complicate the scientific analysis. Effectively, the kind of fat and emulsifier, the presence and kind of center on which the chocolate is coated are all parameters that can affect the formation and shape of bloom. However, fat bloom has been studied since the beginning of the last century, with an increase in the knowledge of when and where it occurs. Numerous theories have been proposed to explain bloom formation, but so far none has covered all the multiplicity of bloom or taken into account all of the scientific data. Furthermore, underlying questions remain: Do the different aspects correspond to the same bloom mechanism? And, is the bloom mechanism similar for the different chocolate compositions?

In this review, we intend to establish a state of knowledge about bloom, to clarify and find some hypothetical links between the multiplicities of bloom, and to propose a diagram to explain the formation mechanism of any bloom. The first two parts describe briefly the properties of the different fats, the chocolate ingredients as well as a brief description of the processes for making chocolates and coatings. These sections are written to provide a common vocabulary and knowledge necessary to understand the rest of the review.

After the brief introduction on chocolate ingredients and processing, we present the different types of bloom according to its origin, its physical-chemical properties and the "remedies" used to avoid the bloom as well as their potential actions. At this point, the different theories of bloom formation will be briefly discussed. Finally, we

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will try to give a global explanation of bloom formation in chocolates and coatings, through a critical analysis of all the data.

2 Characteristic of chocolate and compound coatings

A good knowledge of the different constituents of chocolate and compound coatings is important to understand the mechanisms of fat bloom formation.

2.1 Chocolate *versus* compound coatings

Basically, chocolates and compound coatings are comprised of three main components [2].

- Sugar, crystalline sucrose usually, is one of the major constituents of chocolate.
- Cocoa solids correspond to the nonfat part of the cocoa beans. It can be used as powder (cocoa powder contains not less than 20% cocoa butter, or it is label as fat reduced cocoa powder) or more often as chocolate liquor. Chocolate liquor corresponds to the roasted, hulled, ground substance obtained from fermented, dried cocoa beans.
- Until recently, cocoa butter was the only fat (except milk fat) authorized for chocolate in most countries. Due to the 2000/36/EC directive, 5% of other tropical fats (6 different) can be added in Europe. However, in the United States, the use of other vegetable fats is not allowed in chocolate.

The difference between chocolate and compound coatings is based on the cocoa solids. Chocolate must contain not less than 32% total dry cocoa solids, including not less than 18% cocoa butter and not less than 14% of dry nonfat cocoa solids. Compound coating corresponds to product that doesn't match this definition. In most cases, the use of fats other than CB leads to the name compound coating on a product. Other vegetable fats can be used in order to obtain new flavors, to enhance the physico-chemical properties of the product or to reduce production price. Fats used in coatings can be classified according to their compatibility with CB, under three major family names [3–6]:

- Fats that are totally compatible with CB are called, cocoa butter equivalent, CBE.
- Fats that are partially compatible with CB correspond to cocoa butter replacers, CBR.
- Fats that are incompatible with CB correspond to cocoa butter substitutes, CBS.

2.2 Composition and polymorphic behavior of fats

The triacylglycerol (TAG) composition of a fat is one of the most important parameters since it governs the physical properties as well as the polymorphic behavior of the fat. Polymorphism is defined as the ability of a TAG molecule to crystallize in different molecular packing arrangements (polymorph or polymorphic form) corresponding to different unit cell structures, typically characterized by X-ray diffraction spectroscopy. Since *Chapman* [7], fat polymorphs have been delineated in 3 main forms α, β', β and variations within these main types. The main crystal characteristics of the different polymorphs are summarized in Tab. 1. The TAG composition and polymorphic behavior are presented for the most common fats and oils used for confectionery products in the sections below.

Tab. 1. Polymorphic forms as function of the X-ray diffraction characteristics [8].

	Polymorphic form	Unit Cell	X ray diffraction characteristics
Main forms	α	Hexagonal	One short spacing at 4.15 Å
	β'	Orthorhombic	Two strong short spacing at 3.80 and 4.2 Å
	β	Triclinic	Multiple peaks, and one strong short spacing at 4.6 Å

2.2.1 Cocoa butter

Cocoa butter is the main fat used for chocolate. It has a relatively simple TAG composition that is responsible for a very specific yet complex polymorphism.

2.2.1.1 TAG composition

The precise TAG composition of cocoa butter depends on the geographical growth area and the species of cocoa tree [9–11]. Cocoa butter is made up mainly of monounsaturated TAG. The TAG POS, SOS, POP make up more than 75% of the total amount of TAG (S, stearate; O, oleate; P, palmitate). Typical TAG compositions for cocoa butter are summarized in Tab. 2, as function of the geographical growth area.

Tab. 2. Triacylglycerol composition of cocoa butter from different geographical sources [10] †.

	Malaysia	Ivory Coast	Ghana	Ecuador	Dominican Republic	Brazil
	[wt-%]					
PLO	0.4	0.7	1.0	0.5	0.7	0.9
PLP	1.1	1.7	1.8	1.6	1.8	1.7
OOO	0.1	0.4	0.8	0.7	0.6	0.7
POO	11.0	1.8	2.0	2.7	3.8	5.8
PLS	2.6	3.7	3.6	3.1	4.2	3.9
POP	12.6	15.0	14.5	14.1	14.6	13.9
SOO	1.8	2.3	2.8	3.3	4.4	6.7
SLS	1.6	1.7	2.0	1.6	1.8	2.1
POS	46.9	46.3	42.8	45.4	42.8	40.2
PPS	0.7	0.7	0.8	0.8	0.7	0.6
SOS	29.8	24.0	26.3	24.8	22.8	21.7
PSS	0.4	0.5	0.6	0.4	0.5	0.5
SOA	0.9	0.8	1.0	0.8	1.0	0.9
SSS	0.2	0.4	0.2	0.3	0.4	0.6

† P – palmitic; L – linoleic; O – oleic; S – stearic; A – arachidonic.

2.2.1.2 Polymorphism

Cocoa butter TAG can crystallize into 6 different polymorphic forms, usually denoted either by Greek letter or Roman numeral (or both) [12, 13]. The melting points of each polymorph of CB are summarized in Tab. 3. In lipids, the most unstable polymorphs (α) form the fastest but then quickly transform to the more stable forms (βV and βVI). In cocoa butter, the forms I, II and III are very unstable and are quickly transformed into more stable forms. Form βV is a relatively stable form found after appropriate cooling of a melted chocolate with shelf life often more than one year, but this depends on numerous (sometimes unknown) parameters [20]. The most stable form (βVI) cannot be produced directly from the melted chocolate (except by the addition of βVI CB seeds and under very well controlled conditions [21, 22].

Merken and *Vaeck* [23] and *Aronhime* et al. [12] debated the true existence of form VI. Based on DSC studies, they argued that the most stable β form corresponded to a phase differing in composition. Recent results of *Loisel* et al. [20] seemed to confirm the six different polymorphs, by using an apparatus allowing simultaneous DSC and X-ray diffraction recording. However, in several studies using real-time X-ray powder diffractometer, a clear distinction between the 2 β forms could not be made [22, 24]. Cocoa butter with high content of SSS exhibited no clear difference between the X-ray patterns of βV and βVI, whereas cocoa butter with high degree of unsaturation (C18:1 and C18:2) showed clear differences between the two β forms. The X-ray pattern depended not only on the origin of CB, but also on the way they were crystallized. [20, 22, 24].

However, cocoa butter did not correspond to homogenous crystalline phase. *Loisel* et al. demonstrated that two types of crystals were observed simultaneously. The first and main crystal type was composed of monounsaturated TAG; it had similar polymorph than the whole CB's. Whereas the second type, a minority, was constituted of a high content of saturated TAG and a higher concentration of SOS; it showed a different polymorph than CB and a higher melting point. For example in βV CB, the first crystal type had a βV (3L) polymorph and the second had a βV (2L) polymorph.

This segregation occurred during the cooling step as well as during storage (but at a slower rate due to the poor mobility of saturated TAG in monounsaturated TAG).

Tab. 3. Melting point of different polymorphic forms of cocoa butter determined by different authors.

Vaeck [14]	*Duck* [15]	*Wille* and *Lutton* [16]	*Huygherbaert* and *Hendrickx* [17]	*Lovegren* et al. [18]	*Davis* and *Dimick* [19]
		[°C]			
18.0 (γ)	17.0 (γ)	17.3 (I)	14.9–16.1 (I)	13.0 (VI)	13.1 (I)
23.5 (α)	21–24 (α)	23.3 (II)	17.0–23.2 (II)	20.0 (V)	17.1 (II)
28.0 (β'')	28.0 (β'')	25.5 (III)	22.8–27.1 (III)	23.0 (IV)	22.4 (III)
–	33.0 (β')	27.3 (IV)	25.1–27.4 (IV)	25.0 (III)	26.4 (IV)
34.5 (β)	34.4 (β)	33.8 (V)	31.3–33.2 (V)	30.0 (II)	30.7 (V)
		36.3 (VI)	33.8–36.0 (VI)	33.5 (I)	33.8 (VI)

2.2.2 Cocoa butter equivalent

Cocoa butter equivalent (CBE) fats should be totally compatible with cocoa butter. Compatibility in this context corresponds to the ability of the TAG of two distinct fats to crystallize together without forming a eutectic, although some CBE do not show total compatibility with CB. CBE are usually issued from some exotic fats (from the equatorial, tropical and sub-tropical countries) such as illipee, borneo tallow, shea fraction or fractionated salfat [25]. They can also correspond to synthesized oils, like coberine [26]. The total fatty acid composition of different CBE is presented in Tab. 4. In general, CBE have a similar TAG composition and the same polymorphism as CB, which accounts for their general compatibility with CB.

Tab. 4. Total fatty acid composition of some cocoa butter equivalents [4].

Fatty acid	Ivory coast cocoa butter	Illipe (commercial sample)	Shea butter	Sal fat	Coberine
	[wt-%]				
C12	–	–	–	–	–
C14	–	–	–	–	–
C16	26.8	19.9	5.7	7.6	32
C16:1	–	0.1	–	–	–
C18	35.6	43.7	41.0	42.6	28.2
C18:1	33.5	35.7	49.0	37.0	36.1
C18:2	3.2	0.4	4.3	3.5	2.0
C18:3	–	–	–	1.3	–
C20	0.9	–	–	8.0	–
Other	–	–	–	–	1.7

2.2.3 Cocoa butter replacers

Cocoa butter replacers (CBR) fats may be called cocoa butter extenders, or hydrogenated domestic butter, because they do not replace the full amount of cocoa butter. Their compatibility with CB is lower than for CBE but higher than for CBS. Two main sources of CBR are available: either from hydrogenated or/and fractionated palm oil, or from hydrogenated domestic vegetable oil (soybean, cotton seed, *etc*.).

2.2.3.1 TAG composition

CBR are usually issued from palm oil, so the main fatty acid is palmitic acid. Typical compositions of CBR are summarized in Tab. 5. Tab. 6 compares typical TAG compositions of CB, CBE and CBR.

Tab. 5. Total fatty acid composition of palm oil and 3 different non-identified commercial cocoa butter replacers (CBR) [4].

	Palm oil	CBR-A	CBR-B	CBR-C
	[wt-%]			
C14	1.2	1.3	0.8	0.7
C16	44.0	53.5	42.0	40.2
C18	4.7	18.7	22.5	22.3
C18:1	40.0	25.0	31.3	35.0
C18:2	10.0	1.5	2.8	3.2
C18:3	–	Trace	0.6	0.5
C20	–	–	–	–

Tab. 6. Triacylglycerol composition of cocao butter (CB), cocoa butter equivalent (CBE) and cocoa butter replacer (CBR) [4].

	CB	CBE			CBR		
		Coberine	Choclin	CBE-A	A	B	C
	[wt-%]						
POP†	15.0	35.0	45.0	37.0	58.1	73.8	52.3
POS†	46.3	19.0	14.0	17.9	14.8	9.0	18.3
SOS†	24.0	28.0	21.0	40.3	26.8	17.2	26.2
Others	14.7	18.0	20.0	4.8	–	–	–

† P – palmitic; O – oleic; S – stearic.

2.2.3.2 Polymorphism

According to *Timms* [27], the most comprehensive study on the phase behavior of palm oil has been reported by *Persmark*. Palm oil is characterized by three polymorphs, but its fractions have a greater complexity. The highest-melting point fraction, consisting mainly of trisaturated TAG, showed the classical α, β', β polymorphism. The middle-melting point fraction (rich in POP) has subα, α and β'_1 forms, at low temperatures. At 18 °C, the β'_1 is transformed into a β' form that is transformed into the most stable β form when the temperature reaches 30 °C [28, 29]. *Hong Yap* et al. [30] have described the polymorphic stability of palm oil, palm stearin and hydrogenated palm oil. The hydrogenated oil was very stable in its β' form, whereas the palm stearin had a less stable β' form (transforming then into the β form).

Cottonseed, soybean or rapeseed oils are mainly constituted of C18 fatty acids. After partial hydrogenation, these oils have the same polymorphic behavior as CB [31].

2.2.4 Cocoa butter substitutes

2.2.4.1 Composition

Cocoa butter substitutes (CBS), or lauric hard butter, contains trilaurin (C12) as the main TAG [32]. CBS fats come usually from coconut or palm kernel oils [33].

Coconut and palm kernel oil (PKO) are usually hydrogenated or fractionated to increase their hardness and to improve their melting profile. The olein (or liquid) fraction can also be used directly for ice cream coatings, or after a partial hydrogenation. The stearin (or solid) fraction is used in its native form or after full hydrogenation. In this case, the manufactured products have good properties with a melting profile similar to CB [34–36]. CBS replaces the totality of CB in a coating, except for the CB that is present in cocoa powder. Effectively, the compatibility of CBS with CB is very low (below 5%) due to the significant differences in TAG composition. The total fatty acid compositions of coconut oil and PKO are summarized in Tab. 7 and Tab. 8 compares the composition of fully hydrogenated PKO, fractionated PKO and CB.

Tab. 7. Total fatty acid composition of coconut oil and palm kernel oil [37].

	Coconut	PKO
C8:0	7.5	4.8
C10:0	5.7	3.8
C12:0	47.0	48.0
C14:0	18.5	16.5
C16:0	8.7	8.2
C18:0	3.0	2.6
C18:1	7.5	15.5
C18:2	1.7	2.7
C18:3	–	–

2.2.4.2 Polymorphism

PKO and coconut oil have simple polymorphic behavior, with the β'-2 polymorph predominating. The α polymorph occurs only due to rapid cooling and easily transforms to the stable β'-2 [27]. In a study on PKO products (fractionated, hydrogenated, *etc*.), *Rossell* [40] concluded that the lauric fat had a simple polymorphic behavior in which the transformation plays a minor role, confirming the previous studies of *Riiner* [41] (β'-β transition was not mentioned). However, in 1985, *Rossell* found that bloom corresponded to the β'–β transition [42]. The existence of the β'-β transition for hydrogenated PKO and coconut oil was confirmed by *Timms* [43].

Tab. 8. Acyl carbon number profile of different fats [38, 39].

Acyl carbon number	ICCB	FHPKO	FPKO	Milk fat fraction 17S†	Milk fat fraction 30S†	Winter AMF	Summer AMF
	[%]						
C_{26}	–	1.7	1.6	1.2	1.8	0.3	1.2
C_{28}	–	2.3	2.0	1.3	2.3	0.5	1.3
C_{30}	–	1.9	1.8	1.8	2.0	1.1	1.8
C_{32}	–	4.8	4.7	2.3	2.3	2.1	2.3
C_{34}	–	7.5	7.3	6.0	4.2	5.6	6.0
C_{36}	–	26.9	25.8	15.8	7.4	10.8	15.8
C_{38}	–	22.4	22.1	18.3	8.6	13.4	18.3
C_{40}	–	12.7	13.0	11.6	7.2	10.7	11.6
C_{42}	–	8.0	8.4	6.8	5.9	6.6	6.8
C_{44}	–	4.3	4.6	4.9	7.1	6.2	4.9
C_{46}	–	2.5	2.9	4.4	9.7	6.7	4.4
C_{48}	–	2.2	2.4	5.5	12.4	8.7	5.5
C_{50}	18.0	1.2	1.0	8.7	14.3	11.1	8.7
C_{52}	46.6	1.0	1.0	7.6	10.7	10.7	7.6
C_{54}	35.4	0.8	1.3	3.7	4.2	5.6	3.7

† ICCB, Ivory coast cocoa butter; FHPKO, Fractionated hydrogenated palm kernel oil; FPKO, fractionated palm kernel oil; AMF, anhydrous milk fat.

The hydrogenated fractions of CBS do not need to be tempered, because of the direct crystallization into the stable β' crystal. However, they need proper cooling. Rapid cooling to 10–12 °C initiates crystallization, and removes the latent heat of fusion.

2.2.5 Milk fat

Milk fat is usually present in large amount in milk chocolate, but can also be used at lower extent in dark chocolate (usually under 5%) [44–47].

2.2.5.1 Composition

The TAG composition of milk fat is very complex as it contains more than 100 different TAG with a very broad chain length [48]. It is also very variable and depends on the cow species, the feed and often on the season of production. Milk fat can be considered as an association of three largely independent melting fractions, corresponding to the high, middle and low-melting point fractions [27]. Milk fat can be used in different forms, either in its whole form or after fractionation but it may also be hydrogenated or interesterified [44]. The acyl-carbon number of milk fat and some fractions are summarized in Tab. 8.

2.2.5.2 Polymorphism

Due to its complex composition, the most stable form of milk fat corresponds to the β' polymorph. For the high-melting (HMF) and medium-melting fractions (MMF), the stable polymorph can be β'-2 and β'-2 (plus some β'-3), respectively [49, 50].

2.3 Fat mixtures

In many chocolates and coatings, different fats are blended intentionally or not (oil migration from center into the chocolate, for example). The blend of two fats may have very unpredictable effect on the physical properties of the final product. The phase diagram is used to understand the interactions occurring between two (or more) pure compounds. But fats were constituted by several TAG. However it was possible to draw a pseudo phase diagram by considering fat as single compound.

One form of the pseudo phase diagram that is often used to indicate compatibility between confectionery fats is the isosolid diagram. Two fats are mixed at different concentrations and their solid fat content (SFC) is measured by using pulsed nuclear magnetic resonance (NMR) at different temperatures. Lines are drawn between the mixtures having similar SFC, which correspond to isosolid lines. The shape of the isosolid line indicates the fat compatibility. If isosolid lines vary linearly, the fats are totally compatible and miscible, whereas if a depression occurs in the isosolid line, the fats exhibit some incompatibilities. The isosolid diagrams of the most usual fat mixtures observed in the chocolate industry are presented below.

2.3.1 Cocoa butter and milk fat

The isosolid diagrams obtained with milk fat and CB depend greatly on the nature of the milk fat fraction. Fig. 1 shows the isosolid diagrams obtained by mixing CB with anhydrous milk fat (AMF) and high-melting point fraction (HMF). Each blend exhibited a different eutectic. For example, a eutectic occurred with addition of 30% AMF, whereas a eutectic occurred at lower concentration when HMF was added.

2.3.2 Cocoa butter – Cocoa butter equivalent

The isosolid phase diagram of CB and Coberine is shown in Fig. 2. All the isosolid lines were linear, which demonstrates the total compatibility between these two kinds of fat.

2.3.3 Cocoa butter and cocoa butter replacer

The isosolid diagram of CB and nonlauric CBR is presented in Fig. 3. The addition of CBR to CB softened the

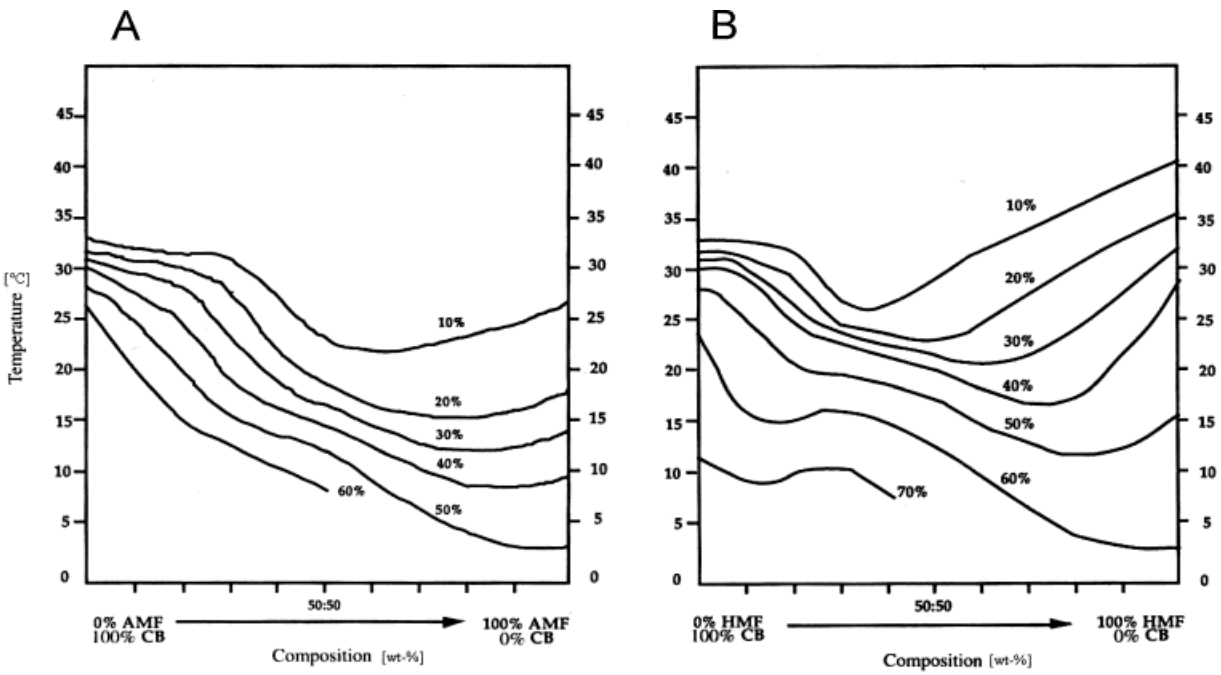

Fig. 1. Isosolid phase diagrams of mixtures of cocoa butter (CB) with (**A**) anhydrous milk fat (AMF) and (**B**), high melting point fraction (HMF) of milk fat [46].

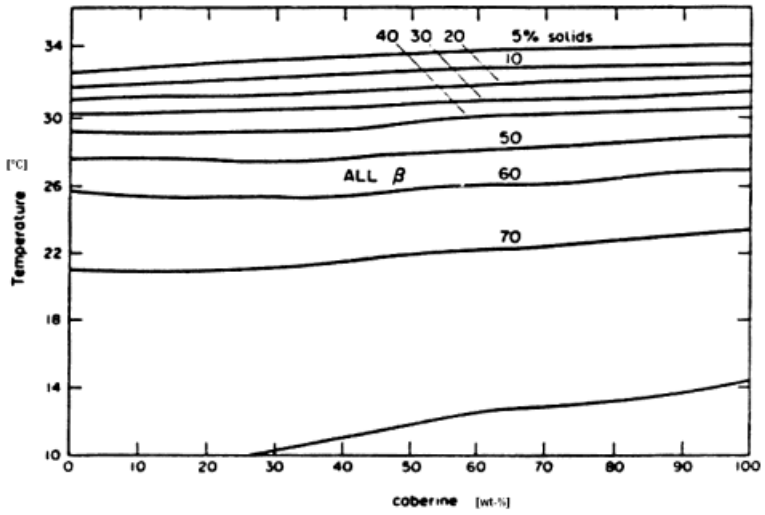

Fig. 2. Isosolid phase diagram of mixtures of cocoa butter and coberine [51].

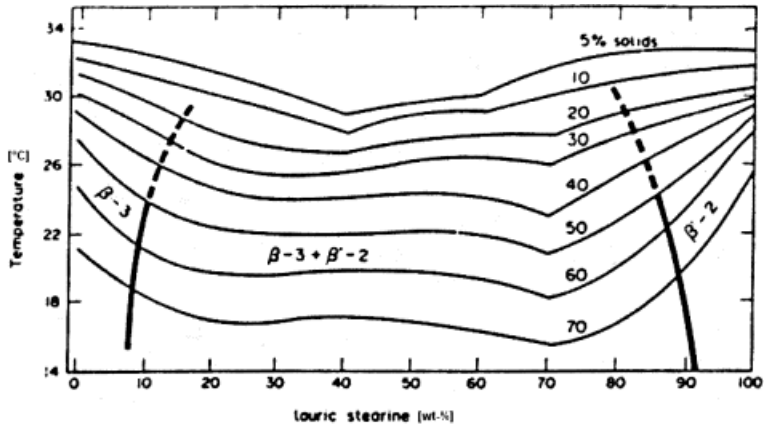

Fig. 3. Isosolid phase diagram of mixtures of cocoa butter and cocoa butter replacer [51].

blend and some eutectic effects were observed. In this case, the two fats exhibit different polymorphism, which usually has a negative effect on the chocolate quality.

2.3.4 Cocoa butter and cocoa butter substitutes

The addition of PKO to CB has a dramatic effect, as seen in the isosolid phase diagram of CB and CBS (PKO) shown Fig. 4. The SFC of CB decreased with addition of as little as a few percent of PKO regardless of the form (hydrogenated, fractionated or both) added. The co-crystallization of short-chain trisaturated TAG of CBS and the long-chain, monounsaturated chain of cocoa butter is very weak. Effectively, the two fats have totally different crystalline forms. CBS crystallizes in the β' polymorph with a double-chain packing, whereas CB forms a βV polymorph with triple-chain packing. The chain packing, also known as chain length structure, corresponds to a repetitive sequence of the acyl chains involved in a unit cell (along the long-chain axis). This difference in crystalline structures is one of the reasons why these two fats are incompatible and it would be better to use degreased cocoa powder to make compound coatings with CBS [52].

2.3.5 Cocoa butter – nut oils

Nut oils are presented in large among in nuts (almond, hazelnut, peanut) and in the fillings (peanut butter, praline). They transfer easily into the chocolate. Fig. 5 shows the isosolid phase diagrams obtained with CB and two nut oils. As the nut oils are liquid at room temperature, no eutectic can be observed when they are blended with solid fat. CB is "simply diluted" in those liquid oils.

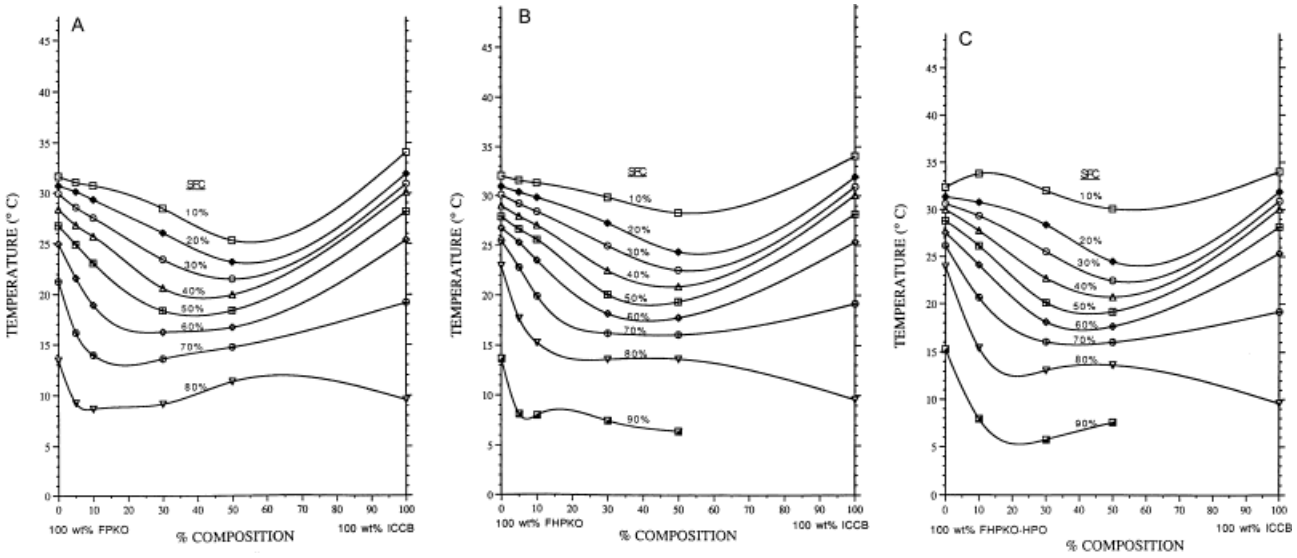

Fig. 4. Isosolid phase diagrams of mixtures of cocoa butter with (**A**) fractionated palm kernel oil (FPKO), (**B**) fractionated hydrogenated palm kernel oil and (**C**) FHPKO with fully hydrogenated palm oil [52].

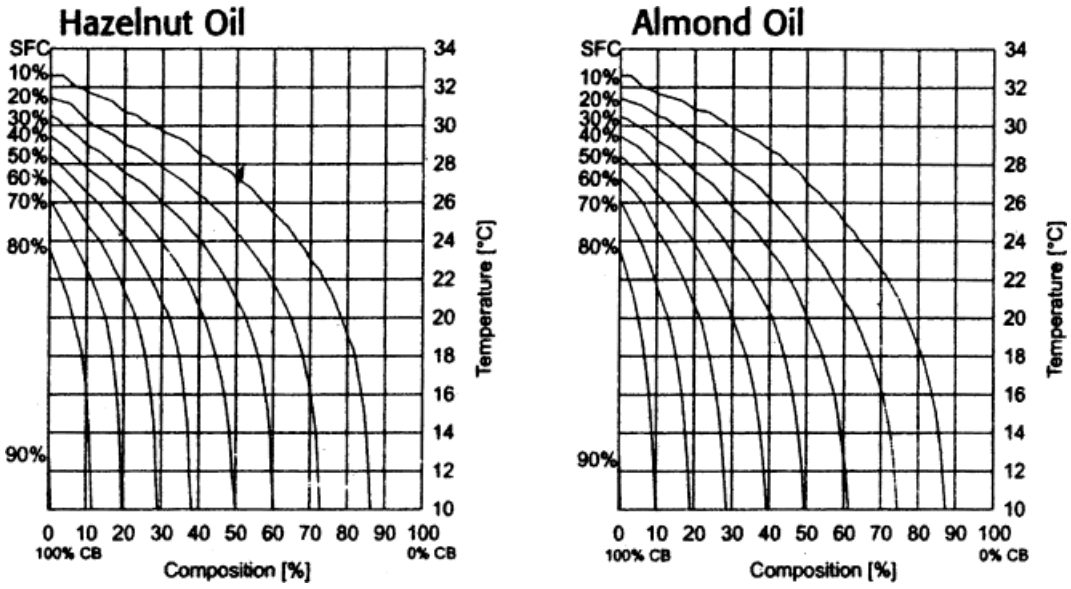

Fig. 5. Isosolid phase diagrams of mixtures of cocoa butter (CB) with nut oils [53].

2.3.6 Cocoa butter substitutes (PKO-based coating) – milk fat fractions

The isosolid phase diagrams of PKO-based coatings and low- and high-melting point milk fat fractions are shown in Figs. 6 and 7, respectively. No eutectic was observed when low-melting point milk fat fraction was added, only a softening effect. The behavior was different with the high-melting point fat fraction, where slight eutectic effects were observed as a function of the solid fat content (at low and medium solid fat content).

2.4 Emulsifiers

Emulsifiers are primarily used to improve the interactions between sugar and fat and thereby reduces the amount of fat needed for a given viscosity. Emulsifiers may also act as bloom inhibitors. They are authorized in chocolate at a level below 1.5% of the total mass; however, a maximal concentration exists for each individual emulsifier (codex alimentarus, standard 147-1985). Soybean lecithin is one of the most common emulsifiers used in chocolates and coatings. However, there are different kinds of emulsifier

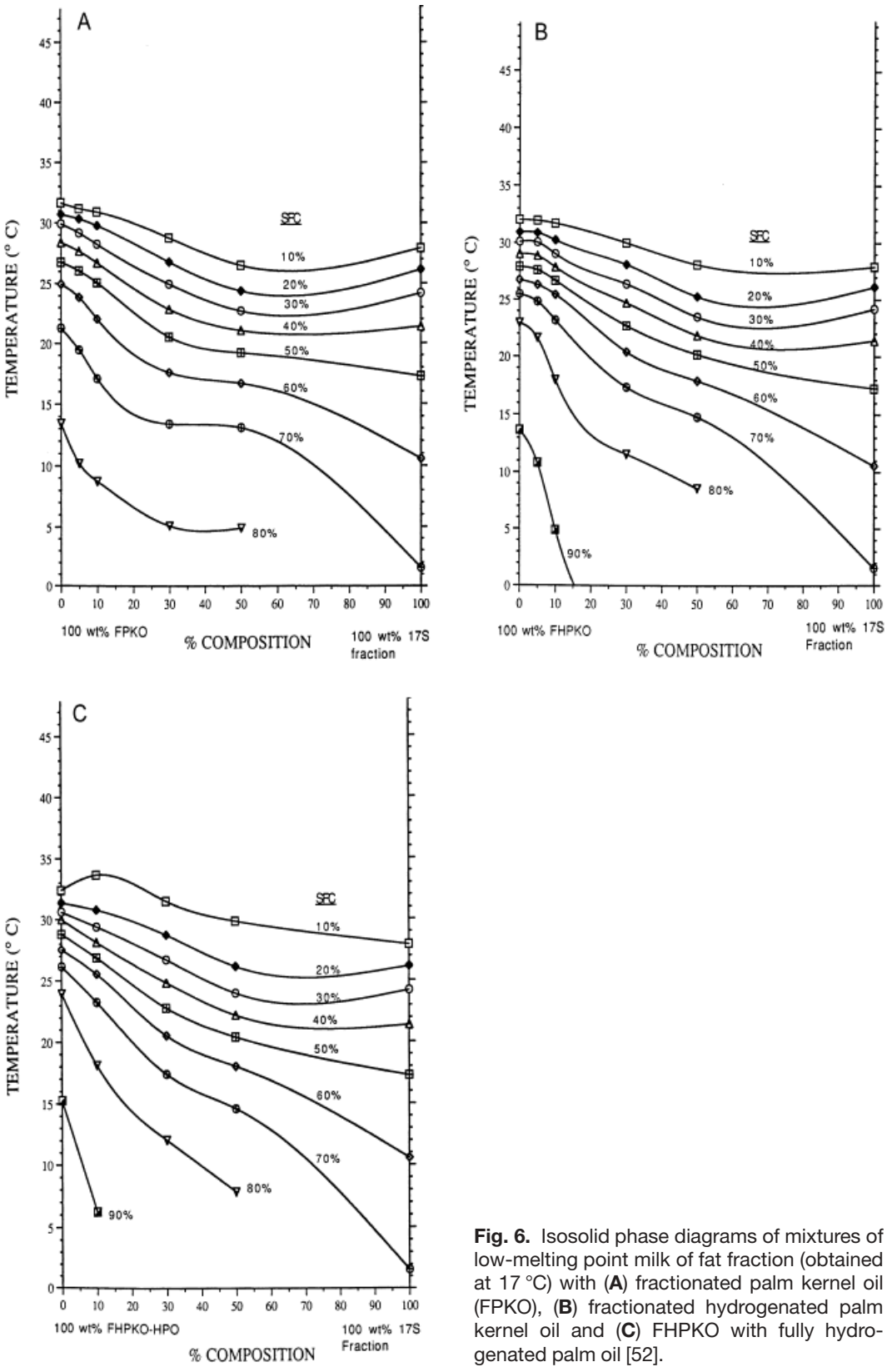

Fig. 6. Isosolid phase diagrams of mixtures of low-melting point milk of fat fraction (obtained at 17 °C) with (**A**) fractionated palm kernel oil (FPKO), (**B**) fractionated hydrogenated palm kernel oil and (**C**) FHPKO with fully hydrogenated palm oil [52].

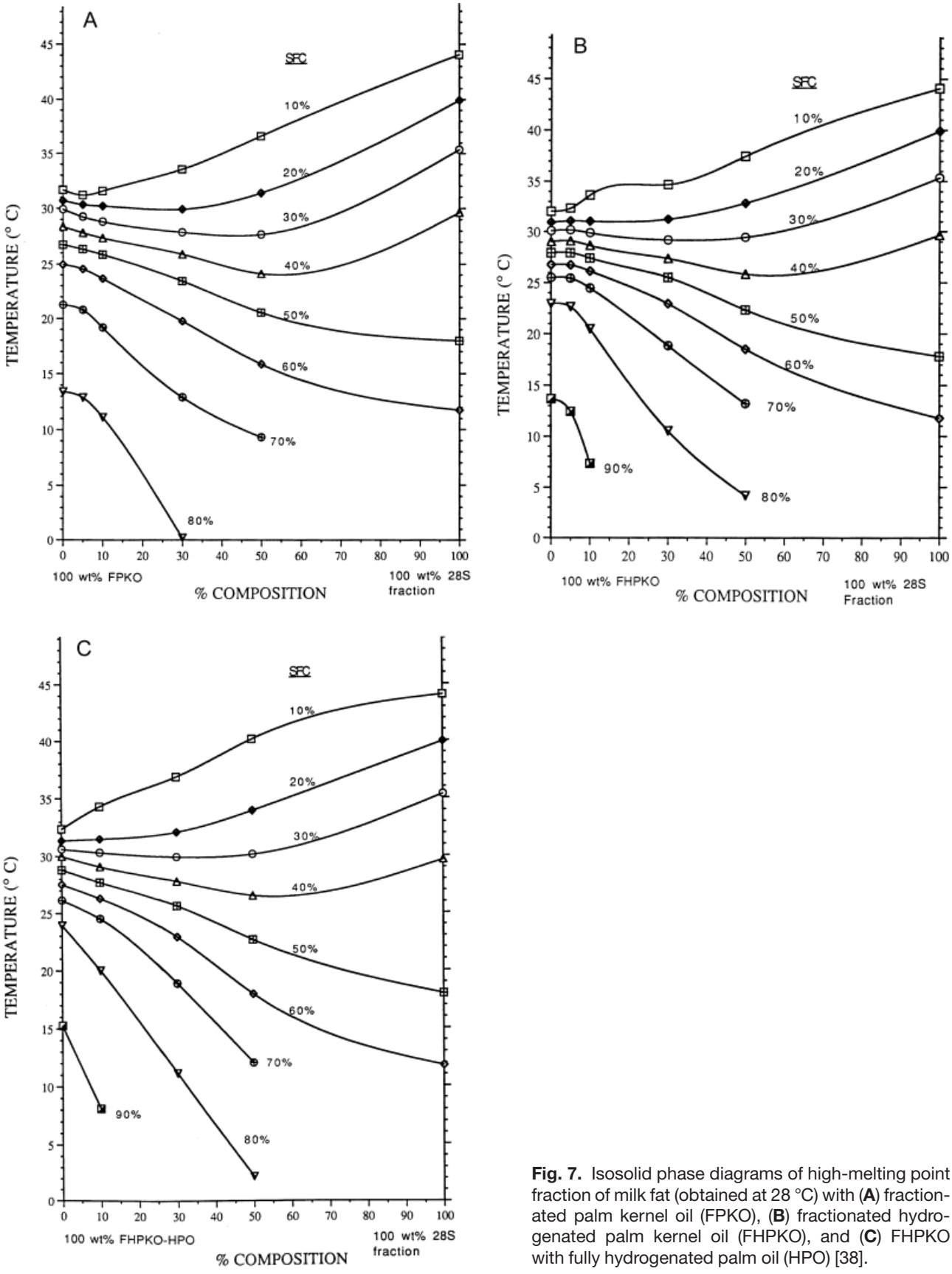

Fig. 7. Isosolid phase diagrams of high-melting point fraction of milk fat (obtained at 28 °C) with (**A**) fractionated palm kernel oil (FPKO), (**B**) fractionated hydrogenated palm kernel oil (FHPKO), and (**C**) FHPKO with fully hydrogenated palm oil (HPO) [38].

that have slightly different effects on chocolates and coatings. The most studied emulsifiers are briefly described [54].

2.4.1 Lecithin

Commercial lecithin is a complex mixture of compounds, containing primarily phosphatidylcholine (PC), phosphatidylethanolamine (PE), and phosphatidylinositol (PI). Free fatty acids (FFA) also represent a major component (usually more than 30%) in lecithin. It is the most common emulsifier in chocolates and is used for its effects on rheology and fat bloom.

2.4.2 Mono- and di-glycerides (MDGS)

MDGS are typically a mixture of monoacylglycerol (MAG), diacylglycerol (DAG) and free glycerol. It also contains a few percent of TAG and FFA. Glycerol monostearate (GMS) is a relatively pure fraction of MAG, usually obtained by distillation. It is sometimes used on coatings, but not in chocolate.

2.4.3 Sugar ester

Sugar esters are made by the esterification of a fatty acid and a sucrose molecule. It has hydrophilic properties (in the case of monoester) and hydrophobic properties (when the esterification number is above two) depending on the position and the number of esterification. It is considered as a fat crystal structure modifier.

Sorbitol esters are a second category of sugar esters of importance in coatings. Sorbitol esters may be either Span and Tweens. Span correspond to a molecule made from sorbitol and a FFA. The most common Span are summarized in Tab. 9. Tweens compounds are ethoxylated derivatives of Span. They are more hydrophilic; however, sorbitan monostearate (SMS), sorbitan tristearate (STS) and polyoxyethylene sorbitan monostearate are the only emulsifiers allowed in foods. STS is sometimes added to compound coatings, in part as a fat bloom inhibitor.

Tab. 9. Some common sorbitol esters.

Name	Acyl chain
Span 20	Monolaurate
Span 40	Monopalmitate
Span 60	Monostearate
Span 65	Tristearate
Span 80	Monooleate
Span 85	Trioleate

2.4.4 Polyglycerol polyricinoleate

Polygylcerol polyricinoleate (PGPR) is one of the most hydrophobic emulsifier and is approved for use in chocolate. It is considered as a rheology controller, primarily because of its effect on chocolate yield value. There have been no studies documenting any effects of PGPR on fat bloom in chocolate.

3 Processing

Although chocolate composition varies slightly depending on the chocolate type, average levels of fat, cocoa solids and sugar are around 30, 20 and 50%, respectively [55, 56]. Flavor and emulsifiers are added at a level below 1%.

Several processing methods exist for making chocolate, but all have 5 basic steps:

– Bulk ingredient mixing.

– Refining. The size of sugar crystals and cocoa solid particles is reduced to obtain the smooth texture of the final product. The chocolate mass is passed through several rollers separated by gaps of decreasing size.

– Conching. Flavor development, moisture decrease and release of volatiles occur during the conching. The paste is continuously agitated to coat the solid particles by the fat phase [57]. Emulsifiers are added to improve the blend and extra fat is added towards the end of the conching step to obtain the desired viscosity.

– Tempering. Chocolate must be tempered to control the polymorphism of cocoa butter [13, 58–60]. The melted chocolate undergoes a temperature cycle to induce the formation of nuclei in βV form (and also to destroy the other unstable forms). The addition of seed is also used to induce the crystallization step. New tempering method used βVI cocoa butter seed. It facilitated greatly this step that is less sensitive to temperature fluctuation, quicker and gives even better final quality [53]. The seed crystals formed during tempering permit the surrounding liquid TAG to crystallize quickly in the right polymorphic form [61, 62]. Effectively, it is more favorable for TAG to attach to a growing crystal face than to find sufficient energy to create new nuclei [63]. When the seed crystal concentration is sufficiently high (0.5 to 2% of total mass), the chocolate can be used for the production of molded or coated products.

– Cooling step. The product is cooled before storage to ensure complete solidification of cocoa butter. Proper temperature control during cooling is critical to growth of seed crystals in tempered chocolate.

4 Causes of bloom

Before discussing the mechanisms of bloom, it is essential to describe and understand all the parameters that can induce or enhance bloom formation. Such a classification (according to the bloom origin) is based on well-known scientific facts and industrial observations. The origins of bloom can be classified according to three main sources: composition, processing and storage conditions. Pictures of bloomed chocolate and compound coatings are presented Fig. 8.

4.1 Composition effects

Two main composition problems tend to induce bloom. The first is when two "incompatible" fats are used in a chocolate or coating. The second composition problem occurs in filled chocolates, where the center is usually rich in oil content.

4.1.1 Use of "incompatible" fats

It is important to differentiate incompatibility of fats due to dilution effects from problems due to eutectic mixing behavior [64]. When two fats are compatible but have different melting points, a dilution effect is observed where the decrease in solid fat content is proportional to the amount of low-melting component added. In contrast, when truly incompatible fats are mixed together, they tend to separate from each other and the solid fat content decreases below that of either individual fat. The concentration at which the two fats separate determines the limits of solubility. Below this concentration, the fats are compatible, but above this concentration they are incompatible and tend to separate. To observe a true incompatibility, both fats must have a certain solid fat content (at the studied temperature). Two such blends can contribute to bloom formation in chocolates and coatings.

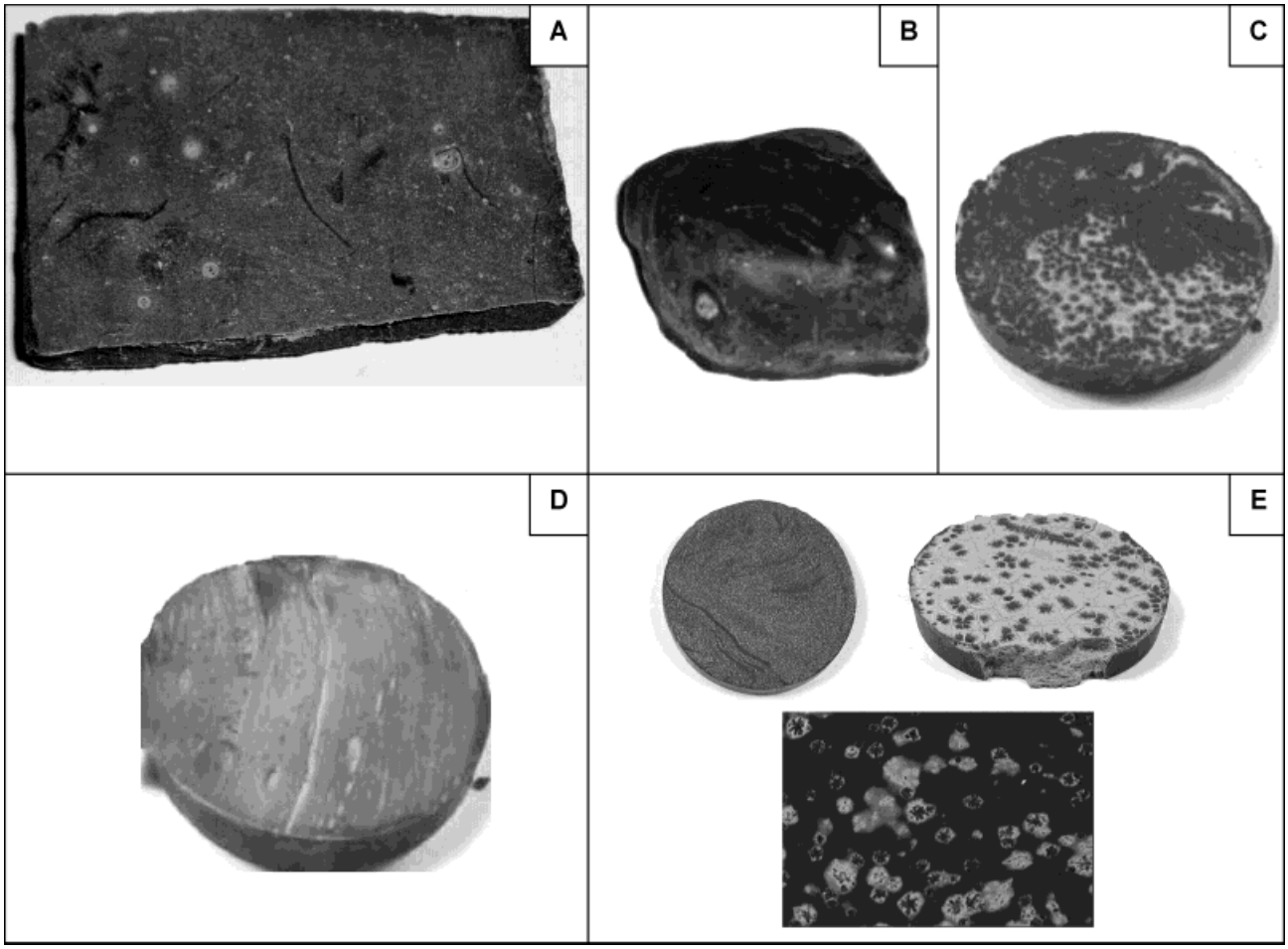

Fig. 8. Pictures of bloomed chocolate due to (**A**) storage, (**B**) fat migration, (**C**) heat hit, (**D**) over-tempering, (**E**) non-tempering.

4.1.1.1 CB with CBS or CBR

4.1.1.1.1 Lauric hard butter (CBS) and cocoa butter

Coatings made with hard lauric butter are very sensitive to the presence of cocoa butter [65, 66]. A eutectic is formed at very low addition levels of CB to CBS. In addition to softening of the mixture, the blend of these two fats promotes bloom formation. A cocoa butter concentration above 4% can result in a bloomed product in a few months and that time drops to less than a week when the concentration is around 10% [6]. If the proportion of CB in CBS is very high, bloom could appear in less than two days [67]. Moreover, in a study comparing FHPKO/CB and FPKO/CB blends, Williams et al. [38] showed that blends with higher SFC had faster bloom formation. The softest compound coatings, so the most affected by the fat incompatibility, were not the most affected by bloom. This effect remains to be explained.

4.1.1.1.2 CBR (hydrogenated domestic vegetable oil) and CB

Fractionated hydrogenated soy and fractionated hydrogenated soy/cotton oils are more tolerant to CB than the lauric hard butter. A eutectic is observed above 15–20% of CB. Moreover, the hydrogenated domestic hard butter was less bloom resistant in comparison to the fractionated hydrogenated domestic hard butter [6].

4.1.1.2 CBS and CBR with milk fat

4.1.1.2.1 Lauric hard butter (CBS) and milk fat

Milk fat and its fractions enhanced the bloom formation when they were added with lauric hard butter products [46, 39, 68]. In this case, harder milk fat fractions led to quicker bloom appearance in coatings made with CBS [69]. This behavior was opposite of that found in chocolate where harder milk fat fractions are known to prevent bloom. However, the isosolid phase diagrams have the same dilution effect for both CBS and CB (below 30% milk fat, as always found in chocolates and coatings).

In a general sense, it appears that the shape of the isosolid phase diagram is not sufficient to predict bloom behavior of a fat mixture. The depression of isosolids lines of CB with addition of milk fat is not associated with bloom, whereas a similar depression of isosolids lines when milk fat is added to CBR leads to bloom formation. Moreover, the absence of a eutectic in the isosolid phase diagram is not automatically associated with the absence of bloom formation as for the case with the milk fat/PKO blend.

4.1.2 Filled chocolate

Filled chocolates are often characterized by a high oil content center. These products are more prone to bloom than plain chocolate. In general, the higher the filling content and the smaller the chocolate part, the greater the possibility of bloom. Similar problems occur when nuts are added to chocolate.

As far back as 1925, *Whymper* and *Bradley* [70] reported that the oil of a biscuit or a center increased the bloom rate. Several researchers have confirmed the acceleration of bloom formation in the case of filled chocolates [71–78]. This type of bloom, in both chocolate and compound coatings, is related to the migration of the most unsaturated TAG from the center to the chocolate surface. Note that the TAG of CB migrate to a lesser extent in the direction of the center.

Kleinert [79] underlined that bloom (for filled products) would automatically appear if the fat phase did not perfectly enrobe the non-fatty solid particles. Thus, conching, and the proper melt viscosity, is the key step to insure continuous coverage of the center.

4.2 Process effects

Two steps in processing, if done incorrectly, may lead to bloom formation, tempering and cooling.

4.2.1 Tempering

In the case of chocolate made with cocoa butter, tempering has long been recognized as one of the most crucial and essential steps in order to achieve a good and stable final product [80]. Since compound coatings made with CBS crystallize directly in the most stable form (β'), they do not need to be tempered prior to cooling. However, some companies choose either to add a nucleating agent (like hardened palm oil) or temper to ensure complete and proper crystallization of lauric-based coatings.

4.2.1.1 Definition

In a review on tempering, *Seguine* [63] gives a definition of "good tempering": "At the end of the tempering, the chocolate must have the largest number of the smallest possible crystals, and those crystals must have the right crystalline form (this means polymorph V)." In this case,

the chocolate crystallizes quickly with maximal contraction (facilitating the mold release), and the final product has a high gloss, with good resistance to fat bloom and fat migration (in the case of the filled chocolate). The principal effect of tempering is to develop a population of seed crystals that are sufficient to avoid heterogeneous crystallization during cooling [21]. To be effective, tempering must provide a seed concentration between 0.1 to 1.15% of cocoa butter mass [81]. *Jewell*, however, reported that larger amounts, 2 to 5% of cocoa butter, of seeds were needed for good temper. This difference may be due to differences in seed size, which affects the number of seed crystals. *Von Drachenfels* et al. [82] specified the importance of crystal size. The smaller and more regular the size of seed crystals, the glossier the chocolate and the greater its bloom resistance. On the other hand, if the crystal size is too large, the crystals tend to re-crystallize during the storage.

4.2.1.2 Under-tempering

Chocolate is considered to be under-tempered when the concentration of nuclei is not large enough to ensure a good crystallization of chocolate mass upon cooling. In this case, the crystallization time increases drastically since nucleation must occur rather than crystal growth. Furthermore, if new seeds are spontaneously generated during cooling, they form in an unstable polymorph, and re-crystallization problems can occur. In such cases, bloom occurs relatively quickly, often in less than two days, and causes a drastic modification of the surface, which appears as large white spots and/or white rings surrounding a black and glossy center.

4.2.1.3 Over-tempering

The term over-tempered is used when the seed concentration in the melted chocolate mass is too high. The seed concentration may increase due to excessive tempering time. In this case, the extent of crystallization in the mold is not sufficient to produce the desired mass contraction. The molded surface is not bright and the unmolded surface turns a gray dull very quickly [80].

4.2.2 Cooling rate

4.2.2.1 Chocolate

For chocolate, the cooling rate is also an important issue in preventing bloom formation. Cooling too fast may induce crystallization of unstable crystal polymorphs as well as formation of hair cracks and pores on the surface. Both effects could promote further bloom. Homogenous heat release, which occurs through the inside as well from the outerlayer, is the best way to avoid any tension on the chocolate surface and consequently, reduce subsequent bloom [79].

4.2.2.2 Compound coating

For coatings, the cooling rate must be quick enough to insure complete crystallization [65, 67]. *Wennermark* and *Carlsson* [83] reviewed the cooling requirements for the crystallization of coatings made with CBR (non-lauric) and CBS (lauric). Parameters like temperature profile, type of cooling tunnel and cooling time must be taken into account. The lower the temperature and the shorter the cooling time, the better the bloom resistance.

4.2.2.3 Filled chocolate

In filled chocolate, the temperature of the center is also very important. The center must be slightly warm before enrobing [79, 84, 85]. Improper temperature during cooling, either too hot or too cold, may cause melting of the chocolate, enhance crack formation, or result in the deposition of moisture (leading to sugar bloom).

4.3 Storage conditions

Even if all the conditions required during processing to avoid bloom are met, fat bloom can still appear at any time and any temperature. Both temperature and temperature fluctuations affect bloom during storage.

4.3.1 Storage temperature

4.3.1.1 Chocolate

For chocolate, three ranges of storage temperature can be distinguished, each with different bloom propensity. The same temperature ranges were also applicable for filled chocolates [71, 86, 87].

4.3.1.1.1 Low temperature (<18 °C)

Cebula and *Ziegleder* [88] reported that storage below 18 °C inhibited storage bloom in chocolate for over one year. The storage of chocolate at low temperature generally minimizes bloom formation; however, even if the storage temperature is low, bloom can occur after more than one year as the chocolate develops a gray dull appearance. In general, the lower the temperature, the lower the bloom risk.

4.3.1.1.2 Medium temperature (18 < T > 30 °C)

In this range of temperature, which is below the melting point of βV crystals, bloom occurs more quickly with an increase in temperature.

4.3.1.1.3 High temperature (>32–34 °C)

When temperature goes sufficiently high, the cocoa butter is partially melted. Upon subsequent cooling, the cocoa butter crystallizes uncontrolled, in unstable polymorphic forms. This is a similar cause for bloom as in under- or untempered chocolate: low seed concentration and unstable polymorph. Thus, bloom will occur very quickly after crystallization and the chocolate will exhibit large white spots.

4.3.1.2 Compound coatings

For compound coatings, the effect of temperature storage is more confusing and less documented. It has been suggested that storage temperatures slightly lower than room temperature (about 18 °C) promotes the most rapid bloom formation in compound coatings. Storage temperatures either higher or lower give better bloom stability. However, no published research documents the effects of different storage temperature on bloom in compound coatings.

4.3.2 Temperature fluctuations

Temperature fluctuations are also important in bloom stability.

4.3.2.1 Chocolate

Temperature fluctuations decrease the bloom induction time and increase bloom rate. In chocolate, even small temperature variations increase the rate of bloom formation. *Hettich* [80] observed a difference in the bloom stability between chocolate stored at 24 °C or at 24 ± 1 °C. However, it is difficult to know which is the prevalent factor inducing bloom, the temperature or its fluctuation. Either way, the chocolate develops a more or less intense gray dull appearance.

Researchers often use temperature cycling to accelerate the rate of bloom formation. The chocolate is submitted to high and low temperature plateaus over a variable time. The time-temperature parameters vary for different researchers. Low temperatures have varied from 15 to 21 °C and high temperatures from 25 to 32–38 °C. The residence times at these temperatures varied between 6 and 24 h. They can be equal for the high and low temperature, or they can differ [87, 89–102].

The time-temperature parameters are generally determined empirically except for the highest temperature. In general, the high temperatures must be under 32 °C to avoid misinterpretation of results due to melting effects. No published research has attempted to define the effects of each parameter and thus, chocolate bloom tests are still not standardized.

4.3.2.2 Compound coatings

Noorden [66] suggested that compound coatings are less sensitive to cycled temperatures than chocolate and such study would require more time. The general perception of the industry is that cycling temperatures tends to promote re-tempering in compound coatings and therefore, most stability studies on coatings are done without controlling temperature fluctuations.

5 Characterization of bloom

Fat bloom can be characterized according to its shape or crystal morphology, composition and polymorphism. In this section, bloom is characterized according to its crystal morphology, composition, polymorphic form of bloom and the porosity of the chocolate.

5.1 Crystal morphology

5.1.1 Under-tempered chocolate

Fat bloom appears very quickly (less than 24 h) when chocolate is under-tempered. It loses its brightness and uniformity, and large white spots develop on its surface [103, 67]. This process corresponds to the formation of large fat crystals separated by crevices that scatter the incident light [104]. Similar shape is observed when the chocolate has been partially or totally melted during its storage.

5.1.2 Bloom during storage

In the case of chocolate, *Whymper* and *Bradley* [70] showed that bloom consisted of numerous small fat crystals growing on the chocolate surface. In 1972, *Jewell* proved, using electron microscopy, that these crystals were 2 to 10 μm long by 0.5 to 2 μm wide by 10 to 50 nm thick [105]. The bloom was not only a surface phenom-

enon, but it was also found in the whole chocolate mass. The inside crystals had a more irregular shape with a size from 1 to 5 μm.

No published research has focused on the shape of bloom on coatings made with pure CBS. However, this bloom also correspond to pure fat crystal growing on the surface.

5.1.3 Bloom due to temperature cycling

Recently, *Hodge* and *Rousseau* [106] used atomic force microscopy (AFM) to study bloom formation at the surface of milk chocolate that was exposed to temperature cycling. The chocolate was cycled between 20 °C and either 32, 33 or 34 °C over a period of 24 h. They showed that the length scale of roughness at the surface increased during cycling, but noted that this roughening did not necessarily correlate with an increase in visual bloom.

5.1.4 Bloom due to incompatible fats

Bloom occurring in coatings made with hydrogenated PKO and 10% CB is similar to that occurring with 100% hydrogenated PKO. This bloom looks like sharp thin sheet crystals [107, 108]. More recently, however, *Arishima* and *Mc Brayer* [109] published images of bloom due to incompatible fats (CBR and CB) where the two fats were segregating and crystallized as a single fat at the surface. He reported similar behavior with CBS mixed with CB (when the CBS concentration was above the eutectic point).

5.2 Bloom composition

Numerous studies have attempted to describe the physical parameters of bloom crystals. However, only a few studies have precisely analyzed the TAG composition of fat bloom on either chocolate or compound coatings.

5.2.1 Under-tempered chocolate

Since *Whymper* and *Bradley* [70], it is commonly accepted that the white powder formed on the surface of under- or untempered chocolate corresponds to fat crystals. Recently, this idea has been contested by *Lonchampt* and *Hartel* [110, 111]. After DSC analysis and polarized microscopic observations of such bloom, they concluded that the whitish powder was essentially cocoa powder and sugar crystals, but not fat. Moreover, the cocoa powder had a higher concentration in the bloom than in plain unbloomed chocolate.

5.2.2 Plain and filled chocolate

According to *Chaveron* et al. [77], bloom composition of filled chocolate did not differ from that of plain chocolate. *Cerbulis* et al. [112] also found that the type of center did not have an effect on the fatty acid composition of bloom, but it affected the bloom rate only.

5.2.2.1 Physical properties

5.2.2.1.1 Melting point

According to *Whymper* and *Bradley* [70], the fat bloom crystals have a higher melting point than the well-tempered chocolate (from 1 to 4 °C higher). *Sachsse* and *Rosenstein* [84] found that the melting point of bloom on well-tempered chocolate was 34 °C, whereas normal chocolate melted at 30 °C. *Whymper* and *Bradley* explained the higher melting point as a result of the separation and further crystallization of a higher-melting fraction of cocoa butter. However, the increase in melting point could also be the result of polymorphic transformation to the most stable β form, a progress that is generally accepted today since all studies have correlated bloom with the βVI polymorph.

5.2.2.1.2 Iodine value

In 1950, *Neville* et al. [113] determined the iodine value (IV) of bloom crystals. They found a difference of 5 in IV between the standard chocolate and the bloom surface, indicating that the bloom had a higher content of saturated TAG than the standard chocolate. This result corroborates the previous studies on the melting point. The same observations were found with filled chocolate [112].

5.2.2.2 TAG and FA composition

Cerbulis et al. [112] determined the fatty acid composition of bloom occurring in different filled chocolates, using an ultraviolet spectrophotometric method (for the linolenic acid). In fat bloom, the concentration of linoleic acid (between 0 and 2.3%) and linolenic acid (between 0.5 and 1.3%) decreased, whereas the concentration of saturated fatty acids increased (from 60% for non-bloomed chocolate to 62% for bloomed).

Steiner and *Bonar* [114] determined the composition of three monounsaturated TAG in bloom with reverse phase paper chromatography that did not allow accurate quantification. The comparison was based only on visual intensity variations of the strips. However, the POP concentra-

tion was found to be much lower in bloom than in the normal chocolate.

Chaveron et al. [77] studied the bloom of a plain and two filled chocolates. The FA analysis, measured by gas chromatography showed a slight increase in C16:0 and C18:1 concentrations and a decrease of C18:0. Different hazelnut oil contents of the centers did not influence the bloom composition. *Adenier* et al. [115] confirmed the *Chaveron* studies, where the composition was very similar between bloom and the initial chocolate.

According to *Loisel* [116], Sato studied the composition of fat bloom on chocolate as a function of the storage temperature. The bloom occurring below 13 °C had a higher POP than POS concentration. The inverse was observed when chocolate was stored above 13 °C (POS was at a higher concentration than POP).

Ziegleder et al. [117] found some differences in bloom composition between plain and filled chocolates. They studied seven different plain chocolates and twenty-two other chocolates with different kinds of centers and found that the filled chocolates had a higher OOO concentration in bloom. However, *Loisel* [116] contested this observation based on lipid mixing rules. According to the phase diagram of SOS and OOO, these two TAG have a very low miscibility at 20 °C, and OOO is liquid under 0 °C [118, 119]. Thus, *Loisel* concluded that the analyzed blooms from *Ziegleder* et al. were contaminated by the underlayer of plain chocolate.

It is difficult to compare each study, because some are expressed in FA concentration, whereas others analyze for TAG, and the results are often contradictory. Either an increase [114, 116] or a decrease [77, 115] in POP was observed, and in some cases a very slight composition difference between bloom and initial chocolate. However, most studies agree that the center has no influence on the bloom composition.

Based on the results available in the published literature, it is difficult to conclude anything about the bloom composition. However, if there is indeed a difference in chemical composition between bloomed and intact chocolate, the differences are very small.

5.2.3 Compound coatings

The bloom of compound coatings made with hydrogenated PKO showed a 10% increase of C12 concentration as well as the C36 TAG concentration. Thus, trilaurin is one of the main TAG of bloom crystals in lauric coatings [6, 108].

When 10% of CB was added to the hydrogenated PKO, the bloom also had higher C12:0 (only 3%), but also higher C16:0, C18:0 and C18:1 concentrations, suggesting that the TAG in CB were also incorporated in the bloom crystals [107]. Similarly, in the case of coatings made with hydrogenated coconut oil and CB, *Traitler* and *Dieffenbacher* [25] found an increase of SOS (coming from the CB) in bloom, indicating a migration of CB to the surface.

In the case of CBR (from soybean or a blend of soybean and cottonseed oils), the fatty acid concentrations of the bloom and the plain chocolate had quite similar values [6].

5.3 Polymorphic form

5.3.1 Chocolate

The polymorph found in chocolate and chocolate bloom depends essentially on the tempering state.

5.3.1.1 Under- or untempered chocolate

The lack of seed that characterizes under-tempered chocolate produces an uncontrolled crystallization of chocolate. After cooling, unstable crystals (β'IV) transform quickly to more stable βV or βVI crystals [120].

5.3.1.2 Well-tempered chocolate

In all studies on well-tempered chocolate, the bloom is found in βVI form. In other words, formation of bloom during storage is always accompanied with a polymorphic transition of cocoa butter from the βV to βVI form. However, the converse of this is not true. That is, chocolate can have a polymorphic transition between the βV and βVI, without the appearance of visual bloom [86, 100]. What remains unclear is why, and in what situations, the polymorphic transition does not lead to visual bloom.

5.3.2 Compound coatings

The polymorphism of bloom found in compound coatings depends on the nature and amount of additional fats. However, inconsistent and sometimes contradictory results can be found in the literature.

According to *Noorden* [66], bloom in coatings made with CBS (lauric hard butter, like PKO) was in the β form, whereas *Timms* [27] found a β' form. *Williams* et al. and *Ransom-Painter* et al. [38, 39] studied the effects of milk fat fractions and cocoa butter on bloom in lauric-based coatings. Both milk fat and CB were found to promote

bloom formation in these coatings, but no evidence for bloom being in the β polymorph was obtained. However, in these studies, the polymorphic form of the bloom crystals themselves was not determined, only that of the mixture of fats. However, *Schmelzer* and *Hartel* [69] showed that the addition of 15% of very high melting fraction of milk fat to palm kernel oil permitted the transition from β' to β form of the fat, after 3 months of storage. No polymorphic transition was observed below 15%.

Liang and *Hartel* [121] could perhaps reconcile these studies. By differentiating the bloom from the whole piece (bloom carefully removed from surface), they were able to observe the β form in the bloom scrapings while the bulk coating was still in the β' form.

In the case of coatings made with CBR, *Paulicka* [122] found a transition from β' to β. In this study, the fat was derived from domestic oils by solvent fractionation. The transition associated with bloom was faster when some CB was added.

Compound coating bloom has not always been correlated to a polymorphic transition of the fat, as is the case with cocoa butter. However, recent studies clearly document that a polymorphic transformation is associated with onset of bloom in PKO-based compound coatings. Further studies on bloom in compound coatings are needed to verify that the onset of bloom is always accompanied by the appearance of the β polymorph.

5.4 Porosity

In many publications, bloom in chocolate is often described as a process involving the migration by capillary action of a liquid fat to the surface [79]. *Loisel* et al. [81] considered the chocolate as a porous material and were able to determine, by mercury porosimetry, the porosity volume of well-tempered dark chocolate (βV), under-tempered (β'V) and over-tempered (mixture of βV and βVI) chocolates. The bubble air volume due to the process was determined with X-ray radiography to be less than 0.1% of the sample volume. The porosity of normal chocolate was about 1% of the total volume and this increased to 2% for the under-tempered chocolate and 4% for the over-tempered chocolate. These results did not allow determination of the precise pore diameter, but suggested that the chocolate does not have open and interconnected pores with mean diameter larger than 0.4 μm at the surface. Moreover, it seems that the pores are filled by the liquid fraction of CB at room temperature. As a result, it is better to talk about empty cavities rather than pores. The presence of mercury at the sample center is not very clear. Mercury was found at the center when a pressure of 180 MPa was used, but not at 80 MPa. The authors explained this by the collapse of structure due to the high pressure used and the low penetration level as the result of the presence of liquid fraction filling the capillaries. So the low level of mercury penetration, as well as the absence of mercury at the center of the chocolate, suggests a poorly connected capillary network. Furthermore, the authors reported that thin dark chocolate layers were totally impervious to gas (at 1 MPa) and no trace of liquid fraction was observed on the surface. Despite these interesting results, many questions remain about the capillary network of chocolate.

Recently, *Khan* et al. [123] highlighted the presence of pores at the surface of milk chocolate by scanning the surface with an atomic force microscope. They estimated the concentration of pores to be thousands/cm^2, with pores of 1 to 2.5 μm of depth randomly distributed on the surface.

6 Bloom inhibition – factors and effects

After having characterized bloom, it is essential to discuss the various factors that can inhibit bloom. Both compositional factors and processing methods, the two major factors that can delay bloom, are discussed.

6.1 Composition factors

Four basic ingredients can provide bloom resistance in chocolates and coatings. These are the main fat composition, additional fat, emulsifier and special compounds.

6.1.1 Composition of main fat

6.1.1.1 Cocoa butter/chocolate

In a general manner, the higher the solid fat content and the lower the liquid fraction, the more resistant a chocolate is to bloom. However, due to organoleptic concerns, it is only possible to increase the melting point of chocolate by only 1 °C [109]. Different ways have been used to increase the solid fat content.

The use of a stearine (high-melting) fraction of CB (after its fractionation) has been found to reduce bloom in chocolate [124]. This fraction has a higher content of SOS (more than 92%), 3% of SSS, and a very low concentration of unsaturated TAG. Added at 20% level, it caused an increase in the heat resistance of chocolate. Similar results were found with filled chocolates [124]. *Wennermark* [125] showed that a high SOS concentration

improved the tempering step, particularly for low-melting point CB. Similar results were obtained with CB removed from its liquid fraction.

Another method used to decrease bloom was to add specific TAG to chocolate. SOS and POP or asymmetrical TAG like SSO or PPO were reported to impede the βV to βVI transition, and consequently inhibited bloom [109, 126].

6.1.1.2 Vegetable fats/compound coatings

Use of specific fractions of vegetable fats (more homogenous) increased bloom resistance in compound coatings in a similar way as with CB in chocolates. A 10% increase of trilaurin content of lauric hard butter (CBS) decreased the induction time of bloom, whereas a 10% addition of dilaurinmonocaprin delayed bloom [107]. For *Noorden* [66], the more fractionated the lauric butter and the lower the concentration of long-chain saturated fatty acids, the smaller the risk of bloom.

Williams et al. and *Ransom-Painter* et al. [39, 52] found that compound coatings made with fractionated PKO (FPKO) were more resistant to blooming than those made with fractionated hydrogenated PKO (FHPKO). This may be related to the solid fat content of the two fats, since in these studies, bloom rate was inversely correlated to the solid fat content of the fat at 25 °C. That is, coatings made from fats that had lower solid fat content seemed to be more resistant to bloom formation.

6.1.2 Milk fat

Milk fat has long been known to have anti-bloom effect when blended with CB in chocolates. However, it is also known to enhance bloom when used with compound coatings, as previously reported.

6.1.2.1 Anti-bloom effect in chocolate

Several papers have reviewed the anti-bloom effect of milk fat [46, 47]. However, the number of publications relating to this effect is quite numerous. Over the years, research has attempted to understand the anti-bloom properties of milk fat and to improve on them by using modified or specific milk fat fractions. The effects are detailed as function of the milk fat kind.

6.1.2.1.1 Hydrogenated milk fat

In 1925, *Whymper* and *Bradley* were one of the first to describe the anti-bloom effect of hydrogenated fat. In the 50's, industrial experience showed that bloom was inhibited by addition of milk fat and this effect was improved by using the high-melting point TAG of milk fat [127]. At that time, use of milk fat fractions were not economically viable, so research focused on use of hydrogenated fat. *Campbell* et al. [128] also investigated the effects of hydrogenated milk fat. Dark chocolate made with addition of 2.5% hydrogenated milk fat was four times more bloom resistant than chocolate made with non-hydrogenated milk fat. Furthermore, fully-hydrogenated fat was more effective than partially-hydrogenated fat [93]. However, the amount of fully-hydrogenated fat was lower in order to avoid incompatible fat problems. *Hendrickx* et al. [129] mentioned, in a study focusing on texture, that substitution of cocoa butter with hydrogenated milk fat delayed or eliminated fat bloom.

6.1.2.1.2 Milk fat fractions

Jebson (1974) showed that incorporation of 3% hard milk fat fraction protected chocolate against bloom two times more than addition of unmodified milk fat. In 1994, *Lohman* and *Hartel* [101] compared 6 different milk fat fractions with whole milk fat. The higher the melting point, the longer the bloom delay. Furthermore, the two lowest-melting milk fat fractions, obtained by solvent crystallization at 0 and 5 °C, enhanced bloom in comparison to regular chocolate. *Dimick* et al. [130] also reported the effect of different milk fat fractions on milk chocolate and confirmed previous results. The percentage of substitution, either 12.2 or 40% of total fat, was higher than with dark chocolate. Chocolate made with the hard milk fat fraction had the highest bloom stability and the higher the percentage of milk fat added, the more stable the chocolate. On the other hand, chocolate made with the lowest-melting milk fat fraction bloomed whatever its concentration.

6.1.2.2 Mechanisms

The effects of milk fat on bloom in chocolates are described in terms of the final physical characteristics of chocolate, the rate of crystallization and the final chocolate polymorphism.

6.1.2.2.1 Physical characteristics of chocolate

The effect of milk fat on the solid fat content (SFC) of chocolate may vary greatly with fraction type and added amount.

When 6.4% (wt/wt) of milk fat fractions having melting points of 51.5, 50.4, and 45.4 °C were added to CB, the mixture had a higher SFC than CB alone. However, SFC of the mixture decreased when the melting point of the

milk fat fraction was below 41.0 °C. The hardness of chocolate with 2% addition of the same milk fat fractions had similar variations as the SFC behavior. Chocolate was harder when made with the fractions having a melting point above 41.0 °C and was softer with milk fat fraction below 41.0 °C melting point [101].

Timms and *Parekh* [131] reviewed the different properties of chocolate, particularly SFC, after the addition of different amounts of milk fat products, including whole milk fat, hydrogenated, fractionated or interesterificated milk fat. The effect of milk fat fraction was dependent on temperature of the chocolate. Below 32 °C, SFC decreased when high-melting point milk fat fraction was added and the decrease of SFC was proportional to the amount added. However, the differences in SFC were quite small between the low-melting point milk fat fractions. Above 32 °C, the SFC of chocolate with added high-melting milk fat fraction increased as compared to pure chocolate. *Jewell* and *Bradford* found similar results [132].

In summary, the addition of a large amount (>10%) of milk fat decreased the hardness of chocolate, but even with a softened texture, this chocolate was more bloom resistant than "normal" chocolate [130].

6.1.2.2.2 Effects on crystallization

Several studies have focused on the effects of milk fat on crystallization characteristics of cocoa butter. Addition of milk fat decreased the rate of bloom formation, crystal size, crystallization rate and also polymorphic transition between unstable and more stable polymorphs [7, 46, 101, 104]. However, the effects were dependent on the milk fat used [133]. Furthermore, *Tietz* and *Hartel* [102] highlighted the effects of minor components (polar lipids) in milk fat on crystallization of CB. They showed that the effect of milk fat on bloom formation could be correlated to its content of minor component (FFA, DG, MG), and that these components had a significant effect on crystal shape.

6.1.2.2.3 Effect on the polymorphism

Cebula and *Ziegleder* [88] reported that dark chocolate with 2 or 5% addition of milk fat did not bloom for more than one year at 23 °C and it remained in the βV polymorph.

Bricknell and *Hartel* [100] found that high-melting point milk fat fraction delayed the βV to βVI transition, but after this delay, the transition rate was quite similar to the control. Chocolate made with the middle-melting point milk fat fraction reduced the transition extent but didn't delay it, whereas no effect was found with the low-melting point fraction.

These results suggest that the mechanism of bloom inhibition of milk fat in chocolate is related to the inhibition of the polymorphic transition of cocoa butter. However, further research is needed to document this effect.

6.1.3 Emulsifiers and other minor lipids

Emulsifiers facilitate the interactions between sugar and fat through adsorption on the sugar crystal surface. The addition of emulsifier decreases chocolate viscosity and may also affect CB crystallization and bloom.

6.1.3.1 Anti-bloom effect

6.1.3.1.1 Chocolate

Easton et al. [89] described the effects of 27 emulsifiers (from lecithin, span, tween to other emulsifiers) on bloom in chocolate. The best bloom inhibition was found with span 60 and tween 60 (poly-oxyethylene sorbitan monostearate) used at 1% level. *Du Ross* and *Knightly* [92] confirmed the action of sorbitan monostearate and polysorbate 60 on bloom. They noted that the emulsifier was more effective when it was intimately dispersed in chocolate and they proposed to add it prior to conching. *Weyland* [134] studied the synergetic effect of lecithin with different emulsifiers, as summarized in Tab. 10. When used individually, sorbitan tristearate and polyglycerol ester were the most effective molecules to improve the initial gloss as well as to keep this gloss after 30 days of cycling between 20 and 30 °C. However, neither of these emulsifiers is allowed for use in chocolates.

6.1.3.1.2 Compound coatings

Anti-bloom effects also were found with sorbitan tristearate, lactic esters of monoglycerides on compound coatings made with fully hydrogenated and fractionated lauric hard butter (CBS) as well for domestic hard butters (CBR) [6, 135, 136]. However, no effect was found with sorbitan monostearate, MDG and MG. Some results are summarized in Tab. 10.

Moreover, numerous anti-bloom patents using emulsifiers are published regularly. Mono- and di-glyceride, monoglycosyl diglyceride, and sucrose fatty acid esters have all been proposed as bloom inhibitors for compound coatings [137–146].

Tab. 10. Effects of emulsifiers on the improvement of bloom resistance in comparison to chocolate or coating made without emulsifier[†].

Fat	DMG	MDG	SMS	STS	STS+lactic ester	PGE	LMD	DATEM	PMD
CB + lecithin [134]		−	−	=		=	−	−−	−
Hydrogenated PKO [135]	+−	=		+	+				
Fractionated PKO [135]	−	=		+	+				
Hydrogenated palm – soybean oils [135]	=	=		++	++				

[†] – bloom development, + bloom delay, = similar than the reference; DMG, distilled monoglycerides; MDG, Mono- and di-glycerides; SMS, sorbitan monostearate; STS, sorbitan tristearate; PGE, polyglycerol esters; LMD, lactic esters of mono and diglycerides; DATEM, diacetyl tartic acid esters of monoglycerides; PMD, sodium salt of phosphated mono/diglycerides.

Minor components of fat should be also discussed. In a recent study, *Tietz* and *Hartel* [102] reported an antagonistic effect of minor components on bloom as function of their concentration. Use of fat having no minor component or a double concentration increased bloom.

6.1.3.2 Potential mechanisms

Emulsifiers affect sugar coating, fat crystallization, crystal growth, crystal polymorphism, and oil migration [147], but have only a slight effect on the final properties of the product (melting point and SFC) [135]. They can inhibit bloom either due to action during the crystallization step or during storage. Most research has focused on the effects of emulsifiers on crystallization.

6.1.3.2.1 Interaction between emulsifiers and sugar or fat crystals

According to *Johansson* and *Bergenstahl* [148, 149] and *Dedinaite* et al. [150], most emulsifiers (phospholipid, sorbitans, mono and diglyceride, and oleylpalmitoylphosphatidylethanolamine) were preferentially adsorbed on sugar crystals rather than fat crystals. A monolayer of emulsifier was adsorbed on fat crystals, whereas several layers were adsorbed on sugar crystals and thus, fat crystals became more polar and sugar crystals became more apolar and less sharp. These studies suggest that the mechanism of emulsifiers on bloom inhibition is perhaps more complicated than it seems and may be related to the interactions between fat and sugar. However, several studies have reported an inhibition of the βV–βVI transition when emulsifiers were added to fat bulk without sugar [151, 152].

6.1.3.2.2 Effect on crystallization

At low water content, emulsifiers have been found to affect crystallization induction time, seed composition, crystal growth rate, and polymorphic transition (*via* melting curve). However, the data are incomplete and the different parameters have not been studied to the same extent for each emulsifier.

Crystallization induction time. *Savage* and *Dimick* [153] noted a difference of crystallization induction time as function of CB origin and found a correlation between crystallization induction time and phospholipid (PL) concentration. They explained their results based on the ratio of LPC (lysophosphatidylcholine) and PI (phosphatidylinositol) over the PC (phosphatidylcholine) concentration. Crystallization induction time was short at a ratio equal to 1, whereas crystallization induction time was longer at a higher ratio, around 3 to 6. The most rapid crystallization of CB had the highest concentration of PC in the first seeds, whereas the seeds of CB having a long induction time had a higher concentration of PI. The authors referred to the self-assembly behavior of PL to explain their results. PC has an inverse hexagonal phase, so the hydrophobic fatty acyl chains are directed to the media, improving the interaction with the TAG. LPC and PI have a normal hexagonal phase, with the polar heads directed in the media. Thus, the TAG should have more difficulties to interact with the more hydrophilic aggregate of LPC and PI.

Diglycerides (DAG) have also been shown to influence crystallization rate. In a study on the crystallization of palm olein, *Siew* and *Ng* [151] found an antagonistic phenomenon of the DAG as function of its configuration. The 1-2 configuration of the DAG delayed nucleation, whereas 1-3 DAG improved crystallization.

Growth rate. *Smith* and *Povey* [152] reported the effect of free fatty acid (FFA), monoglyceride and 1,2- or 1,3-diglyceride on the growth of trilaurin crystals. FFA and monoglyceride increased slightly the trilaurin crystal growth, but decreased the facet and crystal size, whereas 1,2-diglyceride and 1,3-diglyceride (at a higher extent) decreased the crystal growth. The effects were greater when the chain length of glyceride was longer than C12, whereas the used of shorter chain length glycerides did not give as much variation.

The inhibiting effect of DAG (without conformation distinction) on CB crystal growth was previously shown by *Kattenberg* [154].

Melting curve. Addition of minor components can affect fat crystallization, usually decreasing the initial melting point of each polymorph [155]. For example, *Wilson* [135] found that the most effective anti-bloom emulsifiers acted either by reducing the melting curve of the sample or by increasing the general melting temperature of product, whereas the less effective emulsifier tended to enlarge the melting range of chocolate.

Schlichter and *Garti* [156] found that the sorbitan disturbed the initial natural blend between the low- and high-melting point of cocoa butter TAG. They tended to crystallize separately and their melting peak by DSC were more distinct. *Cebula* and *Smith* [157] studied the effect of DAG on crystallization of Coberine (CBE) and found that it enhanced crystallization (occurring sooner) but the following growth rate was reduced.

Seed material. Since phospholipids crystallize at higher temperature than TAG, they could act as nuclei or seeds. According to *Arruda* and *Dimick* [158], the phospholipid concentration was twelve-fold higher in the seeds (first cocoa butter crystals) than in the bulk, with concentrations of 3.9% to 0.34% in seeds and bulk crystals, respectively. The main phospholipids in the seeds were PE (phosphatidylethanolamine) and PC. Thus, emulsifiers may impact bloom formation by promoting formation of many small fat crystals.

Polymorphic effects. In a general review on emulsifiers used in foods, *Krog* [159] confirmed that the sorbitan esters of palmitic and stearic acids stabilized the intermediate form βV of cocoa butter. This effect was more efficient when the ester had more than one acid radical per molecule (sorbitan tristerate was more efficient than sorbitan monostearate).

Garti et al. [155] also studied the effects of sorbitan ester effects (single or mixed with polysorbate 60) on polymorphism of cocoa butter. They found an increase in the β'IV-βV transition rate, but a delay in the βV–βVI transition, as was previously found. The same observation was found with the crystallization of palm oil [160, 161]. However, according to *Garti* et al. [155, 160], the sugar esters must be solid at room temperature (and have a structural compatibility with the fat) to be efficient against the βV–βVI transition. Due to the rigid structures (high melting point), the emulsifiers could hinder the motion of TAG that are consequently entrapped in a rigid network. The polymorphic transition would be directly hindered by the rigidity of the sucrose ester.

Sucrose esters also delayed nucleation and slowed down the β'–β polymorphic transition of hydrogenated sunflower oil [162]. Thus, it would act in the same way as the sorbitan ester.

In general, FFA or diglyceride are known to inhibit polymorphic transitions, even at low concentration (105). *Hernqvist* et al. [163, 164] reported the effect of 1,2-DAG on rapeseed oil phase transition and concluded that DAG delayed the β'-β transition, more by forming a fat crystal network containing DAG, than by disturbing the crystal lattice. They discussed also the optimal chain length, and concluded that the longest stabilization occurred when the DAG chain length was similar to that of the fatty acids in the TAG. The stabilizing effect decreased with shorter chain length and longer chain length could create some co-crystallization problems.

It appears that the most efficient emulsifiers, in terms of bloom inhibition, have three major effects.

1. They improve crystallization by increasing the number of seeds that are formed and reducing the crystal size.

2. They increase the melting point of the fat so the product has a better thermal resistance.

3. They prevent the ultimate polymorphic transition that is always associated with chocolate bloom [165].

These effects are almost similar to the effects of milk fat effects and may be why several authors wondered if the effects of milk fat were due to its minor lipid content, like FFA and partial glycerides, or to the specific TAG composition [86, 102].

6.1.4 Special compounds

6.1.4.1 Prestine

Prestine is a modified vegetable fat (European patent application 530864), marketed at one time in particular to inhibit bloom in chocolate. *Talbot* [166] and *van Dongen* [167] reported the use of the TAG blend called Prestine that inhibited storage bloom in plain and filled chocolate. *Talbot* [166] reported that the oleic chain of SOS in cocoa butter had different conformations in βV or βVI, corresponding to a straight and bent conformation, respectively. Inhibiting the transition of the bent form to the straight form would stop the βV-βVI transition and consequently, inhibit bloom. Prestine was reported to constrain the oleic chains of SOS in CB to its straight conformation, at concentrations as low as 5%.

6.1.4.2 1,3-oleoyl 2-stearoyl glycerol

Koyano et al. [168, 169] showed that a 50/50 blend of 1,3-oleoyl 2-stearoyl glycerol (OSO) and CB prevented bloom. At this concentration, both fats crystallized in a stable β form characterized by a double chain length [109].

6.1.4.3 Sugar particles

Cerbulis [90] screened a wide variety of chemical components as bloom inhibitors in chocolate. He found that anhydrous glucose gave a high bloom resistance when added at 15–20% of chocolate weight. Two anti-bloom patents used the properties of anhydrous glucose [170, 171]. However, chocolate made with glucose would have an undesired aftertaste.

While studying the effects of milk fat on cocoa butter polymorphich transition, *Bricknell* and *Hartel* [100] found that chocolate made with amorphous sugar particles was resistant to visual bloom. The amorphous sugar in this case was a spray-dried blend of sucrose and corn syrup. Although visual bloom was not observed, the chocolate was in the βVI form after storage. Thus, the βV to βVI transition did not correspond to visual bloom formation. Several mechanisms were hypothesized based on sugar crystal shape [100, 172]. One possibility was that the spherical shape of amorphous sugar may have allowed closer packing of the particles, thereby reducing or inhibiting lipid migration and thus, the rate of bloom formation. Also, the inhibition of fat re-crystallization at the surface of the chocolate may be due to the smooth sugar surface hindering the nucleation of fat crystals. Amorphous sugar could also strongly interact with fat and constrain it enough to inhibit lipid migration. Some amorphous compounds are known to reduce the mobility of reactants [173, 174].

6.2 Process factors

As previously mentioned in the section describing bloom enhancers, the tempering and cooling steps are very important to controlling bloom formation. Storage conditions are also important in inhibiting or promoting bloom formation.

6.2.1 Tempering

Different chocolates with different ingredients often require different tempering conditions. For example, it is well known that milk chocolate must be cooled to lower temperatures than dark chocolates in tempering to obtain the same extent of crystallization. The key step for chocolate is to form the right concentration of small βV seed crystals by careful control of the temperatures in the tempering unit [63, 175]. Tempering is of course less important for compound coatings, where tempering is often not needed to form the proper extent of crystallization.

An alternative method of tempering involves addition of seed crystals to chocolate in order to induce crystallization [80, 176]. Seeding decreases the process time as well as many of the temperature constraints involved in the tempering step. One of the earliest studies on seeding was done by *Giddey* [21] who used SOS seed in the βVI form and under proper temperature condition to crystallize CB directly into the βVI form. According to *van Dongen* [167], a chocolate with CB in the βVI form would be impervious to bloom. However, *Adenier* et al. [86] used CB seeds in the βVI form, but were not able to crystallize either CB or dark chocolate directly into the βVI form.

Recently, a new tempering method using βVI CB seeds has been commercialized. This technique allows an easier βV CB crystallization. Even though the chocolate is not in the βVI form, this method increases the bloom stability [53]. The exact effect of seed crystals on the bloom mechanism remains unclear.

A systematic method was used to screen the effect of different seeds: βVI CB, β and β' SOS, β SSS, β' and β BOB (1,3-dibehenoyl-2oleoylglycerol (C22-C18:1-C22). β' BOB and β SSS were ineffective due to the TAG packing difference with CB (2L and 3L, respectively). βVI CB and β SOS improved bloom resistance (with 32/20 °C test cycle) when the concentration used was below 2.5%; above this concentration, the seeding promoted bloom. β BOB seeds improved bloom resistance (32/20 °C and 38/20 °C test

cycle) when seed concentration was above 1% [95–98, 177]. The high-temperature resistance of chocolate made with BOB seeds was explained by the higher melting point of BOB (51.4 °C). Thus, the BOB seeds did not melt and could act as seeds during the cooling.

6.2.2 Cooling

As already discussed, cooling that is too slow or too quick can induce bloom. For example, rapid cooling produces small cracks and pores on the chocolate surface, enhancing bloom [79]. Rapid cooling may also promote formation of unstable polymorphs in the regions that have cooled too quickly. Proper cooling of both chocolates and compound coatings is needed to protect against early bloom formation.

6.2.3 Warm treatment prior to storage

It has been found that a brief period of warming to 32–35 °C protects chocolate against bloom formation. Following his earlier work, *Kleinert* [79] investigated the possibility of exposing chocolate to a brief warm temperature hold to prevent bloom formation. A minimal "treatment" time of 80 min at 32–35 °C was sufficient to protect the chocolate against bloom for more than one year, although a similar hold at temperatures from 28 to 31 °C did not prevent the chocolate from blooming. *Minifie* [175] also noted a similar treatment (32.2 °C for 2 h); however, he described also a second treatment using lower temperature for a longer period of time. Treatment for 2 d at 26.7–29.4 °C for dark chocolate and 22.8–25 °C for milk chocolate also inhibited bloom formation. However, this last method decreased the final gloss. After warm treatment, the chocolate was in the βVI form.

Kleinert [79] suggested that warm treatment (32.2 °C for 2 h) could permit unstable crystals (having a higher concentration of saturated TAG) to equilibrate with the surrounding mass to obtain a homogenous TAG concentration in the CB crystals. The treatment may be compared to the annealing used in the glass industry to eliminate any tension differences (responsible for very weak material). According to *Minifie* [175], this treatment provides a smoother and tighter enrobing surface that could be then compared to a molded surface. Moreover, this treatment allowed transformation of the βV freshly made chocolate into its more stable βVI form [176].

A similar phenomenon is responsible for the bloom inhibition with the second method (2 d at 26.7–29.4 °C). The unstable crystals re-melt and transform to the most stable βVI form, reducing the amount of unstable crystals that could transform during storage.

6.3 Storage conditions

Inhibition of storage bloom is maximal when chocolate is stored at 18 °C or below, as well as without any temperature fluctuations [80, 178]. Chocolate can be stored frozen for a very long time [179]. However, even though the ideal storage conditions that prevent bloom are well known, it is impossible to control the temperature when the chocolate leaves the plant!

7 Bloom theories

Since the 50's, several theories or explanations have been proposed to understand and explain bloom formation [91, 99]. Naturally, these theories have changed as new data has been collected. Moreover, bloom theories often do not take into account the whole complexity of the diverse aspects of bloom formation; most describe bloom occurring during storage and cannot explain all the effects of active components. Theories that relate bloom to phase transition, eutectic effect, crystal demixion, and lipid migration are the most common.

7.1 Polymorphic transition

All chocolates that bloom during storage have lost their initial βV form and the bloom crystals are in the βVI polymorph. This polymorphic transition, which is always observed during chocolate bloom, has been the primary factor to explain bloom and would give rise to needle-like crystals on the surface corresponding to bloom. However, not all chocolates in the βVI form have visual bloom [86, 100]. Recent evidence also suggests that coatings where visual bloom is observed have undergone a polymorphic transition, although more verification of this hypothesis is needed.

The polymorphic transition is certainly one of the most important factors in any bloom theory; however, it should be considered as only one factor responsible for bloom.

7.2 Eutectic effect

In this concept, bloom is explained as the consequence of a phase separation occurring between physically incompatible TAG, which is often based on a two-component phase diagram. It can occur either for TAG within a single fat or for TAG in mixed fats.

7.2.1 Single fat

Whymper and *Bradley* [70] assumed that the highest-melting point fraction of CB separates inevitably from the lowest melting fraction during cooling and storage, and then re-crystallizes as single fats to produce bloom.

Such a separation between low- and high-melting point TAG has been observed during the early stages of crystallization. For example, the initial CB crystals formed had higher concentrations of POP, POS and SOS as well as PE and PC [158, 180] under static conditions and higher PSS, SSS and SOS concentration and a lower POS and POP concentration [181–183] under dynamic crystallization conditions. The general concentration of glycolipids, phospholipids, saturated FFA and DAG in the initial crystals formed was increased [184]. This heterogeneity of the initial crystals suggests a core seed with a high melting point core composed of trisaturated TAG and minor compounds. *Becker* [185] showed that two TAG families, POO+SOO+OOO and POS+SOS+POP, formed a stable solid near the CB melting point, but they tended to separate as temperature decreased (below 16 °C), leading to bloom. Unfortunately, this very interesting theory has been contradicted by several authors [78, 91, 104].

7.2.2 Different fats

Eutectic incompatibilities between two different fats may also explain bloom occurring with incompatible fat blends (*i.e.*, hard butter + CB or milk fat) [64, 186]. However, *Williams* et al. [38] showed that the eutectic extent (between PKO and CB) did not necessarily correlate with bloom development.

7.3 Crystal demixion

From a general point of view, crystal demixion is promoted by the liquid fraction of the fat that acts as solvent for the high-melting TAG. This liquid fraction could reach the surface due to cracks or porosity in the chocolate or coating piece, and then the most saturated TAG would crystallize with the temperature decrease when the most liquid part would draw back in the chocolate [78, 79, 113, 187]. Crystal demixion is closely related to the liquid fat content of the chocolate or coating, which increases with increasing temperature. Another reason for an increase in the liquid fat content is lipid migration from fat-based center into the chocolate.

7.4 Lipid migration

Lipid migration occurs when a chocolate or coating is in contact with a product having a high liquid oil content (*i.e.*, peanut, biscuit, *etc*.). This oil migrates from the center into the chocolate, depending on storage time, temperature, center/chocolate ratio and fat content of chocolate and center [74]. The deleterious effect of liquid oil in chocolate or coatings has been known since 1925 [70].

Qualification and quantification of oil migration was highlighted by *Adenier* et al. [78]. The liquid TAG in the center migrate from into the chocolate at the same time that the chocolate TAG migrate back to the center, but to a lesser extent. Moreover, the migration rate ceases once the equilibrium fat content has been achieved. Oil migration is an attempt to reach an equilibrium state of TAG concentrations between center and coating. Tab. 11 underlines the fatty acid composition of the different parts of a filled chocolate, before and after fat migration.

Tab. 11. Relative proportion of fatty acids composition of each moiety of a filled chocolate, before and after migration [115].

	Chocolate Initial	Filling Initial	Chocolate after fat migration	Filling after migration	Bloom of filled chocolate
C16	25	7.4	17.6	9.5	26.2
C18	34.2	5.2	22.6	6.4	30.1
C18:1	36.5	74.8	52.2	71.2	40.1
C18:2	4.2	12.6	7.6	12.9	3.6

Recent studies have highlighted very precisely the differences of migration as function of temperature by using magnetic resonance imaging to follow liquid TAG [75, 188, 189]. At 19 °C, liquid fat stayed near the filling-chocolate interface, with concentration increasing with time (migration is limited at this temperature). At 28 °C, the liquid fat moved further and accumulated just below the chocolate-air interface. This last observation suggests that the migration mechanism is not only governed by a TAG concentration difference but also by structural differences in the coatings. Similar results were obtained when the samples were storage up-side down, excluding a mechanism based on gravitational forces. The authors proposed that migration could be due to diffusion as well as capillary attraction.

However, for both mechanisms, crystal demixion and oil migration, the main problem is the explanation of the driving force, and how some TAG can crystallize on the surface. *Cousens* and *Wille* [75] hypothesized a lower surface free energy at chocolate surface than the oil's.

The nature of the surface and chocolate porosity may either permit or prevent liquid fat from reaching the surface. For example, it is well known that any scratches on the surface enhance bloom. *Adenier* et al. [86] found that chocolate covered with aluminum foil was protected against bloom. This suggests that liquid fat reaches the surface by capillarity and then crystallizes to produce bloom. Effectively, liquid oil could not reach the surface

when a pressure difference does not exist and, in this way, bloom would be inhibited. The only accurate work related to porosity is from *Loisel* et al. [81]. They found a difference of volume porosity of 1% for normal chocolate and 4% for chocolate in the βVI form. However, the real structure and inter-connectivity of pores are still unknown.

8 Discussion

Numerous theories exist to explain bloom, but so far none seems to cover or explain the entire range of blooms – plain chocolate, compound coatings, filled chocolate, during the storage. Before proposing our final statement about bloom, we discuss the different blooms classfied in four categories:

1. Bloom due to under-tempering or melting of tempered chocolate.
2. Bloom due to over-tempering.
3. Bloom due to a problem of incompatible fats, whether due to the initial fat composition or migration of an incompatible fat.
4. Bloom that occurs over time, or storage bloom.

The first two types of bloom are specific to chocolate (made with CB), whereas the latter two mechanisms may apply to any kind of chocolate or compound coating. All four bloom mechanisms are due to a stability problem of fat crystals, but at different scales. At this point, storage bloom of chocolate and compound coating may be compared, even though there is some question as to whether the bloom mechanism is similar or not for these different fats.

8.1 Bloom due to under-tempering or after melting (>35 °C) of chocolate

Under-tempered chocolate or chocolate that has been accidentally melted and re-crystallized are products where fat crystallization is not controlled. Such crystallization gives rise to one of the less stable polymorphs (βIV). Bloom then appears within a few days when the βIV–βV or βIV–βVI transition occurs. This bloom has distinct characteristics corresponding to large white spots on the surface, which are mainly composed of sugar crystals and cocoa powder and nearly devoid of fat. This phase separation between fat and dry matter has been explained as re-crystallization and mass transfer limitation [111]. Crystals of the most stable polymorph (βVI) re-crystallize from the less stable forms within a few days. When several crystals are growing in the same area, an inter-crystal space, devoid of fat, is formed due to the volume contraction caused by the polymorphic transition. Sugar and cocoa powder are the only components that remain in the inter-crystal space and appear as white spots on the surface. Similar re-crystallization and rearrangement occurs eventually throughout the bulk of the chocolate.

8.2 Bloom due to over-tempered chocolate

With over-tempered chocolate, where either too much seed has crystallized or the seed crystals are too large, bloom develops while the chocolate is solidifying. Bloom is maximum at the end of chocolate solidification and does not vary with time (although storage bloom can occur over time as in any chocolate). Bloom appears as a dull gray surface due only to light diffraction from large CB crystals and not to the presence of pure fat crystal on the surface. During cooling, the large and numerous CB crystals formed during tempering deplete the liquid fat in their vicinity, creating a rough surface with cracks and crevices. Incident light is diffracted on this rough surface (due to the crevices and large crystals), giving a dull, whitish-gray appearance [190].

8.3 Bloom due to a problem of incompatible fats or fat migration

It is well known that certain fat blends (*i.e.*, CB+CBS, CBS + milk fat) tend to bloom quickly and easily. Based on microscopic observations and fat compositional analysis, it has been shown that bloom spots of a single fat (not the mixture of fats) are found on the chocolate or coating surface, corresponding to a separation of the two incompatible fats (usually confirmed by the phase diagrams). In such blends, the crystal network is unstable, TAG are mobile and the liquid fat content is high, which permits and enhances fat separation and re-crystallization of individual fats.

Migration of liquid fat from a center into a chocolate or coating occurs due to the concentration difference in specific TAG between the coating and center (the same driving force as for any mass transfer situation). Diffusion of TAG, from center to coating and from coating to center, occurs due to this concentration driving force. However, capillary forces related to the porosity of the chocolate coating may also draw liquid TAG from center to coating. Once the liquid TAG from the center are absorbed into the coating, the two fats mix according to their phase behavior. Whether due to dilutional softening or a eutectic formation, the solid fat content within the coating occurs as some of the fat crystals in the coating dissolve in the liquid TAG. The dilution of CB crystals leads to a softer coating with more liquid TAG with greater mobility that are more

likely to re-crystallize into a more stable polymorph, initial at the surface, and appear as visible bloom. Once fat migration and softening occur, the bloom mechanism is similar to that which occurs in storage bloom (next section).

8.4 Storage bloom

Bloom, on either chocolate or compound coating, that occurs during storage (and cannot be explained by bad tempering or strong fat incompatibility) is characterized by growth of small fat crystals on the surface (as well as inside the chocolate after longer times). However two main phenomena affect the chocolate during storage.

8.4.1 Phenomena observed during storage

Two phenomena, fat migration and re-crystallization, should be sufficient to explain bloom in almost all cases. Although there may be some disagreement in the literature about the importance of each of these steps, it seems that both must occur to some extent (and perhaps with varying degrees of importance in different situations) for bloom to appear.

8.4.1.1 Fat migration

The migration of liquid TAG is due to external forces on the chocolate or coating. Specifically, temperature fluctuations, even very small ones, are sufficient to cause changes in the amount of fat crystallized. Furthermore, temperature gradients within the chocolate (the surface sees higher temperature fluctuations, which are dampened in the interior) lead to a driving force for liquid TAG to move to the surface. As temperature increases, the amount of liquid TAG increases as does the volume of the system (in reverse, there is a contraction as more fat crystallizes upon cooling). The liquid TAG are pushed (or pumped as some people say) through the chocolate to the surface due to this dilation effect. When the temperature decreases again, not all of the liquid fat is reabsorbed back into the chocolate matrix, leaving a "pool" of liquid fat near the surface. One of the key points in bloom formation is the surface state and whether the liquid fat actually crosses to the surface. As long as the surface of the chocolate or coating remains smooth, compact and free of defects like scratches or crevices, the liquid fat does not cross the surface, as seen in the NMR results of *Guiheneuf* et al. [189], and bloom may be delayed. Once the surface loses its impermeability, however, liquid fat easily crosses to the exterior of the piece and re-crystallization is inevitable. Chocolates that are covered with a package layer or coated with glaze (*e.g.*, panned chocolate pieces) are quite resistant to bloom, likely because the liquid TAG can not cross to the surface.

The rate of migration of liquid TAG may be influenced by numerous factors, including the hardness of the fat (change in liquid fat with temperature), the particulate structure (sugar, cocoa solids, milk solids, *etc.*), emulsifier interactions and the porosity of the chocolate (cracks and crevices providing access to the surface and capillary forces) [191]. Thus, increased porosity of the chocolate due, for example, to crack and crevice formation from cooling too quickly, results in immediate migration of liquid fat to the surface and rapid onset of bloom.

8.4.1.2 Re-crystallization

In general, visual bloom is accompanied by a polymorphic transition, from βV to βVI in bloomed chocolate and from β' to β in many bloomed compound coatings (although suspected, this transition has not been verified to occur in all cases yet). This polymorphic transition, which increases the stability of the fat, occurs naturally, but it appears that "activating" factors like the liquid fat content enhances the re-crystallization. This re-crystallization may appear in the TAG of the liquid fat and/or in the remaining CB crystals.

8.4.1.2.1 Solvent re-crystallization

The high-melting TAG dissolved in the liquid fat content may re-crystallize as temperature decreases (due to lower solubility at the lower temperature). If the solubility is low, the likelihood of re-crystallization is greater. Furthermore, the high-melting TAG dissolved in the liquid component of the fat re-crystallizes into a more stable polymorph (polymorphic transition) and/or a more purified state.

As suggested by *Matsuda* et al., [192], if the solubility of high-melting TAG in the system is high, bloom is less likely to occur than if the solubility is low. Their results on bloom formation in cosmetic products made of stearic acid, oil and wax clearly showed the relationship between the solubility of the bloom forming compound (stearic acid in this case) and the liquid oil. In oils where the solubility of stearic acid was high, no bloom occurred, whereas bloom was rapid when the solubility of stearic acid in the liquid oil was low.

8.4.1.2.2 Spontaneous re-crystallization

The melting of some TAG would disorganize the structure of the remaining CB crystals and would result in a more homogenous composition. The destabilization would en-

hance the re-crystallization. Moreover, if high-melting point TAG are dissolved, this would decrease the energy needed for the phase transition, since the high-melting TAG increase the barrier energy for each polymorphic transition.

8.4.2 Chocolate

In chocolate, storage bloom covers the surface very uniformly and its composition is not substantially different than the initial composition of the CB (even with filled chocolate). *Adenier* et al. (1993), for example, showed that bloom had a similar composition as the liquid fraction obtained at 28 °C. A slight increase of C16:0 and C18:1 and slight decrease of C18:0 fatty acids were observed, but the composition of bloom was not significantly different from the CB composition.

In this case, the polymorphic transition from βV to βVI is always observed. During the early stages of storage bloom, the chocolate is in the βV polymorph [86]. As bloom is initiated and progresses through the early stages, there is an increase in the amount of the more stable βVI polymorph that can be measured by X-ray diffraction. However, scraping the bloom crystals off the surface for analysis reveals that the bloom crystals are all primarily in the βVI form. As proposed before, this re-crystallization could be due to the crystallization of the most saturated TAG of the liquid fat content that crossed the surface and/or by the polymorphic transition of the CB crystals. It is a first step that initiates bloom by creating site of crystallization. However, in order for visual bloom to be observed, re-crystallization must occur so that spiky crystals emanate from the surface to interfere with light reflection, giving the dull and whitish appearance. Furthermore, if re-crystallization could occur so that the crystals form, for example, in layers, as opposed to spiky crystals emanating from the surface, the chocolate would remain without visual bloom despite the polymorphic transition of the fat. This is most likely what occurred in the study by *Bricknell* and *Hartel* (1997), where no visual bloom was observed despite formation of the βVI polymorph. Thus, the polymorphic transition accompanies bloom formation, but by itself is not sufficient to always cause the appearance of visual bloom.

Moreover, formation of crystals on the surface of chocolate would have to be easier than in the interior of the chocolate. The energy needed to change the βV-air to βVI-air interface would be lower than that for the βVI/matter interface. Thus, the first transition would take place on the surface and subsequently move into the bulk of the chocolate.

Once this first step is induced, the formation of a βVI crystal might destabilize the surrounding area and promote additional crystallization of βVI. Moreover, this phase transition corresponds to a mass contraction, which directly affects the cohesion of the mass. The chocolate loses its initial cohesion as empty spaces are created between crystals. It can also lead either to bare sugar surface, or needle-like fat crystals (characteristic of the βVI polymorph). Each of these factors would be sufficient as seeds for further crystallization. The concomitant presence of sites of crystallization and the increase of porosity (from 1 to 4%, permitting the liquid fat content to cross the surface), would permit a quick crystallization of most of the liquid fat content.

This re-crystallization of chocolate mass (CB mass and liquid fat content together) would explain the small difference of composition between initial chocolate and bloom composition. Effectively, based on the fatty acid composition variations between initial chocolate and bloom (+9.9% C18:1, −11.9% C18 and +4.8% C16), it is difficult to explain that bloom would be only due to: (1) the monounsaturated TAG coming from the liquid content of cocoa butter [115] (If such was the case we should have also an increase of C18 corresponding to the C18:1 increase.). (2) the chocolate mass re-crystallization (composition is not exactly similar between chocolate and bloom).

The determination of the TAG composition of the initial site of crystallization (during the first step of bloom formation) would certainly yield interesting information about whether re-crystallization occurs preferentially in the liquid fat content or in the remaining CB crystals.

Fig. 9 summarizes the factors that either promote or inhibit bloom development during storage of chocolate. The primary factors discussed previously are contained within this diagram as either bloom activators or bloom inhibitors. The main points related to the mechanism of bloom formation in chocolates are oil migration (with liquid oils dissolving high-melting TAG) due primarily to temperature fluctuations, leading to re-crystallization of fat at the surface in a more stable polymorph and growing in the proper orientation to scatter incident light.

8.4.3 Compound coatings

Similar to chocolate, compound coating also develops a storage bloom comprised of small fat crystals emanating from the surface. Since compound coatings can be made with three different class of fat, CBE, CBR and CBS, and blends with different fats (CB, milk fat, *etc.*), storage

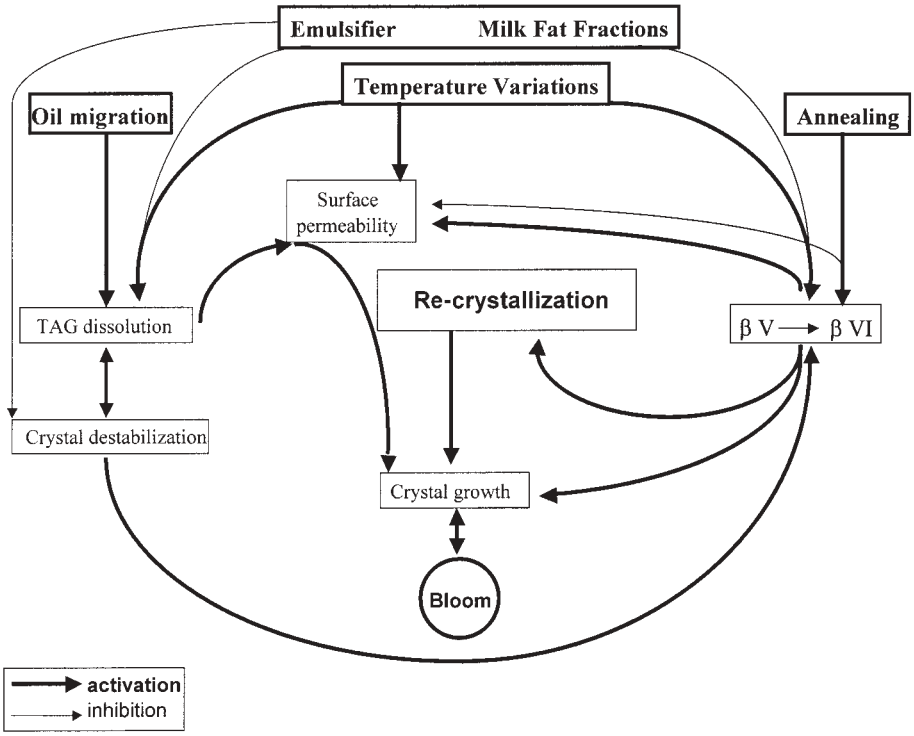

Fig. 9. Bloom mechanism for chocolate.

bloom in coatings is more difficult to summarize. However, most of the studies have focused on bloom occurring with CBS.

8.4.3.1 CBE

No studies relate problems of bloom occurring with CBE (except for synthesized CBE). However, CBE would be expected to have the same bloom behavior and mechanism as chocolate because of the similarity in TAG composition with CB.

8.4.3.2 CBR (non-lauric, hydrogenated or fractionated vegetable oil)

The few bloom studies published for CBR have been related to the problems of fat incompatibility and not storage bloom [6].

8.4.3.3 CBS (lauric vegetable fats)

Numerous studies have reported bloom in coatings made with CBS. Some important differences have been found compared to storage bloom in chocolate (with CB). It has been reported that coatings made with CBS are generally more resistant to bloom than chocolate [66]. In some cases, bloomed compound coatings made with CBS appear to still be in the β' form, although this result is still in question and several recent studies suggest that the β polymorph is present in bloomed coatings. Furthermore, addition of milk fat enhances bloom in compound coatings, whereas it delays storage bloom in chocolate. Another difference in storage bloom formation between chocolate and compound coatings is the effect of storage temperature. In chocolate, it is clear that storage at elevated temperatures and with larger temperature fluctuations promotes bloom formation. However, in coatings, storage bloom often seems to be promoted at temperatures slightly below room temperature (about 18 °C) and inhibited when storage temperatures are higher or fluctuating. For these reasons, the bloom mechanism for coatings is often considered to be different from that of chocolate.

In situations where a polymorphic change is associated with bloom formation in compound coatings, the general outline of bloom formation shown in Fig. 9 should apply in this case as well. Essentially, the same processes can explain the evidence for such bloom in compound coatings, with the exception of the effects of milk fat and storage temperature.

If storage bloom in compound coatings occurs without a polymorphic transformation, a different mechanism is needed to explain this type of bloom. Hypothetically, the

re-crystallization of high-melting TAG could occur in the same polymorph as the bulk of the coating; however, in this case, growth of existing crystals would be favored over formation of new ones. Perhaps the existing β' crystals at the surface simply get larger and this is sufficient to disrupt reflection and give the appearance of bloom. The visual appearance of bloom on compound coatings (larger, grainer spots) suggests that perhaps this is indeed what happens. Further work is needed to document whether bloom can occur in compound coatings without the necessity of the polymorphic transition.

Regardless of whether bloom in compound coatings occurs either with or without a polymorphic transition, the effects of milk fat and storage temperature still need to be understood. Milk fat inhibits bloom in chocolate but promotes bloom in lauric-based coatings. Perhaps the differences in chain length and degree of saturation between CB and PKO can explain their different behavior with milk fat and thus, the different effects of milk fat on bloom formation. Interestingly, milk fat and CB form a eutectic solid at when milk fat content reaches about 30%, whereas milk fat and modified PKO do not. How this phase mixing between the fats influences bloom formation is still unknown.

In chocolate, bloom is promoted at elevated temperatures, where SFC is reduced. However, in lauric-based coatings, bloom is often promoted at about 18 °C and occurs more slowly at both higher and lower temperatures (although it is unknown if this general observation applies in all cases). SFC curves are generally similar for modified PKO and CB, although coatings made with hydrogenated PKO tend to be the most prone to bloom and these fats have the largest difference in SFC with CB. Perhaps this difference in SFC profile is somehow related to likelihood of bloom formation. However, the effect of SFC of the fat on bloom formation in coatings is still largely unknown and further research is needed to address this question.

8.5 Summary of bloom formation

Fig. 10 summarizes the different kinds of bloom that occur for chocolate and compound coatings. Four main bloom mechanisms may be considered for chocolate and three mechanisms for compound coatings:

– On the one hand, under-tempering and melting, and on the other hand, over-tempering, are parameters that act on chocolate bloom principally.

– Bloom due to incompatible fats is common for chocolate and compound coatings, but the incompatibilities are different as function of the main fats.

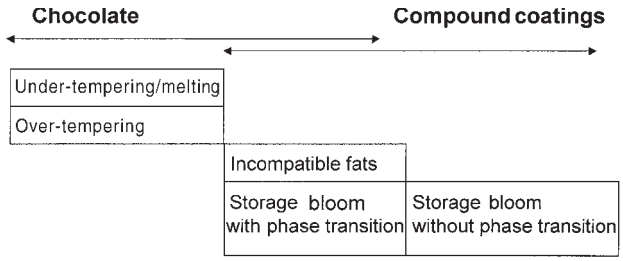

Fig. 10. Different types of bloom as function of chocolate or compound coatings.

– Storage bloom with polymorphic transition is characteristic of chocolate. However it can affect also CC like CBE, and some CBS (hydrogenated PKO).

– Storage bloom without polymorphic transition has only been observed for some compound coatings, although further work is needed verify that this is actually true.

Many factors have been found to affect bloom in chocolates and compound coatings. Some tend to accelerate bloom formation, like oil migration from a coated center, the presence of incompatible fats and improper storage temperatures. Some factors tend to inhibit bloom formation, like the use of milk fat in chocolate and proper storage temperatures.

Despite the years of study of bloom, there are many aspects of this phenomenon that have still eluded a complete understanding.

References

[1] *S. D. Coe, M. D. Coe*: The true history of chocolate. Thanes and Hudson, New York (USA) 1996.

[2] *K. Jackson*: Recipes. In: Industrial chocolate manufactures and use, 2nd edn. Ed. *S. Beckett*, Blackie academic & professional, Glasgow (UK) 1998, pp. 258–280.

[3] *R. Wainwright*: Cocoa butter alternative fat systems for compounds and pastel coating. Manuf. Confect. **66** (1986) 45–49.

[4] *M. Lipp, E. Anklam*: Review of cocoa butter and alternative fats for use in chocolate – Part A. Compositional data. Food Chem. **62** (1998) 73–93.

[5] *J. Pease*: Confectionery fats from palm oil and lauric oil. J. Am. Oil Chem. Soc. **62** (1985) 426–430.

[6] *K. Laustsen*: The nature of fat bloom in molded compound coatings. Manuf. Confect. **71** (1991) 137–144.

[7] *G. Chapman*: Cocoa butter and confectionery fats. Studies using programmed temperature X-ray diffraction and differential scanning calorimetry. J. Am. Oil Chem. Soc. **48** (1971) 824–830.

[8] *K. Larsson*: Molecular Organization in Lipids. In: Food Emulsions, 3rd edn. Eds. S. Friberg, K. Larsson, Marcel Dekker, Inc., New York, NY (USA) 1997, pp. 111–140.

[9] *S. Chaiseri, P. Dimick*: Cocoa Butter – Its composition and properties. Manuf. Confect. **67** (1987) 115–122.

[10] *S. Chaiseri, P. Dimick*: Dynamic Crystallization of cocoa butter. II. Morphological, thermal, and chemical characteristics during crystal growth. J. Am. Oil Chem. Soc. **72** (1995) 1497–1503.

[11] *O. Podlaha, B. Toregard, B. Puschl*: TG-type composition of 28 cocoa buttes and correlation between some of the TG-type components. Lebensm.-Wiss. Technol. **17** (1984) 77–81.

[12] *J. Aronhime, S. Sarig, N. Garti*: Reconsideration of polymorphic transformations in cocoa butter using the DSC. J. Am. Oil Chem. Soc. **65** (1998) 1140–1143.

[13] *P. Dimick*: Principles of cocoa butter crystallization. Manuf. Confect. **71** (1991) 109–114.

[14] *S. V. Vaeck*: Polymorphie einiger Naturfette. Rev. Int. Choc. **6** (1951) 350–354.

[15] *W. Duck*: The measurement of unstable fat in finished chocolate. Manuf. Confect. **44** (1964) 67–72.

[16] *R. Wille, E. Lutton*: Polymorphism of cocoa butter. J. Am. Oil Chem. Soc. **43** (1966) 491–496.

[17] *A. Huyghebaert, H. Hendrickx*: Polymorphism of cocoa butter, shown by differential scanning calorimetry. Lebensm.-Wiss. Technol. **4** (1971) 59–63.

[18] *N. Lovegren, M. S., Gray, R. Feuge*: Polymorphic changes in mixtures of confectionery fats. J. Am. Oil Chem. Soc. **53** (1976) 83–88.

[19] *P. Dimick, T. Davis*: Solidification of cocoa butter. Manuf. Confect. **66** (1986) 123–127.

[20] *C. Loisel, G. Keller, G. Lecq, C. Bourgaux, M. Ollivon*: Phase transitions and polymorphism of cocoa butter. J. Am. Oil Chem. Soc. **75** (1998) 425–438.

[21] *C. Giddey, E. Clerc*: Polymorphism of cocoa butter and its importance in the chocolate industry. Rev. Int. Choc. **16** (1961) 548–554.

[22] *A. van Langevelde, K. van Malssen, R. Peschar, H. Schenk*: Effect of temperature on recrystallization behavior of cocoa butter. J. Am. Oil Chem. Soc. **78** (2001) 919–925.

[23] *G. V. Merken, S. V. Vaeck*: Etude du polymorphisme du beurre de cacao par calorimétrie DSC. Lebensm.-Wiss. Technol. **13** (1980) 314–317.

[24] *K. van Malssen, A. van Langevelde, R. Peschar, H. Schenk*: Phase behavior and extented phase scheme of static cocoa butter investigated with real-time X-ray powder diffraction. J. Am. Oil Chem. Soc. **76** (1999) 669–676.

[25] *H. Traitler, A. Dieffenbacher*: Palm oil and palm oil kernel oil in food products. J. Am. Oil Chem. Soc. **62** (1985) 417–421.

[26] *G. Talbot*: A new generation of cocoa butter equivalents. Confectionary Manufacture and Marketing (1991) 33–35.

[27] *R. Timms*: Phase behavior of fats and their mixtures. Prog. Lipid Res. **4** (1984) 23–38.

[28] S. *Hashimoto, T. Nezu, H. Arakawa, T. Ito, S. Maruzeni*: Preparation of sharp-melting hard palm midfraction and its use as hard butter in chocolate. J. Am. Oil Chem. Soc. **78** (2001) 455–460.

[29] *T. Okawachi, N. Sagi*: Confectionery fat from palm oil. J. Am. Oil Chem. Soc. **62** (1985) 421–425.

[30] *P. Hong Yap, J. deMan, L. deMan*: Polymorphism of palm oil and palm oil products. J. Am. Oil Chem. Soc. **66** (1989) 693–697.

[31] *V. D'Souza, J. deMan, L deMan*: Short spacing and polymorphic forms of natural and commercial solid fats: a review. J. Am. Oil Chem. Soc. **67** (1990) 835–843.

[32] *F. Young*: Palm kernel and coconut oils: analytical characteristics, process technology and uses. J. Am. Oil Chem. Soc. **60** (1983) 326A–331A.

[33] *B. Wainwright*: Oils and fats for confections. An update. Manuf. Confect. **80** (2000) 65–76.

[34] *J. Rossell*: Fractionation of lauric fats and disposal of by-products. Symposium Proceedings **32** (1985) 30–41.

[35] *J. Maarsen*: Edible and uses of coconut and palm kernel oils. Proceedings of "Symposium Palm kernel and coconut oils". The british food manufacturing industries research association **32** (1985) 53–60.

[36] *S. Sabariah, A. Ali, C. Chong*: Chemical and physical characteristics of cocoa butter substitutes, milk fat and Malaysian cocoa butter blends. J. Am. Oil Chem. Soc. **75** (1998) 905–910.

[37] *M. Bockisch*: Fats and oils handbook. AOCS Press, Champaign, IL (USA) 1998.

[38] *S. Williams, K. Ransom-Painter, R. Hartel*: Mixtures of palm kernel oil with cocoa butter and milk fat in compound coatings. J. Am. Oil Chem. Soc. **74** (1997) 357–366.

[39] *K. Ransom-Painter, S. Williams, R. Hartel*: Incorporation of milk fat and milk fat fractions into compound coatings made from palm kernel oil. J. Dairy Sci. **80** (1997) 2237–2248.

[40] *J. Rossell*: Differential scanning calorimetry of palm kernel oil products. J. Am. Oil Chem. Soc. **52** (1975) 505–511.

[41] *U. Riiner*: Investigation of the polymorphism of fats and oils by temperature programmed X-ray diffraction. Lebensm.-Wiss. Technol. **3** (1970) 101–106.

[42] *J. B. Rossell*: Fractionation of lauric oils. J. Am. Oil Chem. Soc. **62** (1985) 385–390.

[43] *R. Timms*: Physical properties of oils and mixtures of oils. J. Am. Oil Chem. Soc. **62** (1985) 241–249.

[44] *B. Campbell, S. Pavlasek*: Dairy products as ingredients in chocolate and confections. Food Technol. **74** (1987) 78–85.

[45] *C. Bystrom, R. Hartel*: Evaluation of milk fat fractionation and modification techniques for creating cocoa butter Replacers. Lebensm.-Wiss. Technol. **27** (1994) 142–150.

[46] *R. Hartel*: Applications of milk-fat fractions in confectionery products. J. Am. Oil Chem. Soc. **73** (1996) 945–953.

[47] *K. Kaylegian*: Milkfat fractions in chocolate. Manuf. Confect. **78** (1998).

[48] *F. Lavigne, M. Ollivon*: La matière grasse laitière et ses fractions. Ol., Corps Gras, Lipides **4** (1997) 212–219.

[49] *E. ten Grotenhuis, G. A. van Aken, K. F. van Malssen, H. Schenk*: Polymorphism of milk fat studied by differential scanning calorimetry and real-time X-ray powder diffraction. J. Am. Oil Chem. Soc. **76** (1999) pp. 1031–1039.

[50] *B. Breitschuh, E. Windhab*: Parameters influencing cocrystallization and polymorphism in milk fat. J. Am. Oil Chem. Soc. **75** (1998) 897–904.

[51] *M. H. Gordon, F. B. Padley, R. E Timms*: Factors influencing the use of vegetable fats in chocolate. Fette, Seifen, Anstrichm. **81** (1979) 116–121.

[52] *S. Williams*: M. S. Thesis, University of Wisconsin, 1996.

[53] *Y. Zeng, P. Braun, E. Windhab*: Tempering, continuous precrystallization of chocolate with seed cocoa butter crystal suspension. Manuf. Confect. **82** (2002) 71–80.

[54] *N. Garti, K. Sato*: Crystallization Processes in Fats and Lipid Systems. Marcel Dekker, New York (USA) 2001.

[55] *S. Beckett*: Industrial Chocolate Manufactures and Use, 2nd edn. Blackie Academic and Professional, Glasgow (United Kingdom) 1994, pp. 242–257.

[56] *L. R. Cook*: Chocolate Production and Use. Catalog and book division, New York (USA) 1964.

[57] *W. Pratt-Johnson*: Conching, Factors affecting chocolate quality. Manuf. Confect. **67** (1987) 52–56.

[58] *N. Gerhard*: Tempering, Coating and cooling of chocolate. Manuf. Confect. **59** (1979) 48–56.

[59] *O. Jocanovic, D. Karlovic, J. Jakovljevic*: Chocolate precrystallization: A review. Acta Aliment. **24** (1995) 225–239.

[60] *N. Kempf*: Crystallization of Cocoa Butter and its Effects on the Properties of Chocolate. In: Industrial Chocolate Manufacture and Use. Blackwell Science Publisher, York (UK) 1949.

[61] *J. Kleinert*: The relationship between temper and cocoa butter constants. Rev. Int. Choc. **20** (1965) 42–57.

[62] *J. Kleinert*: Cocoa butter and chocolate: The correlation between tempering and structure. Rev. Int. Choc. **25** (1970) 386–399.

[63] *E. Seguine*: Tempering – the inside story. Manuf. Confect. **71** (1991) 118–125.

[64] *G. Bigalli*: Practical aspects of the eutectic effect on confectionery fats and their mixtures. Manuf. Confect. **68** (1988) 65–80.

[65] *G. Hogenbirk*: Compatibility of specialty fats with cocoa butter. Manuf. Confect. **64** (1984) 59–63.

[66] *A. C. Noorden*: Fat bloom – causes and prevention when using lauric hard butters. Susswaren Tech. u. Wirtschaft **26** (1982) 318–322.

[67] *E. Seguine*: Diagnosing chocolate bloom. Manuf. Confect. **81** (2001) 45–50.

[68] *G. Hogenbirk*: The influence of milk fat on the crystallization properties of cocoa butter and cocoa butter alternatives. Manuf. Confect. **70** (1990) 133–140.

[69] *J. Schmelzer, R. Hartel*: Interactions of milk fat and milk fat fractions with confectionery fats. J. Dairy Sci. **84** (2001) 332–344.

[70] *R. Whymper, A. Bradley*: The setting of cocoa butter with special reference to the development of bloom on the chocolate. J. Soc. Chem. Ind. **XLIV** (1925) 77–86.

[71] *M. Wootton, D. Weeden, N. Munk*: Mechanism of fat migration in chocolate enrobed goods. Chem. Ind. **32** (1970) 1052–1054.

[72] *G. Ziegleder, C. Moser, J. Geir-Greguska*: Kinetics of fat migration within chocolate products, Part I: Principles and analytics. Fett/Lipid **98** (1996) 196–199.

[73] *G. Ziegleder, C. Moser, J. Geier-Greguska*: Kinetics of fat migration within chocolate products. Part II: Influence of storage temperature, diffusion coefficient, solid fat content. Fett/Lipid **98** (1996) 253–256.

[74] *G. Ziegleder*: Fat migration and bloom. Manuf. Confect. **77** (1997) 43–44.

[75] *P. Couzens, H. Wille*: Fat migration in composite confectionery products. Manuf. Confect. **77** (1997) 45–47.

[76] *J. Wacquez*: Fat migration into enrobing chocolate. Manuf. Confect. **55** (1975) 19–23.

[77] *H. Chaveron, M. Ollivon, H. Adenier*: Blanchiment gras. Migration des matières grasses dans les produits composites. Chocolaterie-confiseries de Frances **328** (1976) 3–11.

[78] *H. Adenier, M. Ollivon, H. Chaveron*: Le blanchiment gras. II. Etude de la fraction liquide. Choc., Confiserie Fr. **322** (1976) 18–22.

[79] *J. Kleinert*: Studies on the formation of fat bloom and methods of delaying it. Rev. Int. Choc. **16** (1962) 201–219.

[80] *A. Hettich*: Experimental basis for the definition of "proper" chocolate temper. Manuf. Confect. **46** (1966) 29–36.

[81] *C. Loisel, G. Lecq, G. Keller, M. Ollivon*: Fat bloom and chocolate structure studied by mercury porosimetry. J. Food Sci. **62** (1997) 781–788.

[82] *H. von Drachenfels, J. Kleinert, E. Hanssen*: A new method of preventing fat bloom. Rev. Int. Choc. **XVII** (1962) 409–410.

[83] *M. Wennermark, M. Carlsson*: How processing conditions affect the appearance of fat bloom. Paper presented at the Specialty Fats Seminar, Orlando, FL (USA) 1994.

[84] *M. Sachsse, J. Rosenstein*: Über den Fettreif der Schokolade I. J. Fette Seifen **55** (1953) 26–29.

[85] *M. Sachsse, J. Rosenstein*: Über den Fettreif der Schokolade II. J. Fette Seifen **55** (1953) 122–124.

[86] *H. Adenier, M. Ollivon, R. Perron, H. Chaveron*: Le blanchiment gras. I Observations et commentaires. Choc., Confiserie Fr. **315** (1975) 7–23.

[87] *A. Ali, J. Selamat, Y. Che Man, A. Suria*: Effect of storage temperature on texture, polymorphic structure, bloom formation and sensory attributes of filled dark chocolate. Food Chem. **72** (2001) 491–497.

[88] *D. Cebula, G. Ziegleder*: Studies of bloom formation using X-ray diffraction from chocolates after long-term storage. Fat Sci. Technol. **95** (1993) 340–343.

[89] *N. Easton, D. Kelly, L. Bartron, S. Cross, W. Griffin*: The use of modifiers in chocolate to retard fat bloom. Food Technol. **6** (1952) 21–25.

[90] *J. Cerbulis*: The effect of various substances on the blooming of chocolate. J. Food Technol. **4** (1969) 133–140.

[91] *W. Andersson*: Fat bloom and phase changes. Rev. Int. Choc. **18** (1963) 92–98.

[92] *J. DuRoss, W. Knightly*: Relationship of sorbitan monostearate and polysorbate 60 to bloom resistance in properly tempered chocolate. Manuf. Confect. **45** (1965) 50–56.

[93] *L. Campbell, P. Keeney*: Developments in fat bloom research on dark chocolate coatings. Manuf. Confect. **48** (1968) 77–82.

[94] *L. Campbell, P. Keeney*: Temper level effects on fat bloom formation on dark chocolate coatings. Food Technol. **33** (1968) 1150.

[95] *I. Hachiya, T. Koyano, K. Sato*: Seeding effects on crystallisation behavior of cocoa butter. Agric. Biol. Chem. **53** (1989) 327–332.

[96] *I. Hachiya, T. Koyano, K. Sato*: Seeding effects on solidification behavior of cocoa butter and dark chocolate. I. Kinetics of solidification. J. Am. Oil Chem. Soc. **66** (1989) 1757–1762.

[97] *I. Hachiya, T. Koyano, K. Sato*: Seeding effects on solidification behavior of cocoa butter and dark chocolate. II. Physical properties of dark chocolate. J. Am. Oil Chem. Soc. **66** (1989) 1763–1770.

[98] *T. Koyano, I. Hachiya, K. Sato*: Fat polymorphism and crystal seeding effects on fat bloom stability of dark chocolate. Food Struct. **9** (1990) 231–240.

[99] *A. Jana, P. Thakar*: Fat bloom in chocolates and confectionery coatings – a review. Indian Food Ind. **12** (1993) 33–39.

[100] *J. Bricknell, R. Hartel*: Relation of fat bloom in chocolate to polymorphic transition of cocoa butter. J. Am. Oil Chem. Soc. **75** (1998) 1609–1615.

[101] *M. Lohman, R. Hartel*: Effect of milk fat fractions on fat bloom in dark chocolate. J. Am. Oil Chem. Soc. **71** (1994) 267–275.

[102] *R. Tietz, R. Hartel*: Effects of minor lipids on crystallization of milk fat – cocoa butter blends and bloom formation in chocolate. J. Am. Oil Chem. Soc. **77** (2000) 763–771.

[103] *W. Duck*: The measurement of unstable fat in finished chocolate. Gordian **67** (1967) 28–31.

[104] *S. Vaeck*: Cacao butter and fat bloom. Manuf. Confect. **40** (1960) 35–74.

[105] *G. Jewell*: Some observations on bloom on chocolate. Rev. Int. Choc. **27** (1972) 161–162.

[106] *S. M. Hodge, D. Rousseau*: Fat bloom formation and characterization in milk chocolate observed by atomic force microscopy. J. Am. Oil Chem. Soc. **79** (2002) 1115–1121.

[107] *T. Kawada, S. Suzuki, F. Kamata, N. Matsui*: The study of lauric hard butter. II. Fat bloom. J. Jpn. Oil Chem. Soc. **20** (1971) 332–335.

[108] *T. Kawada, S. Suzuki, F. Kamata, N. Matsui*: Studies on lauric hard butter. III. Fat bloom (2). J. Jpn. Oil Chem. Soc. **20** (1971) 807–810.

[109] *T. Arishima, T. Mc Brayer*: Application of specialty fats and oils. Manuf. Confect. **82** (2002) 65–76.

[110] *P. Lonchampt, R. W. Hartel*: The sugar/fat interactions during bloom of under- and over-tempered chocolates. 2nd Euro Fed Lipids November 6–8, Strasbourg (France) 2002.

[111] *P. Lonchampt, R. W. Hartel*: Sugar/Fat Interactions during Bloom Formation of Under- and Non-Tempered Chocolates. 94th American Oil Chemists' Society Annual Meeting and Expo May 4–7, Kansas City, Missouri (USA) 2003.

[112] *J. Cerbulis, C. Clay, H. Mack*: The composition of bloom fat in chocolate. J. Am. Oil Chem. Soc. **34** (1957) 533–537.

[113] *H. Neville, N. Easton, L. Bartron*: The problem of chocolate bloom. Food Technol. (1950) 439–441.

[114] *E. Steiner, A. Bonar*: Separation of some glycerides of cocoa butter by paper chromatography. J. Sci. Food Agric. **12** (1961) 247–250.

[115] *H. Adenier, H. Chaveron, M. Ollivon*: Mechanism of Fat Bloom Development on Chocolate. In: Shelf Life Studies of Foods and Beverages. Chemical, Biological, Physical and Nutritional Aspects. Ed. *G. Charalambous*, Elsevier, Amsterdam (Netherlands) 1993, pp. 353–389.

[116] *C. Loisel*: Ph. D. thesis, University of Paris (France) 1998.

[117] *G. Ziegleder, J. Geier-Greguska, J. Grapin*: HPLC-analysis of bloom. Fat Sci. Technol. **96** (1994) 390–394.

[118] *J. Rossel*: Phase diagrams of triglyceride systems. Adv. Lipid Res. **5** (1967) 353–408.

[119] *L. Wesdorp*: Lipid-multiple solid phase equilibria in fats. Theory and experiments. Ph. D. thesis, University of Delft, Delft (The Netherlands) 1990.

[120] *R. Timms*: Oil and fat interactions, theory, problems and solutions. Manuf. Confect. **82** (2002) 50–64.

[121] *B. Liang, R. W. Hartel*: Fat bloom in compound coatings containing palm kernel oil, 94th American Oil Chemists' Society Annual Meeting and Expo May 4–7, Kansas City, Missouri (USA) 2003.

[122] *F. Paulicka*: Hard butter research relates lipid system's phase behavior, fat bloom. Candy Ind. **9** (1970) 5–7.

[123] *R. S. Khan, S. M. Hodge, D. Rousseau*: Morphology of surface pores in milk chocolate. 94th American Oil Chemists' Society Annual Meeting and Expo May 4–7, Kansas City, Missouri (USA) 2003.

[124] *M. Weyland*: Cocoa butter fractions: A novel way of optimizing chocolate performance. Manuf. Confect. **72** (1992) 51–55.

[125] *M. Wennermark, G. Kruiver*: The mechanisms of fat bloom formation in different fat systems. Specialty Fats Seminar May 15–17, Karlshamns Orlando FL (USA) 1994.

[126] *F. Padley, C. Paulussen, C. Soeters, D. Tresser*: The improvement of chocolate using mono-unsaturated triglycerides SOS and POS. Rev. Int. Choc. **27** (1972) 226–228.

[127] *W. Guice, N. Lovegren, R. Feuge*: Addition of Hydrogenated fats to chocolate to improve heat resistance. J. Am. Oil Chem. Soc. **36** (1959) 4–8.

[128] *L. Campbell, D. Andersen, P. Keeney*: Hydrogenated milk fat as an inhibitor of the fat bloom defect in dark chocolate. J. Dairy Sci. **52** (1969) 976–979.

[129] *H. Hendrickx, H. De Moor, A. Huyghebaert, G. Janssen*: Manufacture of chocolate containing hydrogenated butterfat. Rev. Int. Choc. **26** (1971) 190–193.

[130] *P. Dimick, G. Ziegler, N. Full, S. Yella Reddy*: Formulation of milk chocolate using milk fat fractions. Australian J. Dairy Technol. **51** (1996) 123–126.

[131] *R. Timms, J. Parekh*: The possibilities for using hydrogenated fractionated or interesterified milk fat chocolate. Lebensm.-Wiss. Technol. **13** (1980).

[132] *G. Jewell, L. Bradford*: Considerations in chocolate formulation. Manuf. Confect. **61** (1981) 26–30.

[133] *S. Metin, R. Hartel*: Thermal analysis of isothermal crystallization kinetics in blends of cocoa butter with milk fat or milk fat fractions. J. Am. Oil Chem. Soc. **75** (1998) 1617–1624.

[134] *M. Weyland*: Functional effects of emulsifiers in chocolate. Manuf. Confect. **74** (1994) 111–117.

[135] *E. Wilson*: Emulsifiers and their effect on confectionery fats. Manuf. Confect. **79** (1999) 83–88.

[136] *J. Rossell*: Fractionation of lauric oils. J. Am. Oil Chem. Soc. **62** (1985) 385–390.

[137] *T. Katsugari*: Japan Patent JP 11092780 (1999).

[138] *S. Maruzeni, H. Yokobori*: Japan Patent 61040745 (1986).

[139] *N. Suwa, N. Shirota*: Japan Patent 89-71459 (1990).

[140] *N. Suwa, N. Shirota*: Japan Patent 03285644 (1991).

[141] *F. Padley*: European Patent 427309 (1991).

[142] *K. Hokuyo, M. Hayashi, S. Yamaguchi, T. Izumi*: European Patent 676146 (1995).

[143] *H. Gunji, H. Kida, Y. Tashiro, Y. Ebihara*: Japan Patent 05168412 (1993).

[144] *S. Oka, R. Oishi*: Japan Patent 03247240 (2002).

[145] *S. Okada, S. Kometani, T. Nishimura, T. Nakae, H. Takii*: Japan Patent 2001029014 (2001).

[146] *K. Kitabi, Y. Hayashi, S. Yamaguchi, T. Izumi*: Japan Patent 08056572 (1996).

[147] *M. Landis*: Emulsifier to influence crystallization. Paper presented at the Kharlshamns – oils and fats academy, May 15–17, Orlando, FL (USA) 1994.

[148] *D. Johansson, B. Bergenstahl*: The influence of food emulsifiers on fat and sugar dispersions in oils. I. Adsorption, sedimentation. J. Am. Oil Chem. Soc. **69** (1992) 705–717.

[149] *D. Johansson, B. Bergenstahl*: The influence of food emulsifiers on fat and sugar dispersions in oils. II. Rheology, colloidal forces. J. Am. Oil Chem. Soc. **69** (1992) 718–727.

[150] *A. Dedinaite, P. Claesson, B. Campbell, H. Mays*: Interaction between modified mica surfaces in triglyceride media. Langmuir **14** (1998) 5546–5554.

[151] *W. Siew, W. Ng*: Effect of diglycerides on the crystallisation of palm oleins. J. Sci. Food Agric. **71** (1996) 496–500.

[152] *P. Smith, M. Povey*: The effect of partial glycerides on trilaurin crystallization. J. Am. Oil Chem. Soc. **74** (1997) 169–171.

[153] *C. Savage, P. Dimick*: Influence of phospholipids during crystallization of hard and soft cocoa butters. Manuf. Confect. **75** (1995) 127–132.

[154] *H. Kattenberg*: The quality of cocoa butter. Manuf. Confect. **61** (1981) 32–38.

[155] *N. Garti, J. Schlichter, S. Sarig*: Effect of food emulsifiers on polymorphic transitions of cocoa butter. J. Am. Oil Chem. Soc. **63** (1986) 230–236.

[156] *J. Schlichter, N. Garti, S. Sarig*: The bleaching of chocolate in relation to polymorphism of cocoa butter. Ind. Aliment. **23** (1984) 871–877.

[157] *D. Cebula, K. Smith*: Differential scanning calorimetry of confectionery fats. Part II – Effects of blends and minor components. J. Am. Oil Chem. Soc. **69** (1992) 992–998.

[158] *D. Arruda, P. Dimick*: Phospholipid composition of lipid seed crystal isolates from ivory coast cocoa butter. J. Am. Oil Chem. Soc. **68** (1991) 385–390.

[159] *N. Krog*: Functions of emulsifiers in food systems. J. Am. Oil Chem. Soc. **54** (1977) 124–131.

[160] *N. Garti, E. Wellner, S. Sarig*: Effect of food emulsifiers on crystal structure and habit of stearic acid. J. Am. Oil Chem. Soc. **58** (1981) 1058–1060.

[161] *K. Kawamura*: The DSC thermal analysis of crystallization behavior in palm oil II. J. Am. Oil Chem. Soc. **57** (1980) 48–52.

[162] *M. Herrera, F. Marquez Rocha*: Effects of sucrose ester on the kinetics of the polymorphic transition in hydrogenated sunflower oil. J. Am. Oil Chem. Soc. **73** (1996) 321–326.

[163] *L. Hernqvist, B. Herslöf, K. Larsson, O. Podlaha*: Polymorphism of rapeseed oil with a low content of erucic acid and possibilities to stabilize the β'-crystal form in fats. J. Sci. Food Agric. **32** (1981) 1197–1202.

[164] *L. Hernqvist, K. Anjou*: Diglycerides as a stabilizer of the β'-crystal form in margarines and fats. Fette, Seifen, Anstrichm. **85** (1983) 64–66.

[165] *T. Nakae, T. Kometani, T. Nishimura, H. Takii, S. Okada*: Effect of glycolipid fraction on fat bloom in dark and milk chocolates. Food Sci. Technol. Res. **6** (2000) 269–274.

[166] *G. Talbot*: Chocolate fat bloom – the cause and the cure. Int. Food Ingredients **23** (1994) 50–57.

[167] *L. van Dongen*: An end to fat bloom? Source **Issue 14** (1994) 4–5.

[168] *T. Koyano, I. Hachiya, K. Sato*: Phase behavior of mixed systems of SOS and OSO. J. Am. Oil Chem. Soc. **96** (1992) 10514–10520.

[169] *T. Koyano, I. Hachiya, K. Sato*: Physical properties of equally mixed systems of 1,3-dioleoyl-2-stearoylglycerol/Cocoa butter and 1,3-dioleoyl-2-stearoylglycerol-added dark chocolate. J. Jpn. Oil Chem. **G8** (1993) 184–189.

[170] *W. Veatch: US Patent 2188489 (1940).*

[171] *A. Sarotti*: German patent 744863 (1943).

[172] *R. Hartel*: Chocolate: Fat bloom during storage. The influence of structural elements. Manuf. Confect. **79** (1999) 89–99.

[173] *T. R. Noel, R. Parker, S. G. Ring*: Effect of molecular structure and water content on the dielectric relaxation behavior of amorphous low molecular weight carbohydrates above and below their glass transition. Carbohydr. Res. **329** (2000) 839–845.

[174] *R. Tromp, R. Parker, S. Ring*: A neutron scattering study of the structure of amorphous glucose. J. Chem. Phys. **107** (1997) 6038–6049.

[175] *B. Minifie*: Bloom, microbiological and other spoilage problems. Choc., Cocoa Confect. **69** (1989) 495–518.

[176] *W. Duck*: Viscosity increase due to solid fat in tempering chocolate. Manuf. Confect. **38** (1958) 9–12.

[177] *I. Hachiya, T. Koyano, K. Sato*: Observation of seeding effects on fat bloom of dark chocolate. Food Microstruct. **8** (1989) 257–261.

[178] *E. Seguine*: Putting it all together or think like the fat! AACT technical conference, St. Charles, IL (USA) 1994.

[179] *M. H. Mineau*: Stockage aux basses températures de chocolats et articles de confiserie. Revue générale du froid (1978) 91–93.

[180] *P. Dimick, D. Manning*: Thermal and compositional properties of cocoa butter during static crystallization. J. Am. Oil Chem. Soc. **64** (1987) 1663–1669.

[181] *T. Davis, P. Dimick*: Isolation and thermal characterization of high-melting seed crystals formed during cocoa butter solidification. J. Am. Oil Chem. Soc. **66** (1989) 1488–1493.

[182] *T. Davis, P. Dimick*: Lipid composition of high-melting seed crystals formed during cocoa butter solidification. J. Am. Oil Chem. Soc. **66** (1989) 1494–1498.

[183] *D. Manning, P. Dimick*: Crystal morphology of cocoa butter. Food Microstruct. **4** (1985) 249–265.

[184] *S. Chaiseri, P. Dimick*: Dynamic crystallization of cocoa butter. Characterization of simple lipids in rapid- and slow-nucleating cocoa butters and their seed crystals. J. Am. Oil Chem. Soc. **72** (1995) 1491–1496.

[185] *K. Becker*: Über die Fettreif-Bildung bei Schokoladen und Pralinen. Fette, Seifen, Anstrichm. **59** (1957) 636–644.

[186] *A. Herzing*: Eutectic effects of fats. Manuf. Confect. **69** (1989) 83–87.

[187] *W. Reinders, C. Doppler, E. Oberg*: On the melting and solidifying of cocoa butter. Recueil chimique des Pays Bas **LI** (1932) 917–939.

[188] *S. Duce, T. Carpenter, L. Hall*: Nuclear magnetic resonance imaging of chocolate confectionery and the spatial detection of polymorphic states of cocoa butter in chocolate. Lebensm.-Wiss. Technol. **23** (1990) 545–549.

[189] *T. Guiheneuf, P. Couzens, H. Wille, L. Hall*: Visualization of liquid triacylglycerol migration in chocolate by magnetic resonance imaging. J. Sci. Food **73** (1997) 265–273.

[190] *J. Musser*: Gloss on Chocolate and Confectionery Coatings. In: Proceedings of the 27th PMCA Production Conference, PMCA publisher, Lancaster, PA (USA) 1973, pp. 46–50.

[191] *G. Ziegleder*: Fat migration and bloom. Manuf. Confect. **77** (1997) 43–44.

[192] *H. Matsuda, M. Yamaguchi, H. Arima*: Separation and Crystallization of Oleaginous Constituents in Cosmetics: Sweating and Blooming. In: Crystallization Processes in Fats and Lipid Systems. Eds. *N. Garti, K. Sato*, Marcel Dekker, New York (USA) 2001, pp. 485–504.

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