Dynamic Crystallization of Dark Chocolate as Affected by Temperature and Lipid Additives

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ABSTRACT

The dynamic crystallization was studied in a lab-scale Scraped Surface Heat Exchanger by following variations with time of torque applied during different isotherms between 24.9°C and 31.0°C. Crystallization was in two steps for T 26.2°C but it was in one step at T<26.2°C. The first step corresponded to crystallization of about 1% solid fat and was related to that of saturated triacylglycerols (SSS) which segregated from other cocoa butter triacylglycerols (TAGs) because of their low solubility in TAGs. The second step, an abrupt increase of apparent viscosity, leading to complete crystallization was attributed mainly to the monounsaturated TAGs in the β form. Different amounts of tristearin increased the apparent viscosity and reduced the latent time preceding the first step, but did not influence the main crystallization. Stearic acid and distearin additions also influenced chocolate crystallization.

Key Words: chocolate, crystallization, lipid additives, scraped surface, heat exchanger

INTRODUCTION

COCOA BUTTER CONSTITUTES, WITH SUGAR, ONE OF THE MAIN components of chocolate. Its polymorphism, which greatly affects the physical aspect and properties of chocolate products (gloss, snap, contraction and chocolate blooming during storage) through the tempering and crystallization process, has been extensively studied. Six different polymorphic forms, (I to VI), with increasing order of melting points, are generally reported to describe the cocoa butter polymorphism (Wille and Lutton, 1966; Chapman et al, 1971; Huyghebaert and Hendrickx, 1971; Lovegren et al., 1976; Davis and Dimick, 1986; Adenier et al., 1975, 1993). However, the existence of some of these (forms III and VI) has been debated (Merken and Vaeck, 1980; Schlichter-Aronhime et al., 1988; Schlichter-Aronhime and Garti, 1988).

Many earlier studies assumed that cocoa butter crystallizes like a pure compound but others (Manning, 1984; Davis and Dimick, 1989a, b; van Malssen, 1994; Dimick, 1994, Chaiseri and Dimick, 1995a, b; Loisel et al., 1998) have shown that cocoa butter crystallization induces segregation of different lipid families. In a first step, the nucleation process has been postulated to start from complex lipids and trisaturated TAGs (SSS, Saturated-Saturated-Saturated), other TAGs and simple lipids being excluded from seed crystals. Davis and Dimick, (1989a, b) reported that cocoa butter seed crystals formed during early crystallization contained high concentrations of glycolipids (11.1%), phospholipids (6.6%) and triacylglycerols (67.7%). Cocoa butters that contained higher proportions of tristearin seemed to crystallize faster. Chaiseri and Dimick (1995a, b), studied cocoa butters of different geographical origins and found that at the early stages of crystallization under agitation at 26.5°C, cocoa butters solidified into high melting and low-melting fractions. The low melting fraction was composed of polymorphs IV and V of cocoa butter. The high melting fraction at the latter stages of crystallization had DSC endotherms at about 34–36°C (form VI). The concentration of StOSt (1,3-stearoyl-2-oleoylglycerol) in the crystals during growth was higher than that in the original cocoa butter. As crystallization progressed, the proportion of StOSt in the TAGs fraction increased. Cocoa butters characterized by a higher rate of nucleation and crystal growth showed higher stearic acid in their diacylglycerol (DAG) fractions and higher StOSt and POSt (1-palmitoyl-2-oleoyl-3-stearoylglycerol) compared to others (characterized by slower nucleation and growth rates) which showed a higher content of polyunsaturated TAGs (StOO, 1,stearoyl-2,3-oleoylglycerol and POO, 1,palmitoyl-2,3-oleoylglycerol) (Chaiseri and Dimick, 1995a, b). No relation was found between saturated TAGs content of the initial crystals during nucleation and the crystallization behavior of cocoa butters. This confirmed observations of Cebula et al. (1991) that trisaturated TAGs had no effect on chocolate temperability. However, Hachiya et al. (1989) had reported that the seeding of a dark chocolate by the b form of tristearin accelerated cocoa butter crystallization.

In our previous studies (Loisel et al., 1998; Loisel, 1996), monitoring of cocoa butter crystallization by thermal analysis and X-ray diffraction vs. temperature (XRDT) showed that on cooling to different temperatures (0.5 to 5°C/min.), segregation occurred among the TAGs with the formation of high-melting crystals characterized by an increase of SSS content (11% compared to 3% in cocoa butter). XRDT analysis showed that the high-melting crystals, which were formed first during cooling, melted last. They show a 2L (double chain length) long spacing at about 44Å, very close to that of the b form of tristearin, which disappears only at about 37.5°C, i.e. 2–3°C above the melting point of the VI form of cocoa butter (3L, triple chain length).

In order to confirm the fractionated crystallization of cocoa butter in chocolate, a dynamic crystallization test was developed in a lab-scale Scraped Surface Heat Exchanger (SSHE) (Loisel et al., 1997). Chocolate crystallization could be carried out as a function of temperature and time in this SSHE and the nature and quantity of seed crystals be optimized by different temperature cycles. A single crystallization was observed after a slow cooling of chocolate from about 40°C to 26.1°C. No temperature > 26.1°C was directly applied to the melted chocolate during that study. Our present objective was to study chocolate crystallization during different defined isotherms (T_c) between 24.9°C and 31.0°C, reached after direct cooling from 40°C to T_c. The observation of two stages during cocoa butter crystallization and the origin of each were focused on by addition of some minor lipid additives such as saturated TAGs, saturated diacylglycerols and free fatty acids in the chocolate composition. The influence of emulsifiers on chocolate crystallization was also tested.

MATERIALS & METHODS

Materials

The chocolate was a mixture of a low-fat dark chocolate (30.0% fat with 0.4% lecithin), and pure cocoa butter (CB) of the same origin in order to provide a 32.4% final fat content. Each tempering process was conducted using 828g of enriched chocolate (800g of initial choc-

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Table 1—Percent concentration of triacylglycerols in cocoa butter[a]

TAGs	OLO	PLO	PLP	OOO	POO	PLSt	StOO	StLSt	POP	POSt	StOSt	StOAr	StPP	PstSt	StStSt	Total(%)
Cocoa butter	0.4	0.5	1.6	0.4	2.8	1.4	3.4	3	17	36.6	27.3	1.9	1.4	1.1	0.5	99.3
TAGs fractions			polyunsaturated = 13.6						monounsaturated = 83.4				trisaturated =3.0			100

[a]Ar: arachidic acid (C 20:0), L: linoleic acid (C 18:2), O: oleic acid (C 18:1), P: palmitic acid (C 16:0), St: stearic acid (C 18:0).

olate + 28g of CB). The TAGs composition of cocoa butter had been determined by HPLC analysis (Loisel et al., 1998; Loisel, 1996) (Table 1). The composition was calculated assuming that i) unsaturated fatty acids are distributed preferentially in the sn2 position on the glycerol, ii) linoleic and oleic acids are distributed in this position of TAGs having the same HPLC partition number in the proportion given by the fatty acid analysis reported earlier (Loisel et al., 1997). The composition in minor lipids has been determined by GC and reported (Loisel et al., 1997; Loisel el al., 1998). We found TAGs = 97%, diacylglycerols = 1.1%, monoacylglycerols = 0.2%, free fatty acids = 1.6%; phosphatides = 0.15% and others 0.25%.

The influence of minor components on chocolate crystallization was studied by replacing the original cocoa butter by the same amount of tristearin (Sigma, Grade II, purity >90%), distearin or stearic acid (Sigma, Grade I, purity >99%). Weights added were ±0.05g for low-fat chocolate and cocoa butter and ±0.1 mg for tristearin, distearin and stearic acid. Lecithins (Chocotop 50, 100 and 320 and Lecimulthine from Lucas-Meyer) and PRPG (Admul Wol 1403, Quest) were added to increase the emulsifier content from 0.4% to 0.75% (chocolate fat = 32.4%).

Lab-scale scraped surface heat exchanger

Chocolate crystallization was followed in a lab-scale Scraped Surface Heat Exchanger (SSHE) in which torque variation was monitored as a function of chocolate temperature and time (Loisel et al.., 1997; Loisel, 1996). The rotation speed of the SSHE shaft was fixed at 20 rpm during all experiments. The rapid decrease of chocolate temperature from 40°C to the desired temperature (T_c) in the range 24.9–31.0 ± 0.1°C was achieved in about 5 min by switching between two temperature-controlled refrigerated baths (the first bath at 40°C, the second at T_c) which had not been possible during our previous studies. The resisting torque was related to an equivalent viscosity (Pa·s) determined from one standard silicone oil. As the torque-viscosity correlation was found to depend on oil type, we preferred the use of torque units (N·m). The standardization of the SSHE was carried out using a torquemeter (0.1-5N·m ±10%). The following linear relationship was found between the SSHE signal, expressed in arbitrary units (a.u.), and the torque (N·m) ($r^2 = 0.987$)

$$\text{SSHE signal (a.u.)} = 24.7 \times \text{Torque (N·m)} - 15.2$$
$$\text{Torque (N·m)} = 0.04 \times \text{SSHE signal (a.u.)} + 0.62$$

On recordings, the onset of chocolate crystallization was determined graphically as the point (time) at which the tangent to the crystallization curve intercepted the base line (Fig. 1).

Before each crystallization run, chocolate was heated at a temperature between 45°C and 77°C (according to the melting temperature of the additives) for about 2h in order to eliminate any influence of the sample's thermal history. Each experiment was performed in duplicate. With the minor component-containing chocolate, a new sample was prepared for each experiment, we had observed that long exposure to high temperature with blade rotation (e.g., 77°C during 90 min) led to a delay in nucleation of about 20 min, and thus poor repeatability. This delay could be explained by the practice of adjusting the SSHE blades to provide a constant torque value at the beginning of each run. After long periods of stirring at high temperature, the viscosity of the chocolate increased, probably because of degradation of the lecithin, and the blades had to be adjusted. The effect of the blade friction on chocolate crystallization was confirmed by using the SSHE shaft with no blade. A delay of the chocolate crystallization of about 30 min. was observed. For this reason, the initial torque value was imposed at 0.9 ± 0.02 N·m at 40°C at the beginning of each crystallization test in order to standardize the friction of the blades in the SSHE. In addition, viscosity and yield value of chocolates were determined at 40°C at the end of each experiment to verify the absence of degradation. A Rheomat 115 (r1 = 13.6 mm, r2 = 20 mm) was used and Casson-Steiner viscosity and yield value were calculated from the data between 220 s^{-1} and 1 s-1 on the decreasing curve (Casson-Steiner Model). The influence of lipid additives on viscosity and yield value of chocolate was also determined. The conditions of the crystallization tests with additives were similar except that T_c was fixed to 28.2°C as explained below.

Thermal analysis

Thermal analysis of chocolate was carried out using a Perkin-Elmer DSC-7. Samples were taken from the SSHE at several stages of crystallization. They were rapidly put into an aluminium pan (40 µL) stored on a metallic block heated at the same temperature as the chocolate ($24.9<T_c<31$°C). The pan with about 30 mg of chocolate was rapidly placed in the DSC-7 at 21°C and heated at 10°C/min to 50°C. The chocolate mass was accurately determined by the difference between the empty pan weighed before, and the pan with chocolate weighed after thermal analysis. This protocol, by minimizing the cooling of the chocolate before thermal analysis which inevitably induced formation of unstable crystals and made the thermal profile more complex (Manning, 1984), allowed the melting of seed crystals present in the tempered product to be recorded separately from unstable forms. The apparatus was calibrated with lauric acid (purity > 99.9%) at 10°C/min (Grabielle-Madelmont, 1983) (Loisel, 1996). The peak temperatures were taken at the maxima of the endotherms (T_m, indicated by a mark on DSC recordings) instead of the onsets, because of peak

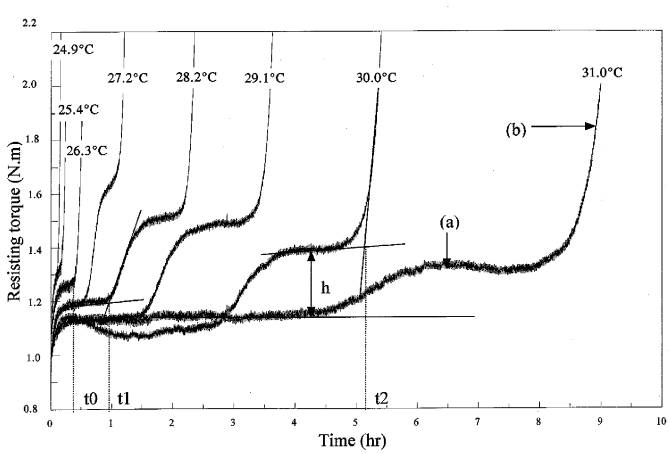

Fig. 1—Change in resisting torque of the SSHE as related to time at temperature (T_c). The first torque increase recorded during the very first minutes, until temperature equilibration, corresponds to the cooling of chocolate from 40°C to T_c. The second and third torque increases resulted from chocolate crystallization. The induction times t1 and t2 corresponding to onsets of crystallization ($T_c \geq 27.2$°C) and amplitude of the torque jump, h, recorded for the first crystallization were determined graphically from tangents to the curve. T0 corresponds to the onset of crystallization for $T_c<27.2$°C. (a) and (b) arrows show sampling points referred to in Fig.3.

overlapping. Therefore, melting points observed for the different polymorphic forms at peak maximum were systematically higher than the published values or those measured at onset. This lag, which was 1 or 2° Kelvin for pure TAGs, reached 4 to 6 K for mixtures such as cocoa butter (e.g. a 10 mg sample of polymorphic form V heated at 5K/min.) displayed onset temperature of 29.1 and maximum of 34.8°C.

RESULTS & DISCUSSION

Standard dark chocolate crystallization

Standard dark chocolate was melted at 45°C and rapidly cooled to 24.9, 25.4, 26.3, 27.2, 28.2, 29.1, 30.0 or 31.0°C (±0.1°C). The torque had to be adjusted (Fig.1) to maintain constant rotation speed (20 rpm) of the SSHE shaft at these temperatures. The torque increase recorded at the beginning of each experiment corresponded to the change in chocolate viscosity observed during cooling from 45°C to the desired temperature (T_c). A time-delay (about 10 min) was necessary to reach this temperature and reach thermal equilibrium as well as constant torque. Although this delay depended on T_c, it was noted that after 5 min., the temperature of the chocolate mass was very close to the desired value (about T_c + 0.3°C). Since nucleation processes, whatever the polymorphic form considered, were expected to start as soon as chocolate temperature was below its melting point, the time of chocolate crystallization reported here was taken from that point. Practically, it has been calculated as the total time from the beginning of the cooling (40°C) to the relevant crystallization onset minus 5 min.

After a constant torque value was reached (Fig. 1), one or two domains of torque variation with time were observed, depending on chocolate temperature. These variations have been interpreted as the development of chocolate crystallization. A single sharp crystallization was observed for T_c=24.9, 25.4 and 26.3°C, while a two-step crystallization clearly appeared for $T_c > 27.2$°C. In most cases, before the onset of crystallization, a first torque plateau was observed, the duration of which was temperature-dependent.

For $T_c > 27.2$°C, the sharp crystallization recorded at lower temperature was no longer observed and was replaced by a more gradual process. The main torque increase observed at the end of each experiment was preceded by a limited torque jump leading to a second plateau for $T_c > 27.2$°C. The mean value of the torque measured during this second plateau was between 1.3 and 1.6 N·m., and tended to decrease when the chocolate temperature increased from 27.2 to 31.0°C. This evolution may have been due to a decrease of chocolate viscosity which is expected when chocolate is heated (Loisel et al., 1997). The dependence of the chocolate viscosity on temperature, determined in our previous study, allowed us to evaluate the torque decrease (about 0.1N·m) expected for a temperature increase of 2.8°C (from 28.2 to 31.0°C). This calculated mean torque variation was close to the decrease observed (0.15N·m) over this range of temperature. However, this torque decrease was not entirely related to chocolate viscosity changes.

A first interpretation of this plateau could be that a polymorphic transition, such as a β′ β transition, occurred during cocoa butter crystallization when $T_c > 27.2$°C. However, the temperature at which the initial (less stable) crystals were formed ($T_c > 28$°C) would rule out the hypothesis of the formation of β′ crystals, which were characterized by a melting point between 25.1 and 27.5°C (Wille and Lutton, 1966; Huyghebaert and Hendrickx, 1971).

The appearance of a second plateau might indicate that no further crystallization occurred and that an equilibrium stage was attained, for instance when crystal growth was exactly compensated by their solubilization in the liquid phase. Another hypothesis is that a fractionated crystallization, corresponding to the first torque jump, may occur in the liquid phase when $T_c > 27.2$°C. The fact that a plateau was attained at all temperatures $T_c > 27.2$°C indicates that a defined amount of crystals was formed at each temperature. The decrease of the torque jump as the temperature increased shows that the amount decreased with temperature. This variation could be attributed to increasing solubility of the crystals in the liquid as the temperature was raised. The weak amplitude of this jump, compared to the torque value recorded at the end of each experiment when the shaft blocked (2.2N·m, Fig. 1), tended to indicate that the crystals formed were made up of a minor lipid fraction of cocoa butter.

For $T_c < 27.2$°C, the single sharp crystallization observed was similar to those reported for a slower cooling to 26.1°C at 0.5°C/min (Loisel et al., 1997). The two-step crystallization and the two plateaus had not been previously observed. The reason for this was that the chocolate was always directly cooled to 26.1°C, which was below the temperature (T_i = 26.2°C), corresponding to the linear curve intercept (Fig. 2) delimiting the two regimes of crystallization, i.e. a single- or double-step. In our previous study, the fast crystallization observed at 26.1°C was attributed to the growth of an unstable form of cocoa butter (form IV). On heating above that temperature, a polymorphic β′ β transition was observed, accompanied by rapid crystal growth at $T_c > T_i$. The rate of this growth was only measured between 30.5 and about 33.0°C, since below that temperature it was too fast to be determined. This fast growth was not observed when chocolate was directly cooled to $T_c > T_i$, without passing below T_i (Fig.1). This confirmed that starting in both cases from liquid chocolate, stable crystals were obtained more quickly at a certain temperature after melting of unstable varieties than by direct cooling to that same temperature. Note that this process is commonly used in the fat industry for crystallization of final products by SSHE.

The induction times, t0, t1 and t2, at which onsets of crystallization were observed, were determined as shown (Fig.1). The logarithm of the induction time (log(t)) for each of the different steps was a function of the chocolate temperature (Tc) (Fig. 2). The three different linear relations were observed, corresponding to different crystallization mechanisms, which confirmed the formation of three types of crystals. Below T_i (26.2°C) only one type of crystals appeared whereas two types formed above the critical limit. The critical temperature limit was probably very close to this value since slight rise was seen on the 26.3°C recording (Fig. 1) when it was observed on an enlarged time scale (not visible on graph at scale shown).

In order to confirm this hypothesis, thermal analyzes were carried out with chocolate samples taken at different times during the crystallization process. The first series concerned samples taken at the beginning of each single crystallization at torque values between 1.3 and 1.6 N·m (at 24.9, 25.4 and 26.3°C). The second series corresponded to samples taken during the first and second steps of crystallization (at 27.2, 28.2, 29.1, 30.0 or 31.0°C). Samples corresponding to the first

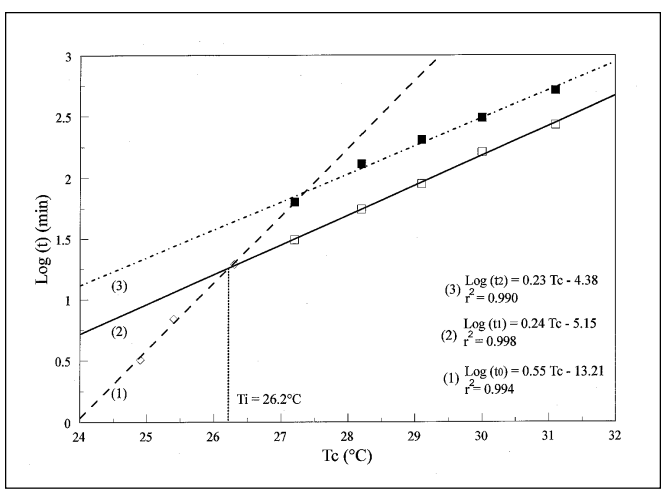

Fig 2—Change in the logarithm of induction times vs temperatures of chocolate crystallization (T_c). ◆ single crystallization which appeared in recordings for $T_c < 27.2$°C and □ first step of the crystallization curves for recordings at $T_c > 27.2$°C; ■ the second step of crystallization. Lines are the corresponding linear fits.

and second step were taken at torque values 1.3-1.6N·m (as for previous samples taken below 27.2°C) and 2 N·m (arrows, Fig. 1). The DSC profiles (Fig. 3) show the melting recordings of samples of tempered chocolate taken at 31.0°C during the first (a) and second (b) step of crystallization. Crystals appearing during the first step were characterized by a higher melting point (36.6°C) than those during the second (34.6°C). All DSC profiles at $T_c > T_i$ were similar to those shown (Fig. 3) and thus confirmed that the crystals which were formed first, melted last (Fig. 4).

The melting point of the crystals appearing during the first step for $T_c \geq 27.2$°C increased regularly from 34.0 to 36.6°C as a function of T_c. Those of the two forms which appeared during the second step were systematically lower and in the ranges 30.5–32.3°C and 34.0–34.6°C, respectively. The occurrence of a series of peaks, the maximum melting point of which was about 31°C, indicated the presence of β′ crystals, probably formed during the cooling of the sample in the DSC apparatus (21°C) (Fig. 3, 4). The melting of these crystals was not considered further, since they were not representative of the solid phase sampled at T_c. In contrast, the presence of two types of crystals, the melting temperatures of which ranged from 34.0°C to 34.6°C and from 34.0 to 36.6°C, indicates the probable existence of two β varieties characterized by different TAG compositions.

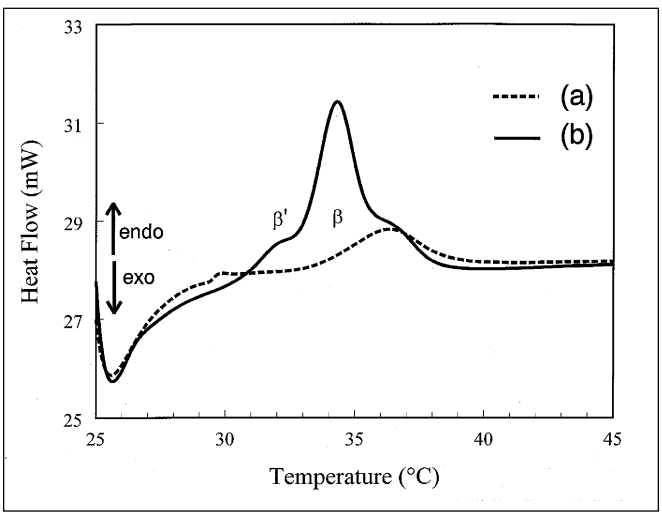

Fig. 3— Melting DSC recordings of the chocolate samples taken during the first (a) and the second (b) steps of the crystallization process (a and b also refers to Fig.1 arrows) for T_c = 31.0°C (sample weight was about 30 mg and heating rate 10°C/min.)

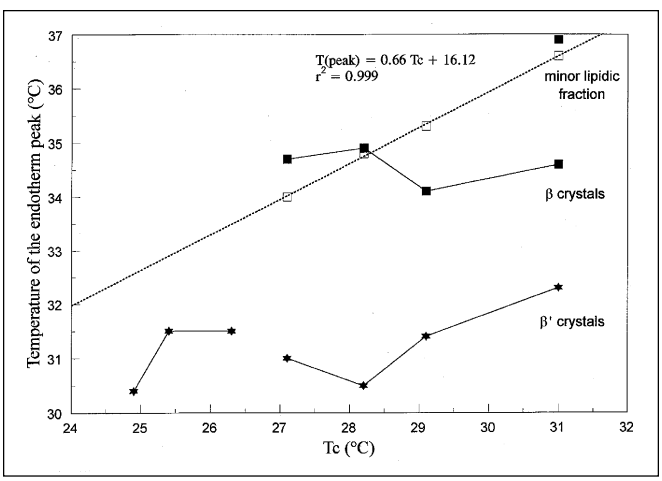

Fig. 4—Melting points observed by DSC of seeds taken during the first and the second steps of the crystallization process at points corresponding to a and b of Fig. 1 as a function of temperature at which chocolate has been crystallized (T_c). □ crystals which appeared during the first step of the crystallization curves for Tc > 27.2°C. ■, crystals which appeared during the second step of these same curves and ⋆ during the single crystallization which occurred at T_c<27.2°C. The dotted line is a linear fit of the melting temperatures found for the high-melting fraction.

An estimation of the amount of crystalline phase formed during the first torque jump was calculated from the DSC recordings during the second plateau using the following formula:

$$\% \text{ (high melting crystals/cocoa butter)} = 100 \times \Delta H / (\Delta H_0 \times 32.4)$$

where: ΔH = experimental melting enthalpy of crystals (J/g); H_0 = 130J/g = mean value of the melting enthalpy of the β forms of cocoa butter determined by DSC from two samples crystallized as forms V and VI, the structures of which have been confirmed by X-ray diffraction in our laboratory. 32.4 = total fat content of chocolate (%).

DSC recordings of the chocolate samples taken during the plateaus (Fig.1) at 27.2, 28.2, 29.1, 30.0 or 31.0°C indicated that only 0.9±0.3% of the cocoa butter was crystallized. Thus, these thermal analyses confirmed the fractionated crystallization of a minor lipid fraction of cocoa butter in the SSHE for $T_i > 26.2$°C.

This fractionation during chocolate crystallization could be attributed to the phase separation of SSS TAGs in cocoa butter as reported by Davis and Dimick (1989a, b) and Chaiseri and Dimick (1995a, b). They have shown that during cocoa butter crystallization, high melting crystals, with a high content of complex lipids and saturated TAGs, may separate from the liquid. This fractionation of the cocoa butter was confirmed by use of X-ray diffraction as a function of temperature and DSC analysis, and may be explained by the low solubility of SSS in mono and polyunsaturated TAGs (Loisel et al., Submitted). The TAG analysis of the high melting fraction has shown that it was enriched in SSS (by four times). In our current results, the high-melting crystal content estimated by DSC (0.9±0.3%) represented only about one third of the SSS content of the cocoa butter (3.0%, Table 1), confirming the partial solubility of saturated TAGs in the chocolate liquid phase.

Taking into account the results of these studies and the fact that this value of about 1% was very close to the content of diacylglycerols (DAGs) (1.1%) and free fatty acids (FFAs) (1.6%) in cocoa butter (Table 2), we assumed that this minor fraction could be mainly composed of such high-melting lipids and we considered their influence on chocolate crystallization.

Influence of lipid additives on chocolate crystallization

Crystallization test determination. Crystallization test were carried out to study the influence of the lipid additives tristearin (StStSt), distearin and stearic acid. The chocolate temperature was fixed at 28.2°C so as to observe the fractionated crystallization of chocolate in< 3 h to perform three different experiments within one day. Another reason for using this temperature was that cocoa butter cannot crystallize under its unstable forms (β′) at 28.2°C. This allowed us to quantify the effects of lipid additives on both steps of chocolate crystallization (induction time as well as torque). The latter step corresponded to the formation of a β form of the monounsaturated TAGs of cocoa butter.

Before starting crystallization tests, we verified that TAG, DAG and FFA incorporation into chocolate did not sharply modify the rheological properties of chocolate, and thus prevent the standardization of blade friction in the SSHE. The effect of rheological properties on the blade adjustment was quantified by recording, at 28.2°C, the dynamic crystallization of three chocolates containing 35%; 32.4% and 30.0% fat. The Casson-Steiner viscosities and the yield values of the chocolates were 1.65±0.02 Pa·s and 6.18 ± 1 Pa (35%), 2.60±0.02 Pa·s and 12.4 ± 1 Pa (32.4%), 4.52±0.02 Pa·s and 17.25±1 Pa (30.0%) respectively. No significant difference was found between the induction times of the different chocolates, regardless of crystallization step. However, we observed that a lower fat content tended to increase the amplitude of the first torque jump. The torque variation decreased

Table 2—Lipid composition of chocolates

Lipid additives in chocolate	Cocoa Butter (g)	Lipid additive amount (g)	Lipid additive (%/chocolate fat)	% of lipid fraction in final chocolate[b]
Chocolate with no lipid additive (800/28/0)	28	0.0	0.00	SSS: 3.0 DAGs: 1.1 FFAs: 1.6
Tristearin (800/23/5)	23	5.0	1.7	SSS: 4.6
Tristearin (800/25/3)	25	3.0	1.0	SSS: 4.0
Tristearin (800/27/1)	27	1.0	0.3	SSS: 3.3
Distearin (800/27.25/0.75)	27.25	0.75	0.3	DAGs: 1.4
Stearic acid (800/26.5/1.5)	26.5	1.50	0.6	FFAs: 2.1
Stearic acid (800/27.250.75)	27.25	0.75	0.3	FFAs: 1.8

[a]The abbreviation 800/X/Y corresponds to the weight ratio of low fat chocolate/cocoa butter/lipid additive.
[b]SSS = trisaturated triacylglycerols; DAGs = diacylglycerols; FFAs = free fatty acids. In this column, except for the first line, only changed compositions have been reported.

Table 3—Main values of the crystallization curves reported in Fig. 5 and 8

	First crystallization			Second crystallization
Experiments	t1 (min)	h (N.m)	Slope (N.m/hr)	t2 (Min)
Dark chocolate	48.5±7.2	0.35±0.09	1.4±0.2	138.8±3.2
SSS TAGs				
3.3%	22±1	0.43±0.05	2.62±0.04	136
4.0%	6.5±0.5	0.73±0.05	4.8 ±0.4	138 ±1
4.6%	2.5±0.5	0.93±0.05	8.6±0.3	146
DAGs				
1.4%	55±2	0.33±0.05	1.23±0.02	189±3
FFAs				
1.8%	55±2	0.33±0.05	1.23±0.02	174±3
2.1%	55±2	0.33±0.05	1.23±0.02	189±1

from h = 0.52±0.05N·m for chocolate with fat content 30% to h = 0.18±0.02N·m for chocolate with fat content 35%. The slope of the first crystallization jump (torque variation versus time) decreased similarly from 1.64±0.05N·m/hr (30%) to 1.23±0.02N·m/hr (35%). The higher torque jump observed for chocolate containing only 30% of cocoa butter could be explained by the appearance of high-melting crystals during the chocolate crystallization with more effect on viscosity in a low-fat, than in a higher-fat chocolate since the mean distance between solid particles would be larger in the higher fat sample (in which the solid-solid interactions are decreased). Then, it appeared necessary to keep a constant value for the chocolate fat content for each crystallization test, in order not to change its viscosity and to be able to compare the specific effects of the lipid additions. For this purpose, a defined quantity of cocoa butter was systematically substituted by the lipid fractions to keep a total fat content of 32.4% (Table 2).

The viscosity and yield value of the different additive-enriched chocolates were checked at the end of each experiment to verify that no deterioration had occurred. For all crystallization tests, the measured values of chocolate viscosities and yield values remained between 2.61 and 2.77 Pa·s and 12.1 and 15.1 Pa, respectively. These values were very close to those of the dark chocolate (2.60 ±0.02 Pa·s and 12.4 ±1 Pa). Therefore, no significant effects of rheological parameters on crystallization changes were expected.

The repeatability of the crystallization test was reported (Table 3) as standard deviations of the parameters measured for three different samples corresponding to the same chocolate without additives (32.4% fat) (pure dark chocolate). All results with different lipid additives were compared to this control.

Influence of tristearin addition

The effects of the addition of 0.3, 1.0 and 1.6% tristearin (StStSt) on chocolate crystallization at 28.2°C were compared (Fig. 5). The main parameters determined from these crystallization curves (Table 3) showed the addition of tristearin reduced t_1 and increased h. The crystallization process was very sensitive to this effect and even a small increase of saturated TAGs from 3.0 to 3.3% sharply accelerated the onset of fractionated crystallization (t1 was reduced by half). This confirmed that the first jump observed (Fig.1) was related to the fractionated crystallization of SSS. Changes in the induction times, t_1 and t_2 were also compared (Fig. 6) as a function of total SSS concentration (noted [SSS]) in the chocolate fat (Table 2). A small increase of [SSS] decreased t_1 without affecting t_2 significantly. Two asymptotic curves were observed for the plot of t_1 vs [SSS]. At high [SSS], t_1 was so short that it indicated a spontaneous crystallization of the minor lipid fraction. At low [SSS], t_1 was so high that we could assume [SSS] asymptotically tended towards its limit of solubility in the undercooled liquid phase. This solubility limit in chocolate (about 2.1%) could be evaluated as: [SSS fat content] (3.0%) - [high-melting fraction](0.9%) at 28.2°C.

The solubility of SSS in the liquid chocolate at 28.2°C was determined by plotting the torque jump amplitude (h) vs the amount of StStSt added (Fig. 7). The torque jump was linearly dependent on the amount of tristearin crystallized in the domain in which the additions were made. Assuming that this linearity extended to the null concentration of SSS, the extrapolation to null torque jump (h = 0) yields a negative value (about 1.0%) which corresponds to the amount of crystallized SSS (such a plot is commonly used for evaluation of concentrations of minor components in a complex mixture by analytical techniques).

The amount of crystallized SSS in the dark chocolate at 28.2°C represents about 1% of the total fat content of chocolate or about one third of the trisaturated TAGs. This is very close to the quantity of solid phase which had been determined by thermal analysis (0.9±0.3%). Therefore the amount of solubilized SSS was about 2.0%. This is comparable to the concentration found by HPLC analysis (2.3%) for a sample in which the phase crystallized at 30±0.5°C had been removed prior to analysis (Loisel et al., Submitted). Taking into account the slight increase in solubility expected at the higher temperature, there was good agreement between all these determinations. These values also confirmed results of Cebula and Smith (1992), who observed by thermal analysis that addition of trisaturated TAGs to Coberine™ (Loders Croklaan's, Netherland) (a cocoa butter substitute with close TAGs composition) accelerated the crystallization and also raised the temperature of nucleation of the fat.

The fractionated crystallization we observed for chocolate, as well as that previously found in pure cocoa butter, may be partly explained by the very low solubility of the trisaturated TAGs in the liquid phase, which is mainly composed of monounsaturated TAGs. This result is similar to that for fractionation of pure cocoa butter (Loisel et al., Submitted). This fractionation, which has been studied by different techniques, and its dependence on temperature, can be explained in the same way. The coexistence and phase separation of the two fractions is similar to the behavior of TAGs representative of the two fractions, such as StStSt and StOSt for the SSS and SUS respectively. The StStSt/StOSt phase diagram, (reported by Rossell, 1967), illustrated this behavior. Note that the phase diagram PPP/POP is similar to that

of SSS/StOSt except for a temperature shift (Rossell, 1967; Ollivon, 1992). Then, we assumed that the behavior of mixtures of the two series of TAGs would not be very different from that of the pure compounds. These phase diagrams have in common that the limit of solubility in the solid state of SSS in SUS is extremely low, while that of SUS in SSS is quite high. The StStSt/StOSt phase diagram indicated that for [StOSt] > 80% and T > 45°C, the StStSt composition of the solid phase (and thus, its melting temperature) in equilibrium with the liquid phase, mainly composed of StOSt, was highly temperature-dependent. A small increase of temperature at which crystals are obtained would result in a large change in solid phase composition. The amount of solid phase formed is increased and the initial and maximum melting points are shifted towards higher temperatures when T_c is decreased (Fig. 4).

In addition, our previous results showed that the high-melting crystals from the liquid phase after storage for 3 wk at 30±0.5°C were composed of about 11% of SSS (compared to the initial SSS content of cocoa butter, 3.0%). The enrichment of the crystals in SSS confirmed the probable homology of the SSS/SUS phase diagram of cocoa butter (unknown) with StStSt/StOSt (Rossell, 1967).

Also, in the range studied, whatever their concentration, trisaturated TAG crystallization had no effect (Fig. 5) on the crystallization of the monounsaturated TAGs of cocoa butter which occurred later, since t_2 could be considered as constant (Table 3). Above 27.2°C, during this dynamic process, both trisaturated and monounsaturated TAGs crystallized directly under their β form, since T_c was above the melting point of the β' form of cocoa butter and that the α−>β transition of trisaturated TAGs in cocoa butter occurs below 28°C (Loisel et. al, 1998). These results show that the crystallization of SSS in a β form (2L) did not accelerate the formation of β crystals of the monounsaturated TAGs (3L) of cocoa butter. This confirmed results of Cebula and al., (1991) but not those of Hachiya et al., (1989) who observed that dark chocolate crystallization was slightly accelerated by adding StStSt (form β).

The SSS effect we observed could be related to our previous results (Loisel et al., 1998) which showed DSC and X-ray diffraction data as a function of temperature. The α form of SSS (d_{001} = about 50 Å; d_{001} refers to first order spacing of the $d_{hkl = 001}$ planes) did not accelerate the crystallization of the monounsaturated TAGs of cocoa butter under their unstable forms (subα, d_{001} = 53Å and α d_{001} = 49Å).

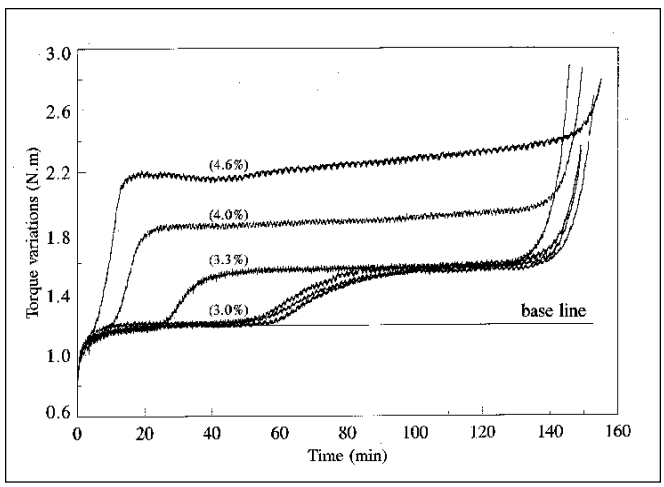

Fig. 5—Influence on chocolate crystallization recorded at T_c=28.2°C of the addition of different amounts of tristearin. Percentages correspond to the content of trisaturated TAGs in chocolate fat after tristearin incorporation. The base line drawn shows the reference from which the amplitude of the torque jump h was graphically determined as in Fig. 1.

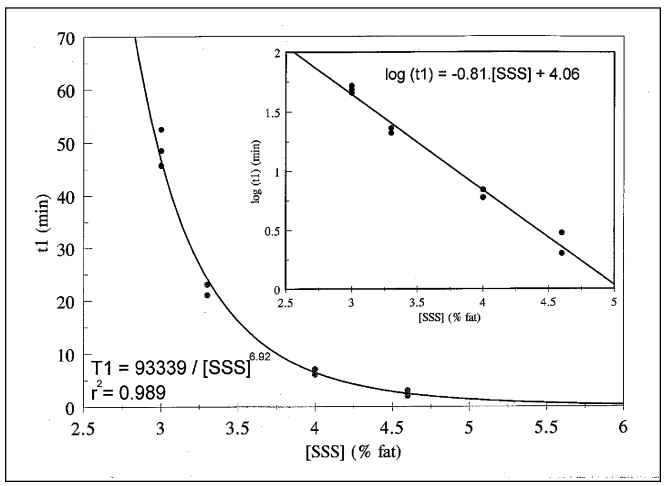

Fig. 6—Influence of addition of trisaturated TAGs (% of chocolate fat) on induction time of the first jump (t_1) (3% correspond to the pure dark chocolate with no addition of tristearin) (• , experimental points). The curve fit (solid line) tends towards both axis asymptotically.

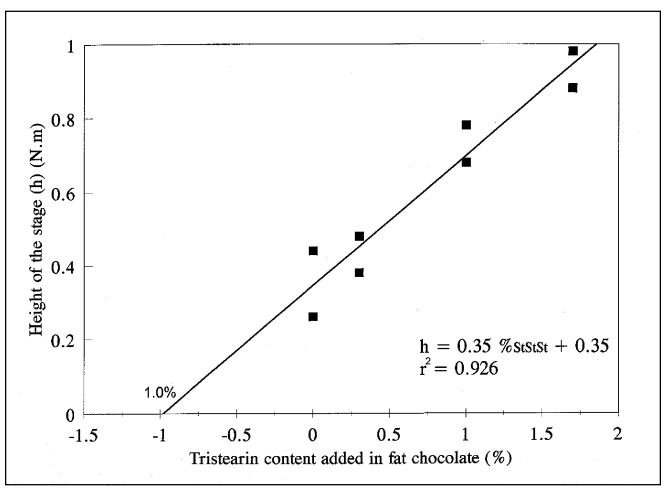

Fig. 7—Relationship between amplitude of the torque first jump observed during chocolate crystallization (Fig. 5) and the tristearin amount added (g/g of chocolate fat). The value of 1% corresponds to the quantity of tristearin which crystallizes at 28.2°C in the dark chocolate (with no tristearin addition).

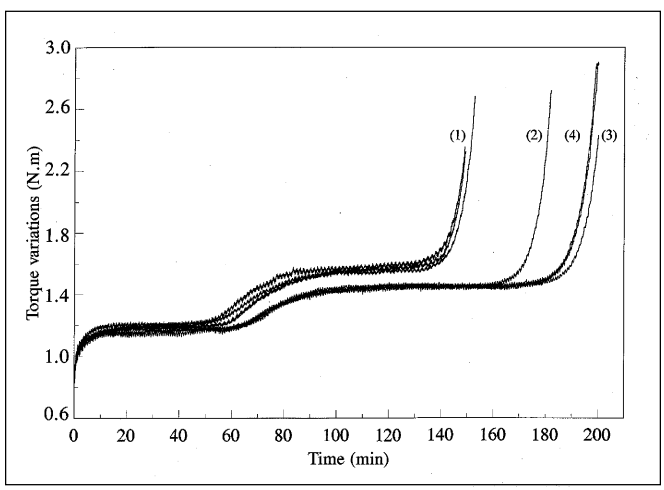

Fig. 8—Effects of stearic acid or distearin addition on chocolate crystallization at 28.2°C. (1) corresponds to chocolate repeatability with the pure dark chocolate, (2) and (3) to chocolate with addition of 0.3 and 0.6% of stearic acid, respectively, and (4) to chocolate with 0.3% of distearin (Table 2).

Fast crystallization of the SSS observed during that same study for a rapidly cooled (-2°C/min) cocoa butter sample, as well as a short t_1 found at low T_c (Fig.6) tend to show that during this dynamic process, the crystallization of trisaturated TAGs occurs even for T_c<27.2°C, but the rapid crystallization of the monounsaturated TAGs under their β' form did not enable their formation to be detected (Fig.1). The crystallization of the minor SSS was masked by that of the main TAGs.

Influence of distearin or stearic acid addition

The effects of adding stearic acid or distearin on the dynamic crystallization of dark chocolate at 28.2°C were compared (Fig. 8) The influence of these additives on the crystallization parameters, t_1, t_2 and h, (Table 3) indicated that the first jump amplitude was not modified by addition of free fatty acid (FFA) and diacylglycerol (DAG) and that t_1 was only slightly modified. Thus, the trisaturated TAGs crystallization was neither directly affected by the presence of these compounds nor related to their concentration in chocolate. On the contrary, results showed that FFAs and DAGs slowed the second step of chocolate fat crystallization. These effects confirmed the observations of Cebula and Smith (1992) by thermal analysis that diacylglycerols slowed the subsequent velocity of growth and retard the TAG polymorphic transitions on heating.

Influence of emulsifiers additions

Emulsifiers, such as lecithins and PRPG (polyricinopolyglyceroesters), were added to the pure dark chocolate to study their influence on crystallization. However, this could not be studied in the SSHE because their introduction in the cocoa butter modified both the overall rheological behavior of chocolate (Casson-Steiner viscosity was reduced and yield value was increased for lecithins; while the reverse was observed for PRPG) and, as a result, the blade friction onto the SSHE surface. Due to a large decrease of blade friction, it was necessary to increase considerably their pressure on the SSHE surface. Thus, results recorded with emulsifiers were not directly comparable with those recorded with pure dark chocolate, although excellent repeatability of the recordings was found. However, no significant difference was observed for t_1, saturated TAGs tending to crystallize in the same way as with the pure dark chocolate. Moreover, a faster crystallization of the monounsaturated TAGs of cocoa butter was never observed, t_2, for the enriched-chocolate, even when friction was increased, which would indicate that emulsifier addition always delayed crystallization.

Concerning the influence of additives on chocolate crystallization in general, our observations confirmed those of Davis and Dimick (1989a, b). They reported, during cocoa butter crystallization, some minor components, as trisaturated TAGs, crystallized separately from the other TAGs. Moreover, assuming reliable comparisons between cocoa butter and chocolate, the absence of connection between crystallization of the high-melting TAGs and that of the monounsaturated TAGs of the chocolate fat explains why Chaiseri and Dimick (1989a, b) reported that the behavior of cocoa butter from different geographical origins was not related to SSS, but rather depended on StOSt, POSt, StOO and POO concentrations.

CONCLUSION

CHOCOLATE CRYSTALLIZATION DURING A DYNAMIC PROCESS IS A two-step process for T_c>26.2°C but it is a one step process at T_c<26.2°C. The first step was related to crystallization of part of the saturated (SSS) TAGs, about 1% of the whole fat chocolate (1/3 of SSS), while the second or main crystallization, mainly corresponded to the monounsaturated TAGs (SUS). The SSS solubility in the liquid phase of chocolate (about 2%) could be calculated from data by DSC and dynamic crystallizations in SSHE of chocolate with different amounts of tristearin. This technique made it possible to study the behavior and effects of chocolate additives. No relationship occurred between the amount of saturated TAGs and the rate of crystallization in the β form of monounsaturated TAGs. Incorporation of stearic acid and distearin slightly decreased the growth rate of SSS crystals and delayed their formation. The induction time of crystallization of monounsaturated triacylglycerols under their β form increased almost linearly with concentration. The influence of emulsifiers such as lecithin could not be reliably studied in this way since their introduction in the cocoa butter modifies blade friction and overall rheological behavior. Cocoa butter crystallization cannot be considered as that of a pure compound, although it is largely influenced by its three main monounsaturated triacylglycerols (POP, POSt and StOSt). Fat fractionation, which was observed for the first time in chocolate, occurs during cooling and results from low solubility of saturated triacylglycerols in the monounsaturated major fraction. This confirms, for chocolate, results obtained recently with pure cocoa butter by synchrotron X-ray diffraction and DSC (Loisel et al., 1998).

REFERENCES

Adenier, H., Chaveron, H. et Ollivon, M. 1993. Mechanism of fat bloom development on chocolate. In *Shelf life studies of foods and beverages; Chemical, biological, physical and nutritional aspects*, G. Charalambous (Ed.). Elsevier Science Publishers B.V.

Adenier, H., Ollivon, M., Perron, R., and Chaveron, H. 1975. Le blanchiment gras.I. observations et commentaires. Chocolaterie Confiserie de France. 315: 7.

Arruda, D.H. and Dimick P.S. 1991. Phospholipid composition of lipid seed crystal isolates from Ivory Coast butter. J. Am. Oil Chem. Soc. 68: 385.

Cebula, D.J., Dilley, K.M., and Smith, K.W. 1991. Continuous tempering studies on model. confectionery systems. 45th P.M.C.A. Production Conference: 42.

Cebula D.J. and Smith K.W. 1992. Differential scanning calorimetry of confectionery fats: Part II—Effects of blends and minor components. J. Am. Oil Chem. Soc. 69:992.

Chaiseri, S. and Dimick, P.S. 1995a. Dynamic crystallization of cocoa butter. I. Characterization of simple lipids in rapid- and slow-nucleating cocoa butters and their seed crystals. J. Am. Oil Chem. Soc. 72: 1491.

Chaiseri, S. and Dimick, P.S. 1995b. Dynamic crystallization of cocoa butter. II. Morphological, thermal and chemical characteristics during crystal growth.. J. Am. Oil Chem. Soc. 72: 1497.

Chapman, G.M., Akehurst, E.E., and Wright, W.B. 1971. Cocoa butter and confectionery fats-studies using programmed temperature X-ray diffraction and differential scanning calorimetry. J. Am. Oil Chem. Soc. 48: 824.

Davis, T.R and Dimick, P.S. 1986. Solidification of cocoa butter. Proc. PMCA Prod. Conf. 40: 104.

Davis, T.R. and Dimick, P.S. 1989a. Crystals formed during cocoa butter solidification. J. Am. Oil Chem. Soc. 66(10): 1488-1493.

Davis, T.R. and Dimick, P.S. 1989b. Lipid composition of high-melting seed crystals formed during cocoa butter solidification. J. Am. Oil Chem. Soc. 66(10): 1494-1498.

Dimick, P.S. 1994. Influence de la composition sur la cristallisation du beurre de cacao. La cristallisation - applications au sucre et aux produits sucrés (Alliance 7 et le CEDUS) nov. Paris.

Grabielle-Madelmont, C. and Perron, R. 1983. Calorimetric studies on phospholipid-water systems. J. Colloid Interface Sci. 95: 471.

Hachiya I., Koyano, T., and Sato, K. 1989. Seeding effects on solidification behavior of cocoa butter and dark chocolate. I. Kinetics of solidification. J. Am. Oil Chem. Soc. 66: 1763.

Huyghebaert, A. and Hendrickx, H. 1971. Polymorphism of cocoa butter, shown by differential scanning calorimetry. Lebensm.- Wiss. U. Technol. 4: 59.

Loisel, C., Keller, G., Lecq, G., Launay, B., and Ollivon, M. 1997. Tempering of chocolate in a scraped-surface heat exchanger. J. Food Sci. 62: 4.

Loisel, C., G., Lecq, G., Keller G, Bourgaux C., and Ollivon, M. 1998. Phase transitions and polymorphism of cocoa Butter, J. Am. Oil Chem. Soc. In press.

Loisel C. 1996. PhD thesis, Physico-Chimie du chocolat : Cristallisation du beurre de cacao et propriétés structurales, E.N.S.I.A., Massy, France.

Lovegren, N.V., Gray, M.S., and Feuge, R.O. 1976. Polymorphic changes in mixtures of confectionery fats. J. Am. Oil Chem. Soc. 53: 83.

Manning D.M. 1984. Thermal and compositional properties of cocoa butter during static and dynamic crystallization. Ph.D thesis, The Pennsylvania University, State College, PA.

Merken, G.V. and Vaeck, S.V. 1980. Etude du polymorphisme du beurre de cacao par calorimétrie DSC. Lebensm.- Wiss. U. Technol. 13: 314.

Ollivon, M. 1992. Manuel des Corps Gras, in *Mélange de triglycérides*, A. Karleskind (Ed.), p. 491-503. Tec. et Doc, Lavoisier.

Rossell, J.B. 1967. *Advances in Lipids Research*. (5): 353-408.

Schlichter-Aronhime, J. and Garti, N. 1988. Solidification and polymorphism in cocoa butter and the blooming problems. Ch. 9. In *Crystallization and Polymorphism of fats and fatty acids*, Surfactant Science Series, vol 31, N. Garti and K. Sato (Ed.), p. 363-393. Marcel Dekker Inc., New York.

Schlichter-Aronhime J., Sarig S., and Garti N. 1988. Reconsideration of polymorphism transformations in cocoa butter using DSC. J. Am. Oil Chem. Soc. 65(7): 1140-1143.

Sidisky, L.M. and Dimick, P.S. 1993. Further characterization of steryl glucosides and esterified steryl glucosides in cocoa butter and seed crystals nuclei. Inform 4: 504.

van Malssen K.F. 1994. Real-time X-ray powder diffraction applied to cocoa butter and graphite intercalates. Ph.D thesis, Amsterdam University

Wille, R.L. and Lutton, E.S. 1966. Polymorphism of cocoa butter. J. Am. Oil Chem. Soc. 43: 491.

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