Polymorphism and Phase Transitions of Cocoa Butter: Composition, Crystallization, and Implications for Chocolate Quality

Abstract

Cocoa butter is the main fat in chocolate and is responsible for its texture, gloss, melting behavior, and shelf stability. These properties arise from its specific triacylglycerol composition and its ability to crystallize into several polymorphic forms. Among these forms, Form V is the most desirable for chocolate production, while conversion to the more stable Form VI is closely linked to fat bloom. This review summarizes current knowledge on the polymorphism and phase transitions of cocoa butter, with emphasis on the roles of triacylglycerol composition, geographical origin, and processing conditions such as cooling rate, thermal history, and tempering. The review also discusses memory effects in cocoa butter and their relevance to industrial tempering and bloom control. In addition, recent advances in analytical techniques, including differential scanning calorimetry, X-ray diffraction, and Raman spectroscopy, are outlined for their use in identifying and monitoring polymorphic forms. A clear understanding of these factors is essential for improving chocolate quality, enhancing processing control, and reducing the risk of fat bloom during storage.

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But still Slightly descriptive; could emphasize novel synthesis and gaps

Keywords: - Cocoa butter; Polymorphism; Phase transition; Triacylglycerols; Tempering; Fat bloom; Chocolate quality

1. Introduction

Cocoa butter is an essential ingredient in the chocolate industry and known for its unique physical and thermal characteristics. Cocoa butter predominately consists symmetrical-triglyceride composition and a melting range of 32-35°C, which makes it semi-solid at room temperature. Almost 80% of its triglycerides consist of mainly three large triglycerides: 1,3-dipalmitoyl-2-oleoyl-glycerol (POP), 1-palmitoyl-2-oleoyl-3-stearoyl-glycerol (POS), and 1,3-distearoyl-2-oleoyl-glycerol (SOS) (Loisel et al., 1998). Among these three, POS is very dominant in regulating the polymorphic behaviour of cocoa butter and improve functionality in chocolate products. The unique ability of cocoa butter to crystallize in different states is mainly responsible for the texture, stability, and sensory properties of chocolate. This characteristic molecular arrangement confers cocoa butter a sharp melting range close to human body temperature (32-35 °C), enabling chocolate to remain solid at ambient conditions while melting rapidly in the mouth (Shukla, 1995). The polymorphic behaviour of cocoa butter is linked to its TAG composition and processing conditions such as cooling rate, shear, thermal history, and storage temperature (Van Malssen et al., 1996; Marangoni & McGauley, 2003). In addition, the composition of TAG also varies with geographical origin which affects crystallization kinetics, polymorphic stability, and tempering requirements (Chaiseri & Dimick, 1989; Ghazani & Marangoni, 2021). The polymorphic characteristics of POP and SOS have been well documented, and very little research has been conducted on the polymorphic properties of POS (Ghazani & Marangoni, 2021).

Advances in analytical techniques have substantially improved the understanding of cocoa butter crystallization and polymorphism. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) have long been used to characterize thermal transitions and crystalline structures. Recent applications of Raman spectroscopy have enabled detailed molecular-level differentiation between polymorphic forms, particularly Forms V and VI (Bresson et al., 2011; Simone et al., 2023). These complementary techniques provide valuable insights into phase transitions, structural rearrangements, and order-disorder phenomena, supporting improved

control of chocolate processing and storage stability. This review aims to provide a comprehensive and integrated overview of cocoa butter polymorphism, emphasizing the molecular mechanisms underlying phase transitions. It also describes the influence of TAG composition and geographical origin, and the implications for chocolate quality. Particular attention is given to the role of POS in polymorphic behaviour, the application of advanced analytical techniques, and the relationship between tempering, polymorphic stability, and fat bloom formation.

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This introduction is Condense repetition.
Please move foundational explanations to earlier sections and focus later sections on mechanistic depth and implications to improve transitions between sections to guide the reader

2. Chemical Composition of Cocoa Butter

Cocoa butter is the lipid fraction extracted from the seeds of *Theobroma cacao* and is widely recognized as one of the most structurally distinctive fats used in food systems. It forms the continuous fat phase of chocolate and is largely responsible for its characteristic texture, gloss, snap, and melting behaviour (Ribeiro et al., 2012). Cocoa butter is used as a key ingredient in chocolate industry due to its unique properties. It consists of symmetrical triglycerides, with over 75% of oleic acid at the sn-2 position. Approximately 20% of its triglycerides remain liquid at room temperature, and it starts to soften in a temperature range of 30-32°C (Shukla, 1995). The physical and thermal characteristics of cocoa butter are depended upon composition of triglycerides (TAG). Unlike other animal fats, which contain complex mixtures of triglycerides, cocoa butter has a simpler structure. It is made up of mainly three types of triglycerides: saturated, monounsaturated, and polyunsaturated. Among these, monounsaturated triglycerides dominate, and contribute to more than 80% of the total content (Loisel *et al*., 1998) as discussed in Table:1

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Could better connect composition to later polymorphic transitions

Table:1 Composition of cocoa butter (%w/w)

Triacylglycerol	Cocoa butter (%w/w)
POL	0.5
PLP	1.4
PLS	2.3
POO	2.8
POP	15.4
PPP	0.4
SOO	3.1
SLS	1.2
POS	38.8
PPS	0.5
SOS	27.7
PSS	0.6
SOA	1.6
SSS	0.3

Source: Ghazani & Marangoni, (2021)

Abbreviations: P- Palmitic acid; O- Oleic acid; L- Linoleic acid; S- Stearic acid; A- Arachidic acid.

Among all TAG, 1,3-Dipalmitoyl-2-oleoyl-glycerol (POP), 1-Palmitoyl-2-oleoyl-3-stearoyl-glycerol (POS), 1,3-Distearoyl-2-oleoyl-glycerol (SOS) are three major triglycerides present in cocoa butter which contribute up to 80% of total triglycerides composition. The distinct melting and crystallization characteristics of cocoa butter are mainly due to its triglyceride composition. The fatty acid profile of cocoa butter consists mainly of palmitic acid (C16:0), stearic acid (C18:0), and oleic acid (C18:1), which together account for approximately 95% of

total fatty acids (Loisel et al., 1998). The relatively high proportion of long-chain saturated fatty acids would ordinarily yield a rigid, high-melting fat. However, the near-universal incorporation of oleic acid into cocoa butter TAGs depresses the overall melting range to approximately 32-35 °C. Linoleic and arachidic acids occur only in minor amounts but contribute to plasticity and influence oil migration behavior during storage (Mustiga et al., 2019). The functional uniqueness of cocoa butter arises not only from its fatty acid composition but also from the highly ordered regiospecific arrangement of these acids on the glycerol backbone. Natural cocoa butter exhibits a strongly non-random sn-1,3-saturated and sn-2-unsaturated (SUS) configuration. In this configuration, palmitic and stearic acids occupy the outer positions while oleic acid is esterified almost exclusively at the sn-2 position (Jia et al., 2019). This arrangement enhances molecular packing efficiency and promotes the formation of stable crystalline lattices. This positional specificity also influences lipid digestion. Pancreatic lipase mainly breaks down fatty acids at the sn-1 and sn-3 positions of triacylglycerols, releasing saturated fatty acids that are absorbed less efficiently. On the other side, sn-2 oleic acid remains as a monoacylglycerol and is readily absorbed. The released free stearic and palmitic acids often react with calcium and magnesium in the gut to form insoluble salts that are excreted rather than absorbed. This mechanism explains why cocoa butter has a relatively neutral effect on serum cholesterol despite its high saturated fat content (Stonehouse et al., 2020).

The molecular arrangement of these triglycerides enables cocoa butter to adopt different crystalline forms. This polymorphic behaviour is key to its functional properties in chocolate and other food applications. Investigating the polymorphic behaviour of triglycerides, mainly POS, will provide important insights into chocolate crystal structure, polymorphism, melting behaviour, and stability (Ghazani & Marangoni, 2021).

3. Influence of geographical origin on cocoa butter composition

The triglyceride composition of cocoa butters from different geographical origins. A total of 64 samples were analysed that included 15 from South America, 8 from North and Central America (one sample was from Mexico), 17 from Africa, and 24 from Asia (20 from Malaysia). The results showed that the level of POP triglycerides did not differ significantly from region to region. The levels of POS triglycerides were significantly higher in the cocoa butters from Asia than in cocoa butters from South America which had the lowest levels. Levels of SOS triglycerides were highest in cocoa butters from Asia, then Africa cocoa butters followed by America containing the least SOS triglycerides. Some other triglycerides such as POO and SOO had significant regional differences in concentration, Asian cocoa butters containing the least concentration, African samples containing medium levels, and cocoa butters from the Americas sample containing the highest concentrations (Chaiseri and Dimick, 1989) These studies concluded the effect of geographic origin on the chemical composition of cocoa butter and significant differences were noted between regions which are summarized in Table: 2. Environmental temperature during pod development (approximately 95 to 115 days after pollination) strongly modulates desaturase activity, with higher temperatures favoring saturated fatty acid accumulation and producing harder cocoa butter (Mustiga et al., 2019).

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Table:2 Triglyceride composition of cocoa butter across geographical origins

Triglycerides	South America (%)	North and Central America (%)	Africa (%)	Asia (%)
POP	19.0	18.6	18.4	18.6
POS	38.0	38.9	39.1	40

SOS	26.0	26.9	28.2	30.8
AOS	0.5	0.6	0.6	0.8
POO	34	2.7	2.2	1.2
SOO	5.7	5.3	4.7	2.9
PLP	1.1	1.0	1.0	0.8
PLS	3.5	3.3	3.2	2.9
SLS	2.8	2.7	2.5	2.2

Source: (Chaiseri & Dimick, 1989)

4. Polymorphism in Cocoa Butter

Polymorphism is the capacity of a substance to crystallize into multiple distinct forms, primarily alpha (α), beta-prime (β′), and beta (β). Each form consists of a unique arrangement of molecules in the solid state. This phenomenon occurred due to variations in temperature, pressure, and cooling rates of the material. Wille and Lutton (1966) conducted a study on the polymorphic behaviour of cocoa butter, and identifying six different crystalline forms, labelled I to VI, arranged in order of their increasing stability as shown in Table:3. It was observed that Form I is least stable, and has the lowest melting point (17.3°C), while Form VI, was found most stable with melting point of 36.3°C. Moreover, Form VI does not crystallize directly from the melting of cocoa butter but, it gradually converted to from less stable Form V. This transition involves only minor structural changes, and no significant differences were observed in X-ray diffraction patterns. Among all polymorph states, Form V is most acceptable for chocolate production, contributing to its desirable texture, glossy finish, and optimal melting properties. Van Malssen et al. (1999) reported a classification comprising five polymorphic forms, including the identification of a previously unrecognized low-melting γ (gamma) form. Subsequent studies, such as Sato and Koyano (2001) and Fessas et al. (2005), suggested the existence of six polymorphic forms of cocoa butter. Over time, Form V can convert to the more stable Form VI that leads to fat bloom. This defect involves the migration of fat crystals to the surface, which results in an unattractive whitish appearance that lowers the visual appearance and sensory quality of chocolate (Sato, 2001). Hence, understanding and controlling these polymorphic conversions is essential for achieving optimum chocolate quality and stability for a long time.

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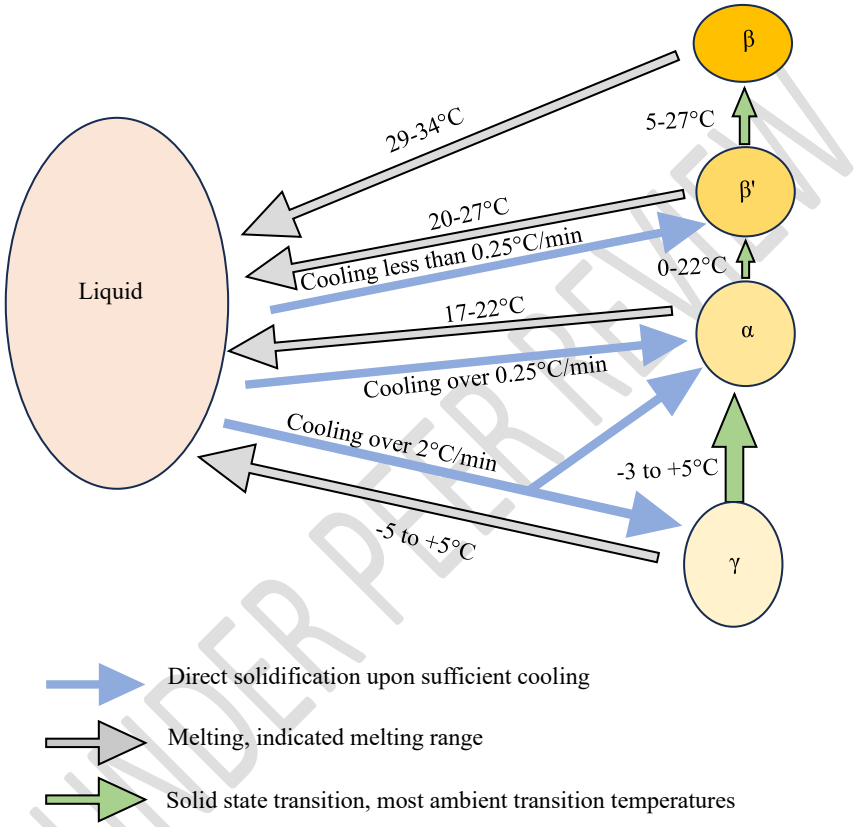
Table:3 Polymorphic forms of Cocoa butter and their melting point

Polymorphic form			**Melting Point**	
Wille & Lutton (1966)	Larsson (1966)	Van Malssen *et al.* (1999)	Wille & Lutton (1966)	Van Malssen *et al.* (1999)
Form-I	(β'_2)	γ	17.3°C	–5 to +5°C
Form-II	(α)	α	23.3°C	17–22°C
Form-III		β′ range	25.5°C	20–27°C
Form-IV	(β'_1)		27.5°C	
Form-V	(β'_2)	β-V	33.8°C	29–34°C
Form-VI	(β_1)	β-VI	36.3°C	

5. Phase transition in cocoa butter

The phase transitions of cocoa butter under static isothermal conditions, categorise into four primary polymorphic forms: γ, α, β', and β with a melting point of -5 to 5°C, 17-22°C, 20-27°C, and 29-34°C respectively. The γ, α, and β' forms crystallize directly from the melt and

subsequently undergo gradual transformation into a more thermodynamically stable form, as shown in Figure: 1 (Van Malssen *et al*., 1999). The β' form acts as a temporary intermediate phase, showing a variable X-ray diffraction patterns. Additionally, the β phase does not form directly from the melt, but it develops by the transformation of the metastable β' phase (Wille and Lutton, 1966). Furthermore, Van Malssen *et al*. (1999) suggested that, due to their slight structural variations, Forms V and VI, can be considered as subphases of the β polymorph.



Source - Van Malssen et al. (1996)

Figure: 1 Phase transition in cocoa butter

During fat crystallization, interactions among the acyl chains, methyl-end stacking, and the conformation of the glycerol backbone of triacylglycerols (TAGs) play a key role in determining polymorphic form and crystal stability. The mixing and crystallization behavior of TAG mixtures can be explained using phase diagrams, which describe the equilibrium melting behavior of binary or multicomponent TAG systems. Based on phase diagrams, four main types of mixing behavior are commonly observed: continuous solid solution, eutectic, monotectic, and molecular compound formation. In a continuous solid solution, TAGs with similar melting

temperatures, molecular structures, and polymorphic forms are completely miscible in both the liquid and solid states, resulting in a single solid phase across all compositions. A typical example is the POS-SOS system, which crystallizes in the β polymorphic form and shows a continuous change in melting temperature with composition (Sato & Ueno, 2005). In contrast, eutectic systems exhibit complete miscibility in the liquid state but limited miscibility in the solid state, as observed for POP-POO and SOS-SOO mixtures. The eutectic point corresponds to the lowest melting temperature of the mixture (Sasaki et al., 2012). Monotectic behavior represents an intermediate case between solid solution and eutectic systems, where partial miscibility occurs in the solid phase. In molecular compound formation, TAGs co-crystallize in fixed stoichiometric ratios to form a distinct crystal structure. In such systems, steric effects and packing constraints caused by the coexistence of saturated fatty acids (palmitic and stearic acids) with unsaturated oleic acid chains favor the formation of double-chain-length (2L) crystal structures. This behavior has been reported in systems such as POP-OPO, SOS-OSO, and SOS-SSO (Floeter et al., 2018).

6. Memory effects in cocoa butter

The memory effect of cocoa butter refers to the influence of its prior thermal and crystallization history on subsequent crystallization behavior, polymorphic form, and physical properties. This phenomenon arises from the persistence of stable crystal nuclei that are not eliminated during melting and can act as templates during recrystallization. In cocoa butter, the survival of such crystals leads to crystallization at low degrees of undercooling, with seed crystals enriched in tristearin rather than SOS. Only when crystal memory is retained, the stable β polymorphic form crystallizes directly from the melt. The melting points and characteristic short and long-spacing values of the various cocoa butter polymorphs, as reported by Wille and Lutton (1966), are summarized in Table:4.

Table:4. Melting points and short spacings of the different polymorphs found in cocoa butter

Polymorphs	**I (2L) sub-α**	**II (2L) α**	**III (2L) β′$_2$**	**IV (2L) β′$_1$**	**V (3L) β$_2$**	**VI (3L) β$_1$**
Melting point (°C)	17.3	23.3	25.5	27.5	33.8	36.3
Long spacings (A˚)	54.5	49	49	45	63.8	64.1
Short spacings (A˚)	4.19 (vs)	4.24 (vs)	4.62 (w)	4.35 (vs)	5.4 (m)	5.43 (m)
	3.7 (s)		4.25 (vs)	4.15 (vs)	5.15 (w)	5.15 (w)
			3.86 (s)	3.97 (m)	4.58 (vs)	4.59 (vs)
			4.62 (w)	3.81 (m)	4.23 (vvw)	4.27 (vw)
					3.98 (s)	4.04 (w)
					3.87 (m)	3.86 (m)
					3.75 (m)	3.7 (s)
					3.67 (w)	3.36 (vw)
					3.39 (vw)	NA

Abbreviations: m, medium peak intensity; NA, not available; s, strong peak intensity; vs, very strong peak intensity; vw, very weak peak intensity; vvw, very very weak peak intensity; w, weak peak intensity. Source: Wille & Lutton (1966).

From a technological perspective, the memory effect has important practical implications. When deliberately controlled, it is utilized in seed tempering, where stable Form V crystals are

introduced to direct cocoa butter crystallization. In contrast, when uncontrolled, residual crystal memory can lead to defective crystal networks, resulting in fat bloom, surface dullness, softer texture, and reduced shelf stability. Therefore, industrial tempering processes are designed to eliminate undesirable crystal memory through complete melting, typically at 45-50 °C, followed by controlled cooling and reheating to establish a new and stable crystalline structure. An understanding of the memory effect is also crucial when formulating chocolates containing cocoa butter equivalents (CBEs), cocoa butter replacers (CBRs), or milk fat, as these fats exhibit different polymorphic behaviors and can modify or weaken the inherent memory effect of cocoa butter.

7. Advanced analytical techniques for studying cocoa butter polymorphism

The cocoa industry is facing a problem in providing good cocoa butter with unique flavour and sensory qualities. This is due to its derivatives providing many health and functional benefits, which are essential for their economy. The quality of cocoa butter depends on the triglycerides and fatty acid composition (Alotaibi et al., 2024). To check the polymorphism of cocoa butter, advanced analytical tools are required, like Raman spectroscopy, Differential Scanning Calorimetry, and X-ray diffraction (XRD). In this section we are going to discuss the advanced analytical tools to study cocoa butter polymorphism.

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7.1 Raman spectroscopy

Raman spectroscopy has proven to be a powerful tool for analysing the polymorphic forms and liquid state of cocoa butter. It is a vibrational spectroscopic method that depends on the phenomenon of Raman scattering. Raman spectroscopy is commonly used in various field like, food safety assessment, quality control, and identification (detection) of adulteration in edible fats and oils. These are all possible due to its non-destructive nature, high degree of sensitivity, and real-time detection capability (Wang et al., 2021). Spectral analysis is done by raman spectroscopy in the fingerprint region, spacing 945-1600 cm^{-1} (Castro et al., 2022). The use of raman spectroscopy has enable the chocolate industry to create many different combinations of fat with specific physical and organic characteristics. Some research studies highlighted different Raman signatures in the ester carbonyl stretching region (1800-1700 cm^{-1}), enabling clear differentiation between forms V and VI, which is crucial for understanding fat bloom in chocolate. Recent literature demonstrates that form V is preferable in commercial chocolate, whereas form VI is related to fat bloom. The C-H stretching region, which ranges from 3000 to 2700 cm^{-1}, was useful in tracking order-disorder transitions. While forms IV and V exhibit changes before their melting points, form VI was stable until melting. Furthermore, this study indicated the existence of form III, and its polymorph displayed different signatures in Raman and XRD analysis. The polymorphic transitions in cocoa butter involved gradual structural changes. (Bresson, et al., 2011)

7.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is based on the precise measurement of heat flow related to melting, crystallization, and solid-solid interaction of fat crystals as a function of temperature. All polymorphic forms of cocoa butter have different characteristic like thermal stability and melting behavior. During DSC analysis, melting of polymorphic forms appears as endothermic peaks, while crystallization during cooling is observed as exothermic peaks. The quantitative nature of DSC arises from the fact that the area under each thermal peak is directly proportional to the enthalpy change (ΔH) associated with the phase transition (Sato, 2001). The polymorphs of cocoa butter melt within a specific temperature range, so integration of individual melting peaks enables estimation of the relative proportion of each polymorph present in the sample. DSC also allows quantitative monitoring of polymorphic transformations

during storage, such as the gradual conversion of Form V to Form VI, which is closely linked to fat bloom development (Afoakwa et al., 2008). This transformation is detected as a shift of the melting peak toward higher temperatures along with an increase in enthalpy associated with the more stable form.

7.3 X-ray diffraction (XRD)

X-ray diffraction (XRD) is an important structural tool for determining the crystal packing and identifying polymorphic forms in cocoa butter by measuring the position and intensity of bragg reflection (Ghazani & Marangoni, 2021). XRD tells us about the lamellar spacing, unit cell symmetry (triclinic/monoclinic/orthorhombic motifs), and the distinct peak patterns that differentiate α, β′, and β crystal families (forms I-VI). XRD can be used both qualitatively and quantitatively (Simone et al., 2023).

8. Tempering and Polymorphic Stability in Chocolate

Tempering is a crucial step in the manufacture of chocolate, where the aim is to promote the nucleation and crystallization of cocoa butter in its stable form β-V. The tempering process ensures that the fat phase crystallizes uniformly and produces optimal texture and appearance. For example, during the ice cream coating process, when the chocolate is cooled rapidly, the cocoa butter may crystallize into unstable forms. Since ice cream coatings are stored at much lower temperatures between -18°C and -20°C, no significant change was observed in the crystal form. Different research studies revealed that the β-VI form is the most stable form among other forms. Instead, crystallization into β-V is the most achievable stable form required for chocolate production conditions. The transition from β-V to β-VI is slow under normal storage, and this process can lead to fat bloom defect. During tempering, chocolate is cooled from its molten state above 50°C, where it remains fully liquid. If trisaturated triglycerides are present, they may begin to crystallize, as they do not contribute to tempering. Further cooling to 26–27°C initiates the nucleation process of both unstable β′ and stable βV forms. By raising the temperature slightly, the unstable forms melt away, leaving only the stable βV crystals to act as seeds for further crystallization (Stobbs et al., 2025). The final temperature adjustment depends on various factors, such as the fat composition of chocolate. During processing of dark chocolate, the temperature is increased to 30-31°C. This temperature rise depends upon origin of cocoa butter, lower temperature is used for South America compared to Asian countries. On the other hand, during the processing of milk chocolate temperature is kept in the range of 28-29°C because it contains 3.5% to 5% milk fat. This process ensures the formation of stable βV crystals form, which is essential for producing high-quality chocolate with the desired gloss, and resistance to fat bloom (Garti & Widlak, 2015). A clear distinction exists between dark and milk chocolate tempering behaviour. Dark chocolate, composed mainly of cocoa butter and cocoa solids, generally requires higher tempering temperatures (final tempering range ~31-32 °C) because of its higher cocoa butter content and absence of milk fat. In contrast, milk chocolate contains milk fat, which acts as a softening agent and interferes with cocoa butter crystallization by depressing melting and crystallization temperatures. As a result, milk chocolate is tempered at lower temperatures (typically 29-30 °C) and exhibits broader crystallization ranges (Afoakwa et al., 2008). These compositional differences necessitate different tempering curves to ensure adequate formation of Form V crystals. However, Cocoa butters with higher SOS content typically crystallize at higher temperatures and show increased stability of β crystals, requiring slightly higher tempering temperatures compared to butters richer in POP or POS (Ghazani & Marangoni, 2021).

9. Fat Bloom in chocolate

Fat bloom is a significant quality defect in chocolate, characterized by a grayish-whitish haze on the surface, which diminishes consumer appeal and product quality. This phenomenon mainly results from complex interactions between cocoa butter polymorphism, fat migration, and the microstructure of other chocolate components, such as sugar and milk fat (Sonwai & Rousseau, 2010).

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9.1 Polymorphic Transition and Liquid Fat Migration

Cocoa butter (CB) forms the continuous lipid phase in chocolate, in which solid particles such as cocoa solids, sugar crystals, and sometimes milk solids are dispersed (Lipkin et al., 2025). CB exhibits polymorphism, allowing it to crystallize into several forms with different melting points and stabilities. Form V is the most desirable for chocolate, providing a smooth texture and characteristic snap. During unfavorable storage conditions, it can transform into more stable but undesirable Form VI with larger crystal size (Nightingale et al., 2011; Bricknell & Hartel, 1998). These crystals are often larger than 50 μm, which scatter light diffusely, producing the characteristic whitish appearance on the chocolate surface. This process is driven by the migration of liquid triglycerides to the surface, where they recrystallize as βVI, leading to increases in the whiteness index (WI) and white area percentage (WA%) (Watanabe et al., 2021). For instance, exposure to temperatures slightly above the cocoa butter Form βV melting point (35-37 °C) followed by gradual cooling can induce fat bloom through partial de-oiling on chocolate surfaces (Sato et al., 2020). In filled chocolates, such as pralines, oil migration from the filling into the chocolate shell is considered a major driver of fat bloom (Böhme et al., 2021). The rate of temperature cycling significantly influences fat bloom formation. A faster cooling rate, for example, has been shown to retard fat bloom formation by limiting fat migration, suggesting that rate-induced crystallization behavior plays a critical role in controlling fat migration. This indicates that controlling the thermal history of chocolate products is crucial for preventing fat bloom (Zhao et al., 2025).

9.2 Role of Sugar Microstructure

The microstructure of non-fat particles, particularly sugar, significantly influences fat bloom formation and oil migration in chocolate. Chocolate is a suspension of these solid particles in a continuous cocoa butter phase. The characteristics of sugar particles, such as their size, shape, and surface properties, can affect the overall porosity and fat absorption capacity of the chocolate matrix (Shen et al., 2023). Crystalline sugar forms discrete particles within the chocolate matrix. Research indicates that modifying the surface of crystalline sugar can reduce fat bloom. Model chocolates formulated with modified sucrose surfaces showed a reduction in bloom, as evaluated by changes in whiteness index and white area percentage (Jin et al., 2024). Similarly, controlling the particle size distribution (PSD) of sucrose affects bloom formation, with reductions in the D90 particle size leading to decreased surface roughness and bloom extent (Shen et al., 2023). Amorphous sugar, on the other hand, exists in a non-crystalline, glassy state, and its direct role in fat bloom formation is less clearly defined. Replacing cocoa powder with sugar particles in chocolate model systems with different types of sugar, such as sucrose, maltitol, corn syrup solids (CSS), and polydextrose (PD), affected bloom extent, with all three bloom evaluation methods (ΔWI, white area percentage, and visual bloom level) showing similar trends (Jin & Hartel, 2020). The physical properties of chocolate, including fat bloom, are influenced by the morphology, content, and distribution of the sugar particles, which form the dispersed phase (Konar et al., 2024). Smaller sugar particles tend to form a more compact chocolate structure that restricts fat migration, whereas larger particles create more void spaces that facilitate lipid movement toward the surface. (Dahlenborg et al., 2015).

9.3 Impact of Milk Fat and High-Melting Fractions

Milk fat (MF) and its various fractions are commonly incorporated into chocolate formulations to modify texture, melting properties, and crucially, to inhibit fat bloom. MF is a complex lipid composed of diverse triacylglycerol (TAG) and non-TAG components, which interact with cocoa butter to alter its crystallization behavior (Schmelzer & Hartel, 2001). The addition of milk fat to chocolate has been shown to inhibit fat bloom formation. Milk fat reduces the formation of large surface crystals and limits surface roughness by slowing the growth and solidification of cocoa butter deposits (Sonwai & Rousseau, 2010). This effect occurs because certain triacylglycerols present in milk fat interfere with cocoa butter crystallization, thereby hindering the development of large and unstable βVI crystals (Metin & Hortel, 1996). High-melting fractions of milk fat are particularly effective in reducing fat bloom. When high-melting milk fat fractions incorporated into chocolate it can stabilize the desirable βV polymorph of cocoa butter (Pajin & Jovanovic, 2004). Similarly, hydrogenated milk fat has been shown to inhibit fat bloom, where fully hydrogenated forms are more effective than partially hydrogenated milk fat (Campbell et al., 1969). This effect is attributed to the ability of these fats to act as crystallization modifiers, influencing the nucleation and growth of cocoa butter crystals (Ribeiro et al., 2013).

Other additives, such as cocoa butter stearin (CBSt) and sorbitan monostearate (SMS), have been reported to delay fat bloom formation, particularly under fluctuating temperature conditions. CBSt, a high-melting fraction of cocoa butter, and SMS help stabilize the chocolate fat phase, highlighting the importance of high-melting components in bloom prevention (Buscato et al., 2018). Similarly, mangosteen seed fat (MSF), which is rich in 1,3-distearoyl-2-linoleoyl-glycerol (StLSt), has been shown to reduce fat bloom by blending effectively with the symmetrical monounsaturated triacylglycerols present in cocoa butter (Hou et al., 2025).

10. Conclusion

The polymorphic behavior of cocoa butter represents a major technological challenge in chocolate manufacture. Small changes in crystal form can lead to large differences in texture, appearance, and storage stability. This review shows that polymorphic stability is not controlled by composition alone, but by the combined effects of thermal history, tempering conditions, and crystal memory. In particular, the persistence of metastable crystals and the slow transformation to more stable forms explain why fat bloom remains difficult to prevent under practical storage conditions. Advances in analytical techniques have made it possible to monitor these transformations with greater precision, allowing better control of crystallization during processing. A deeper understanding of less-studied triacylglycerols, especially POS, may further improve predictive control of cocoa butter behavior. Overall, integrating compositional knowledge with processing and analytical tools is essential for producing chocolate with consistent quality and long-term stability.

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General Notes for this manuscript:

1. Tables compile valuable data but lack **interpretive commentary**.
2. Table numbering and formatting are inconsistent in places.
3. Figure 1 is referenced but not fully discussed in the text.
4. For each table, explicitly state what new insight it provides
5. Clarify how Table 4 advances understanding beyond Table 3
6. Expand the discussion of Figure 1 to emphasize kinetic vs thermodynamic control.

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