

# POLYMORPHOUS TRANSITIONS IN COCOA BUTTER

## A quantitative DSC study

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Large experimental evidence was collected on polymorphous transitions of triacyl glycerols (TAG) in cocoa butter by means of DSC investigations. The cooling treatment (in conditions close to those of the industrial practice) and the annealing temperature significantly affect the overall crystal fraction and the distribution of the various polymorphs. These data allowed a quantitative, although purely phenomenological, kinetic parameterization of polymorphous transitions of cocoa butter. The evaluation of the relevant kinetic constants and their dependence on the temperature allowed prediction of the yield in every polymorph after a given thermal history. Similar evidences were attained for cocoa liquor and dark chocolate where TAG are sided by other ingredients. These results can be the basis for an industrial exploitation.

**Keywords:** calorimetry, chocolate, cocoa butter, crystallization, DSC

### Introduction

Polymorphism of triacyl glycerols (TAG) is a thoroughly investigated property in a number of natural fats and synthetic lipids [1] since it affects the compliance of these products to thermal and mechanical treatments aimed at preparing specific foods, like chocolate, anhydrous milk fat, spreads, etc., and underlies phenomena, like the chocolate blooming, that can compromise the market performance of the final product.

In recent years Narine and Marangoni [2] demonstrated that TAG polymorphism is the molecular level of a hierarchical scale of structural features: tiny TAG crystals aggregate to form roughly spherical crystal domains (spherulites) which are interconnected to one another so as to yield a fractal network hosting a liquid phase within its meshes. The macroscopic properties of the product (e.g. its rheology) can be related to the fractal dimension of this network, which depends on the size of the spherulites and therefore on the growth extent of the specific TAG polymorph of their crystal elements. As a consequence of this intriguing model, one has to control TAG crystallization in view of the higher hierarchical structure levels that directly affect the process compliance of the raw material and the stability of the final product. These authors showed that suitable cooling rates and annealing temperatures allow the formation of a single rapidly nucleating TAG crystal form which produces a spherulitic network with a small fractal dimension and a final product with a high elastic modulus; slow cooling rates and low annealing

temperatures will instead allow coexistence of various TAG polymorphs, and produce a more disordered network with large fractal dimension and a final product with a small elastic modulus.

Further advancements of this state of the art therefore imply a thorough and quantitative description of the TAG polymorphous transitions and their dependence on cooling rate and annealing temperature. An important contribution to this progress is the recent work by Loisel *et al.* [3] who reported the results of diffraction of synchrotron radiation coupled with DSC investigations on cocoa butter. This study confirms the polymorph series, I–VI (in order of increasing melting point) proposed by Wille and Lutton [4], but reveals that phase separations take place when cocoa butter is annealed and that annealing allows the irreversible transformation of polymorph IV into polymorph V, the high melting TAG crystal form, VI being a mixture of different crystal types, again as a result of a phase separation. The work of Loisel *et al.* can indeed be referred to as a substantial progress of the current understanding of TAG polymorphism, allowing a firmer confidence in the Wille and Lutton classification of TAG polymorphs and enhancing the vision of a kinetic rather than thermodynamic way to describe the transformations that take place in fats.

Cocoa butter is a mixture of fats the composition of which depends on many factors, including the vegetal origin of the product. The mass fractions of the three main TAG however are rather similar in any cocoa butter, with a predominance of POS (Palmitic-Oleic-Stearic triglyceride). An important

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synthesis of the state of the art is reported by Sato and Koyano [5] who determined the regions of the ternary (SOS, POS and POP triglycerides) phase diagram where either a single phase or a mixture of phases is expected: it can be easily recognized that a multi-TAG product, like cocoa butter in the state with the highest melting point (polymorph V), can be referred to as a solid solution. Such TAG mixtures behave like a pseudo single-component system, inasmuch as a suitable thermal treatment, namely cooling the melt at a given rate and annealing the solid at a given temperature for a given time, produces a material with predictable properties, like crystal structure, melting point and viscosity, which seem not affected by the minor differences in the composition. That is why comparable values of these properties have been so far reported by different authors who investigated cocoa butter of different origin [6–8].

The present work is in line with these recent fundamental assessments [3] and aims at a quantitative description of the kinetics of the TAG polymorphous transitions in cocoa butter, cocoa liquor and chocolate cooled from the molten state at cooling rates close to those of the industrial practice, so as to allow prediction of the specific polymorph type produced with a given thermal history. This result should be of interest either to perfect the fractal model of fat crystallization [2] or to improve the industrial practice for cocoa-based products.

DSC technique is of rather simple use in any industrial laboratory for routine controls, but can also be of help to get adequate information about structural transitions, so far approached mainly with much more sophisticated techniques. In the present work, some hundred DSC traces were used as the experimental fundament for a reliable picture of the changes experienced by the material during a given thermal history and for a reliable kinetic parameterization of the TAG polymorphous transitions in cocoa butter and chocolate samples. A side scope of the present paper was indeed to show how much can the application range of DSC data be extended when they are processed with an adequate mathematical treatment.

## Materials and methods

Cocoa butter, cocoa liquor and dark chocolate were supplied by a chocolate industrial producer.

The TAG content of cocoa butter was: 40% POS, 25% SOS, 20% POP, and an overall 4.9% including POO, PLiS, SOO, SLiS, SOA and PLiP, where O, P, S and Li stand for Oleic, Palmitic, Stearic and Linoleic acids, respectively; free fatty acids accounted for less than 0.5%.

The overall cocoa butter content in cocoa liquor was 53.5% (mass/mass), the rest of the material being starch, vegetal fibers, polyphenols and proteins in amounts not declared by the supplier.

Dark chocolate was a product industrially prepared from the cocoa butter and the cocoa liquor described above. Its overall cocoa butter content was 32% (mass/mass).

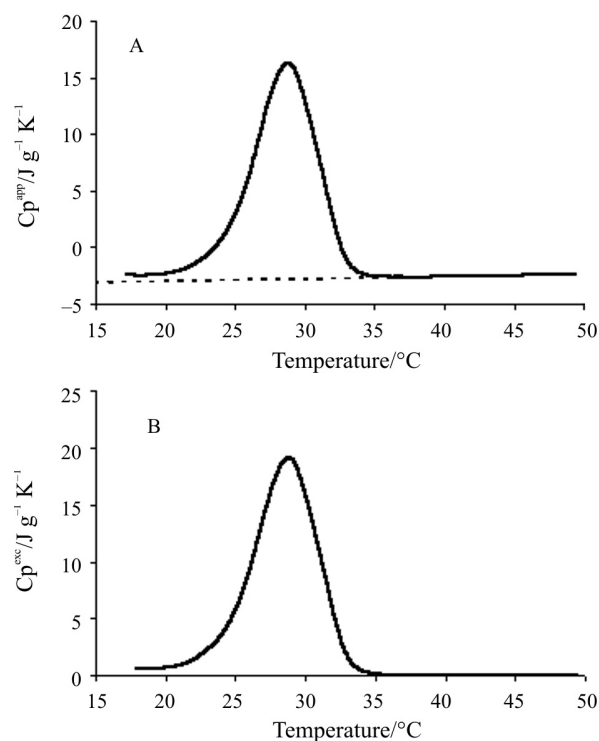
## DSC

The instrument used was a Perkin Elmer DSC6. Aluminum pans were used. Twice distilled water was used as the reference material and 40 mg samples were used for the investigations.

All these samples were sealed in the DSC pan and heated up to 50°C and rest for 5 min to allow the whole mass to melt: this treatment was directly monitored recording the relevant the DSC signal that attained a straight line trend, corresponding to the apparent heat capacity of the molten state. The preliminary equilibration in the molten state at 50°C was found sufficient to cancel any previous thermal history, as long as the repeated DSC runs with a given sample gave completely overlapped traces.

Starting from the molten state, the samples were cooled at various cooling rate down to different temperatures, where they were let at rest for different annealing times. All the samples were then DSC investigated at a heating rate,  $\beta$ , of 2 K min<sup>-1</sup>. This was a reasonable compromise between lower  $\beta$  values, that would allow a better splitting of the DSC signals, and the need of collecting a large number of traces to encompass a wide range of possible thermal histories. Because of the number of these and the rather long time required for each DSC run (mainly because of the rest time at the given annealing temperature), replicas were performed on a fraction of the samples examined, which nonetheless was large enough to assess the reproducibility of the results and allow satisfactory (less than 2% for enthalpy) confidence limits.

The output signal in mW units was divided by the sample mass·heating rate product to be converted into apparent heat capacity  $C_p^{app}$ , in J g<sup>-1</sup> K<sup>-1</sup> units. The trace of  $C_p^{app}$  was finally scaled with respect to the baseline to obtain the excess heat capacity with respect to the molten state,  $C_p^{exc}$ . The straight line fit of the  $C_p^{app}$  vs.  $-T$  trend for the molten cocoa butter was used as the baseline of the trace (Fig. 1). Due to the units selected, namely [J g<sup>-1</sup> K<sup>-1</sup>] and [K], the area underlying the recorded peaks directly corresponded to the relevant enthalpy drop in J g<sup>-1</sup> units. This normalization procedure allowed comparison between records obtained from different samples.



**Fig. 1** DSC trace of a heating run for a thoroughly annealed cocoa butter sample (A). The linear trend relevant to the molten state was selected as the baseline to be subtracted from the whole trace to give the final trace (B),  $C_p^{\text{exc}}/\text{J g}^{-1} \text{K}^{-1}$  vs.  $T/^\circ\text{C}$

The deconvolution of these traces was performed with the software PeakFit v4 released from Jandel Scientific Software using Gaussian functions (see Results and discussion).

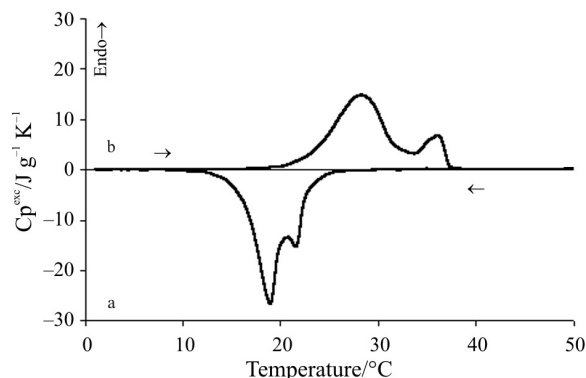
#### Kinetic parameters

The same software program (PeakFit v4) was used to evaluate the kinetic parameters of the polymorphous transitions through a best-fit treatment of the data obtained from the deconvolution of the DSC traces according the kinetic model (see results and discussion).

## Results and discussion

The DSC trace (Fig. 2a) of a cocoa butter sample cooled at  $0.1 \text{ K min}^{-1}$  from  $50^\circ\text{C}$  (where it was completely molten) down to  $1.0^\circ\text{C}$  showed an exothermic peak with onset around  $26^\circ\text{C}$  and minimum around  $21.5^\circ\text{C}$ , followed by a second exothermic peak with minimum around  $19.0^\circ\text{C}$ .

These peaks are related to the separation of crystal phases. Peculiarities of crystallization mechanism and types of crystals formed are fully described in the literature [1, 3, 5]. After 1 min rest at  $1^\circ\text{C}$ , the sample

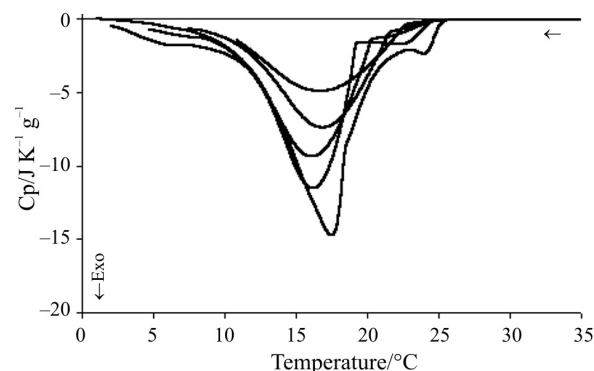


**Fig. 2** a – DSC traces of cooling and b – after 1 min rest at  $1^\circ\text{C}$ , heating runs performed at  $0.1 \text{ K min}^{-1}$  for a cocoa butter sample

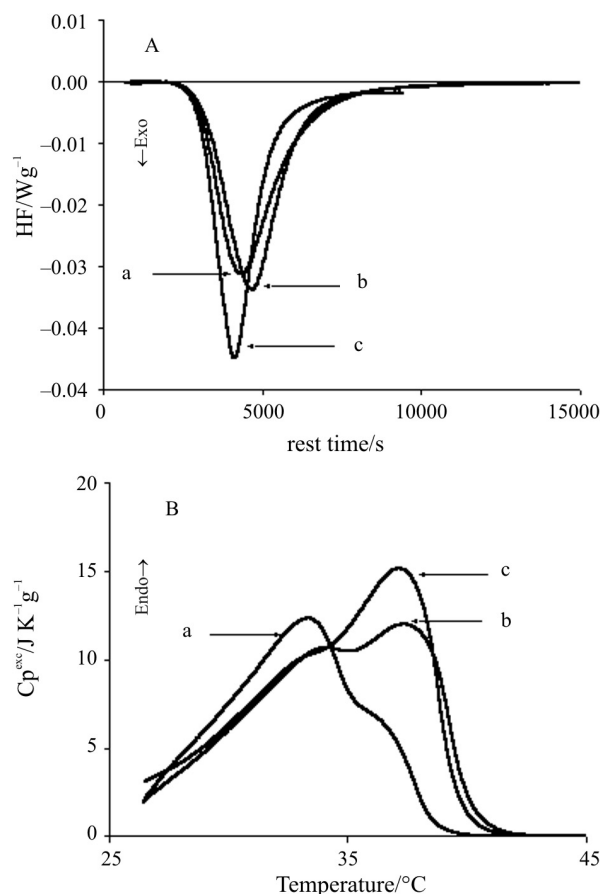
was heated up (at  $0.1 \text{ K min}^{-1}$ ). The corresponding DSC trace (Fig. 2b) showed at least two endothermic peaks with several shoulders across a wide temperature range. These peaks are related to the fusion of the various crystal types formed on cooling. The relevant enthalpies referred to one gram of sample,  $\Delta H=116\pm 3 \text{ J g}^{-1}$  and  $\Delta H=115\pm 3 \text{ J g}^{-1}$  for trace a and b, respectively, indicate that the low cooling rate allows an almost complete crystallization (the progress of the polymorph transition being negligible during the DSC heating run; see below).

A much different picture appears when different cooling rates are considered (in the industrial practice they are larger than  $10 \text{ K min}^{-1}$ ). The DSC traces relevant to cocoa butter samples cooled from  $50^\circ\text{C}$  at various cooling rates, i.e.,  $0.5, 2, 4, 6, 8 \text{ K min}^{-1}$  (Fig. 3) indicated that the exothermic crystallization signal (on cooling) was strongly affected by the cooling rate either for the overall crystallized mass fraction, which drastically decreased with increasing cooling rate, or for the type of polymorph formed, which are singled out by inspecting the trace of the DSC heating run (see below).

In a first attempt, isothermal calorimetry, IC, was used to follow up the growth of the crystal phases



**Fig. 3** DSC traces of cooling runs performed at various scanning rates ( $0.5, 2, 4, 6, 8 \text{ K min}^{-1}$ ). The smaller the cooling rate, the larger the crystallization exothermic peak and the earlier its onset



**Fig. 4** A – IC traces (25°C) relevant to the growth of crystals in cocoa butter samples previously cooled from 50°C down to 25°C at 10 (a), 5 (b) and 2 (c)  $K min^{-1}$ . B – DSC traces (heating run at 2  $K min^{-1}$ ) of the same samples (after 20 h rest at 25°C)

during the annealing period at 25°C. Figure 4A shows the relevant traces obtained from samples cooled at 10, (a), 5 (b) and 2 (c)  $K min^{-1}$  from 50°C down to 25°C and kept at this temperature.

A single exothermic well-shaped signal was observed in all the experiments, although the relevant thermal effects were different from one another, thus confirming that crystallization is affected by the cooling rate. However these signals did not allow any split between different cocoa butter polymorphs, mainly because the relevant crystallization enthalpies are very close to one another (Table 1).

Standard DSC heating runs (at 2  $K min^{-1}$ ) performed on samples cooled from 50°C down to 25°C and kept at this temperature for 20 h showed the endothermic peaks related to the fusion of the crystals formed during cooling and rest time (Fig. 4B). The shoulders of these peaks suggested the presence of various crystal types that melt at slightly different temperatures. These preliminary results indicated that the standard DSC is more adequate than the IC to check the presence of the TAG polymorphs.

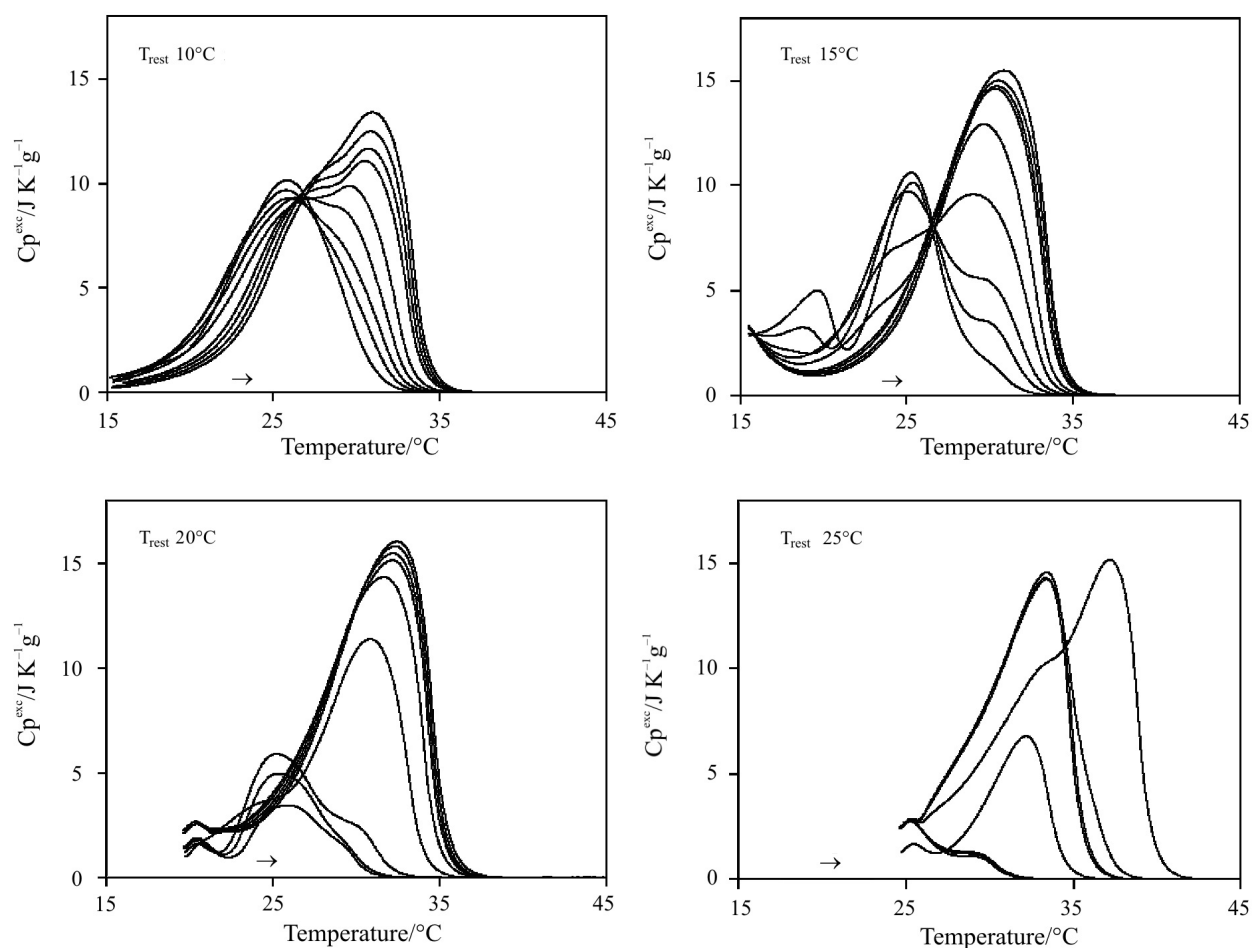
**Table 1** Column A: fusion temperatures of TAG polymorphs of cocoa butter obtained from the auto-consistent deconvolution procedure (see text). Column B: fusion enthalpies of TAG polymorphs from [3]

TAG crystal form	A	B
	$T_{fus}/^{\circ}C$	$\Delta_{fus}H/J g^{-1}$
II	23.5±1.0	86.15
III	26.0±0.5	112.47
IV	29.0±0.5	117.57
V	31.3±0.5	136.73
VI	36.0±1.5	148.02

The information drawn from one DSC run is however limited to a single thermal history experienced by the sample. For this reason, a comprehensive investigation plan must include a large number of samples, each with a given thermal history, so as to encompass a wide region of the temperature – time plane. For the present work, cocoa butter samples were previously cooled at 2, 5 and 10  $K min^{-1}$  from 50°C down to five different annealing temperatures (5, 10, 15, 20 and 25 °C) where they rested for various lapses of time (5, 10, 15, 30, 60 min, 3, 5, 10, 20 h). The overall investigation plan therefore implied 135 cooling rate/annealing temperature combinations, for each of which a DSC run was performed at 2  $K min^{-1}$  heating rate. Collected data included replicas for many of them (see section Materials and Methods).

The results from samples cooled at 2 and 10  $K min^{-1}$  are reported in Figs 5 and 6. Analogous results were collected for samples cooled from the molten state at 5  $K min^{-1}$ . The maximum enthalpy observed, 121  $J g^{-1}$ , corresponded to a cooling rate of 2  $K min^{-1}$  and 20 h rest at 25°C

The DSC endothermic signal related to the fusion of cocoa butter samples was split in different fusion peaks centered at the expected melting points of the six TAG polymorphs proposed in the literature. These peaks were given a Gaussian shape as a reasonable approximation of the expected trend for a cooperative process, like fusion, of a small mass sample. Other functions that correspond to slightly skewed peaks, which may be closer to the actual shape of these contributions to the overall DSC signal, do not imply a significantly improved confidence of the deconvolution treatment. More empirical approaches [9] led to similar qualitative conclusions that cannot be of help for a reliable parameterization of the polymorphous transitions. An important source of uncertainty is related to the choice of a reliable value of the melting temperatures,  $T_{fus}$ , of each cocoa butter polymorph, because of the many discrepancies between relevant literature [3, 4] data (which may be due the different experimental methods used for their



**Fig. 5** DSC traces (heating run at  $2 \text{ K min}^{-1}$ ) of cocoa butter samples cooled from the molten state ( $50^\circ\text{C}$ ) at  $2 \text{ K min}^{-1}$  and kept at rest for various lapses of time (5, 10, 15, 30, 60 min, 3, 5, 10, 20 h) at four different resting temperatures  $T_{\text{rest}}$  (10, 15, 20 and  $25^\circ\text{C}$ )

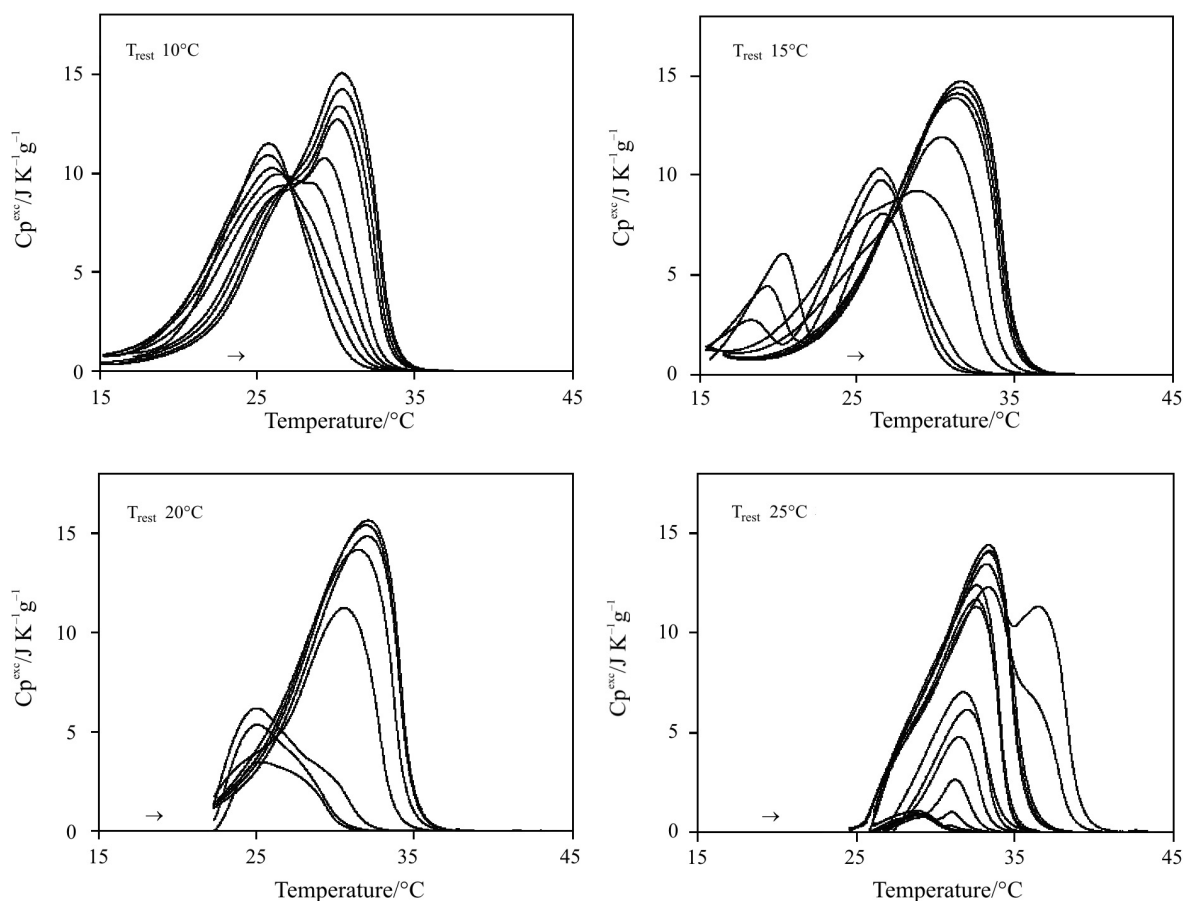
determination). This is why the literature  $T_{\text{fus}}$  values were used as a starting estimation to be adjusted through the deconvolution routine. Having collected a huge number of thermograms, the deconvolution treatment was planned to achieve both a satisfactory fit of each DSC trace and a reliable self-consistency of the set of the six  $T_{\text{fus}}$  (Table 1), which was therefore applied to all the DSC traces of the present work. An example of deconvolution is shown in Fig. 7.

The six  $T_{\text{fus}}$  found with this approach are in the range of those reported in the literature; none the less they should be referred as ‘apparent’ fusion points as far as they are indeed affected by the heating rate ( $2 \text{ K min}^{-1}$ ) and the sample mass. The area underlying each Gaussian directly gave the relevant fusion enthalpy of the corresponding crystal form. The mass fraction,  $\alpha_i$ , of each polymorph actually present in the sample was determined by dividing the area of the relevant Gaussian peak by the fusion enthalpy of the corresponding pure polymorph (Table 1) reported in the literature [3],

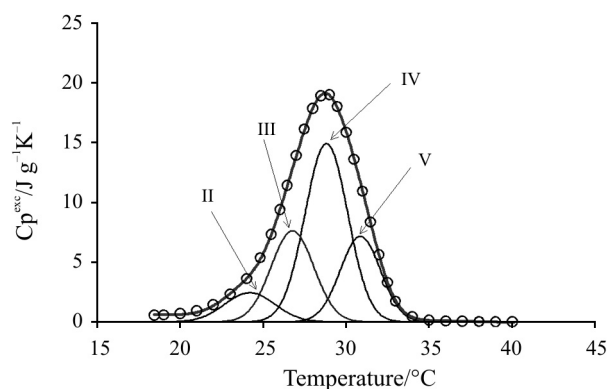
$$\alpha_i = \frac{\text{area of the } i^{\text{th}} \text{ gaussian peak}}{\text{fusion enthalpy of the pure } i^{\text{th}} \text{ crystal form (Table 1)}}$$

where ‘ $i$ ’ stands for I, II, III, IV, V and VI. The evaluation was repeated for every cooling rate and annealing temperature in order to monitor the rise and the decline of each TAG polymorph in cocoa butter during the rest time. The evolution of the crystal forms III, IV, V, VI, in samples cooled at 2 and  $10 \text{ K min}^{-1}$  are reported in Figs 8 and 9. Form II was detected only in samples annealed at 5, 10 and  $15^\circ\text{C}$  and its fraction was monotonically decreasing in all the cases. Form I ( $T_{\text{fus}}=19\pm 2^\circ\text{C}$ ) was detected very seldom. Analogous results were collected for samples cooled from the molten state at  $5 \text{ K min}^{-1}$  and not annealed.

Inspection of the data reported in Figs 8 and 9 allowed definition of the events that took place during the thermal history experienced by each sample. Cooling rate and annealing temperature have different effects on the growth of the various polymorph types. For the cooling rates considered, only some polymorph types can be observed at a given annealing



**Fig. 6** DSC traces (heating run at  $2 \text{ K min}^{-1}$ ) of cocoa butter samples cooled from the molten state ( $50^\circ\text{C}$ ) at  $10 \text{ K min}^{-1}$  and kept at rest for various lapses of time (5, 10, 15, 30, 60 min, 3, 5, 10, 20 h) at four different resting temperatures  $T_{\text{rest}}$  (10, 15, 20 and  $25^\circ\text{C}$ ). For  $T_{\text{rest}}=25^\circ\text{C}$  the rest times considered were: 35, 40, 45, 50, 55, 90, 150 min and 40 h (shown by the arrow)



**Fig. 7** Deconvolution of the DSC trace (heating run at  $2 \text{ K min}^{-1}$ ) of a cocoa butter sample cooled from the molten state ( $50^\circ\text{C}$ ) at  $5 \text{ K min}^{-1}$  and kept at rest for 60 min at  $T_{\text{rest}}=10^\circ\text{C}$ . The Gaussian contributions were centered at the fusion temperatures reported in Table I to single out the contribution from each polymorph type. A small contribution was also found to account for polymorph I

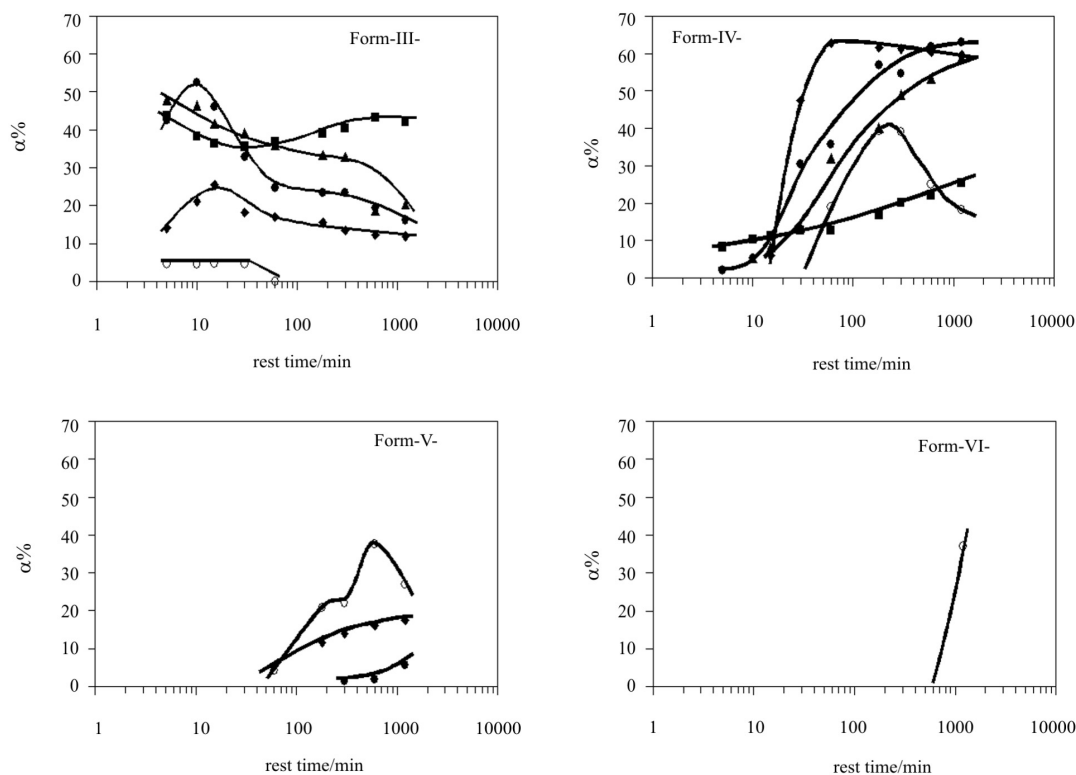
temperature within a reasonable (for the industrial practice) lapse of time, ought to their metastable character and the overwhelming effect of kinetic factors. Furthermore some of them do not directly arise from

the liquid phase. Looking at the rise and decline of the various forms, one can easily recognize that V stems from IV and is the precursor of VI. A summary of these results can be represented with a qualitative scheme of the transitions that take place (after cooling from the molten state) during the rest of the sample at a given  $T_{\text{rest}}$  (Fig. 10).

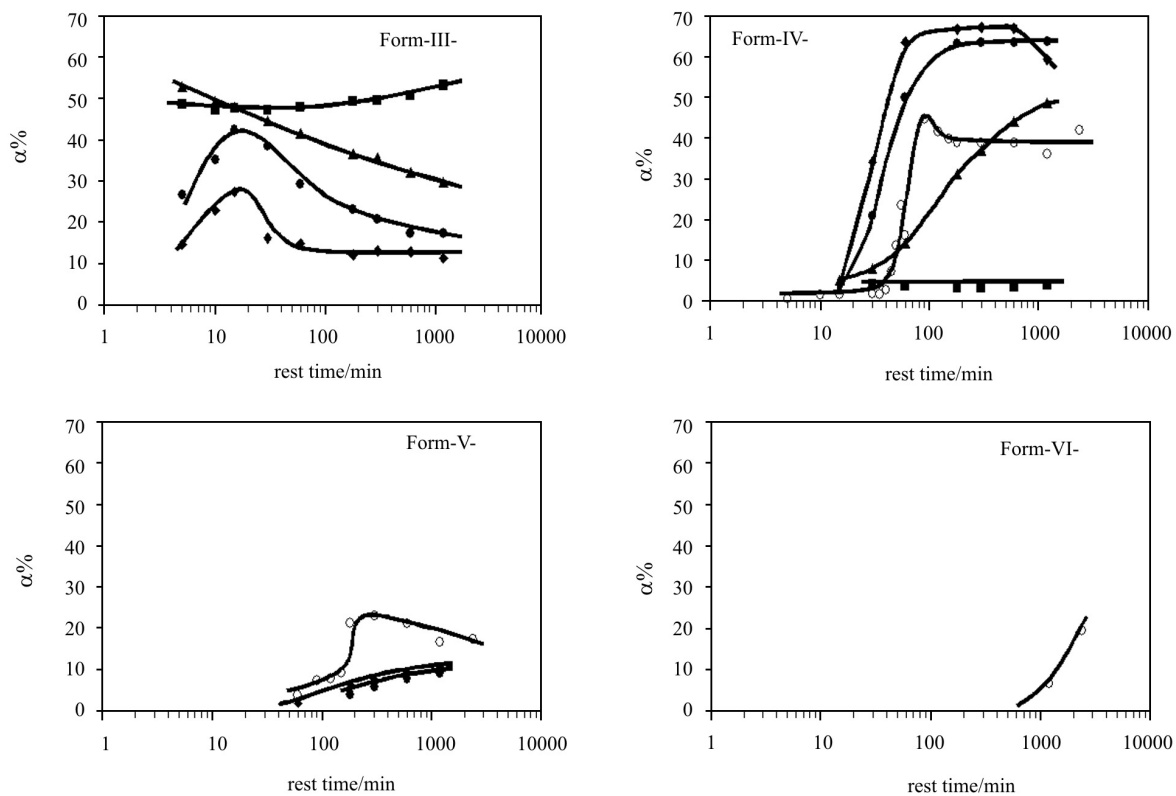
The increase of the overall crystal mass fraction,  $\alpha = \sum_i \alpha_i$ , of cocoa butter therefore follows a complex pattern implying the decline of some polymorph and the rise of some else (Fig. 11).

The value of  $\alpha$  never exceeded 0.9, namely, the overall TAG content of the cocoa butter (90%, see Material and Methods), and therefore indicated that no extra phenomena, but just the TAG transitions, were responsible for the DSC signal. Whichever the previously experienced cooling rate, the condition  $\alpha \sim 0.9$  was attained in samples annealed at  $20^\circ\text{C}$  earlier than in samples kept at any other rest temperature. However this  $\alpha$  level did correspond to different distributions of polymorphs as a result of the cooling conditions: fast cooling was indeed followed by growth of polymorphs with lower melting temperatures (mainly IV after the longest rest), while slow cooling was ac-

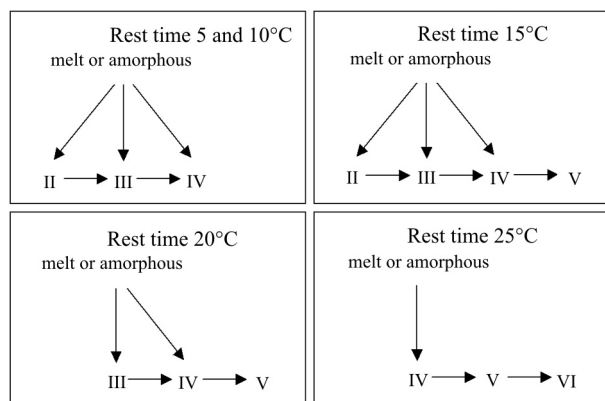
POLYMORPHOUS TRANSITIONS IN COCOA BUTTER



**Fig. 8** Trend of the crystal fractions  $\alpha$  of TAG polymorphs formed at various rest temperatures,  $T_{\text{rest}}$ , in cocoa butter samples previously cooled from the molten state down to  $T_{\text{rest}}$  at  $2 \text{ K min}^{-1}$ . Squares, triangles, full circles, romps and open circles correspond to  $T_{\text{rest}}=5, 10, 15, 20$  and  $25^\circ\text{C}$ , respectively



**Fig. 9** Trend of the crystal fractions  $\alpha$  of TAG polymorphs formed at various rest temperatures,  $T_{\text{rest}}$ , in samples previously cooled from the molten state down to  $T_{\text{rest}}$  at  $10 \text{ K min}^{-1}$



**Fig. 10** Qualitative scheme of the transitions that take place in cocoa butter sample annealed at a given  $T_{rest}$  after a previous cooling from the molten state

accompanied by much higher yields of polymorphs V and VI. It is of industrial interest (tempering process) to notice that the longest lag-time before the onset of the crystal growth was observed for  $T_{rest}=25^{\circ}\text{C}$ , no matter the rate of the previous cooling treatment (Fig. 11).

Because of the number of polymorphs that concur to the overall crystal fraction, a formal kinetic model is not simple to assess. In particular the classical Avrami approach may not be applied to  $\alpha$  in a straightforward way. The following example can elucidate this point.

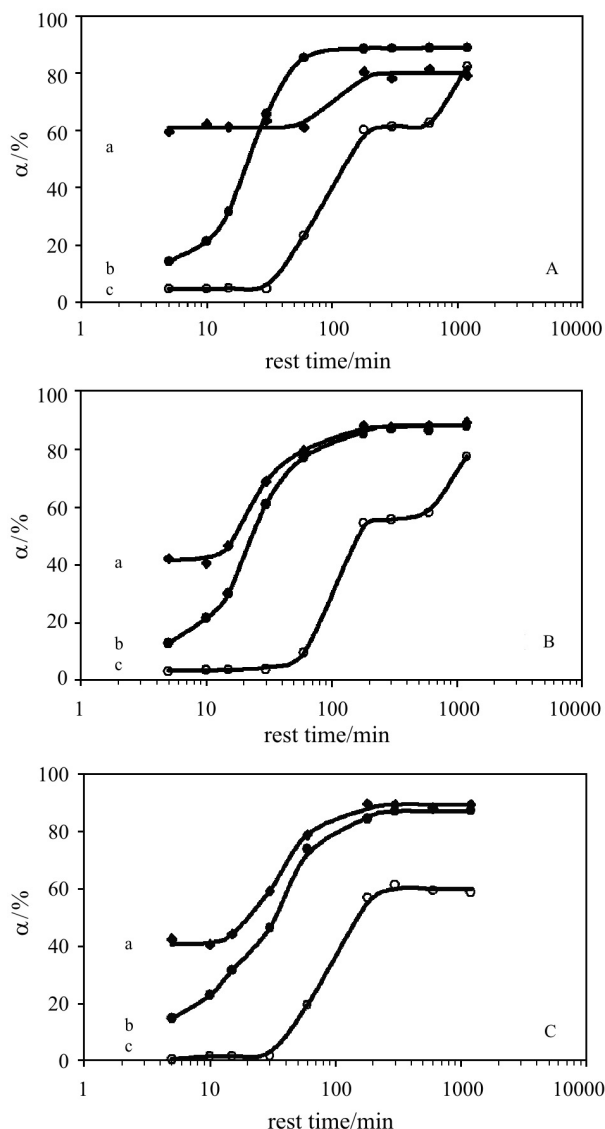
Figure 12 shows the  $\alpha$ -vs.- $t$  trend (where  $t$  stands for annealing time), relevant to samples cooled at  $2\text{ K min}^{-1}$  and annealed at  $20^{\circ}\text{C}$ . A rising branch is followed by a plateau, just as in any nucleation/growth process described with an Avrami model,

$$\alpha = 1 - \exp(-kt^n)$$

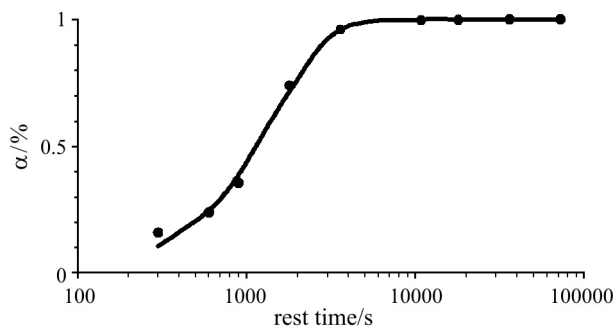
The best fit was found for  $n=1.36$  and  $k=4.82 \cdot 10^{-5}\text{ s}^{-n}$ .

Such fit was however misleading since the sample hosted a mixture of polymorphs (Fig. 8): polymorph IV predominates in the earliest part of the process (there are also minor amounts of III) and steeply increases, while almost no V is yet present. After about 100 min annealing the IV mass fraction declines being almost exactly counterbalanced by the rise of the mass fraction of V. This example suggests that, when dealing with cocoa butter (and other natural fats), one should be careful in applying simplistic models [10] that may be not reliable at all.

The evidence collected shows that the evolution of a cocoa butter sample in the solid state strongly depends on the starting conditions, namely the mass fraction of the various polymorphs formed during the cooling from the molten state and the amount of amorphous material [11].



**Fig. 11** Trend of the overall crystal fraction at various rest temperatures (a –  $15^{\circ}\text{C}$ ; b –  $20^{\circ}\text{C}$ ; c –  $25^{\circ}\text{C}$ ) in cocoa butter samples cooled from the molten state ( $50^{\circ}\text{C}$ ) at various cooling rates (A –  $2\text{ K min}^{-1}$ ; B –  $5\text{ K min}^{-1}$ ; C –  $10\text{ K min}^{-1}$ )

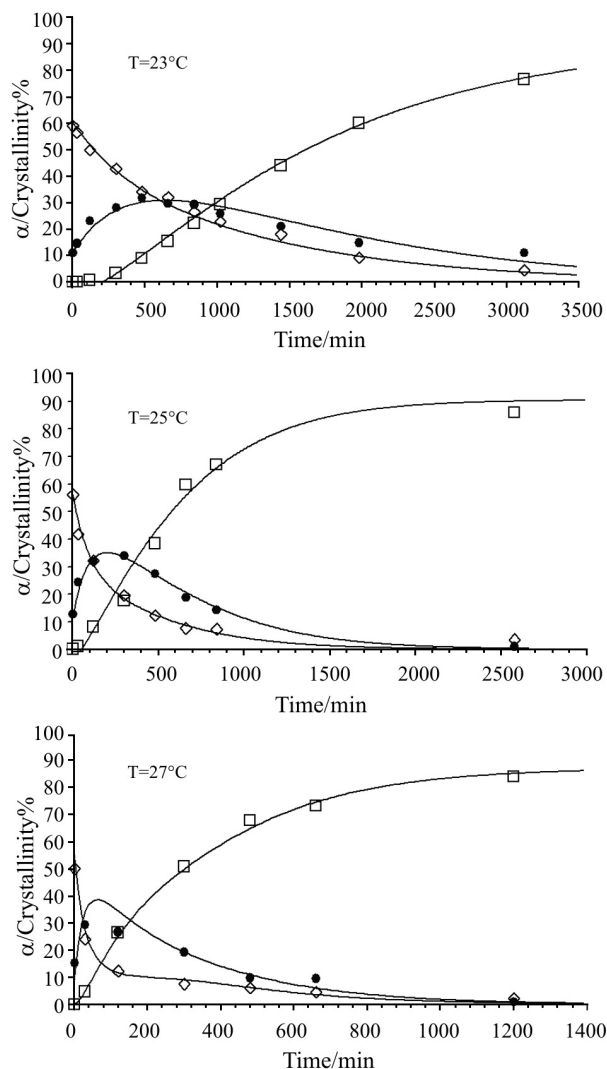


**Fig. 12** Fictitious Avrami fit of the crystal growth within a cocoa butter sample (see text)



To account for all the transitions that take place in the real production of a stable solid, a number of parameters should therefore be determined. In order to single out the effects of the polymorphous transitions from the overall change that implies the formation of crystals from the amorphous and/or liquid fractions, our attention was focused on samples pre-treated so as to contain a rather small fraction of amorphous material and low melting crystals and known fractions of polymorphs IV, V and VI.

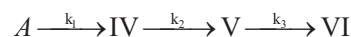
On the basis of the data collected (Fig. 9), the most suitable pre-treatment seemed the one that implies a 20 h rest at 15°C after cooling at 10°C min<sup>-1</sup> from the molten state, as far as it produced about 60% mass fraction of IV in a 6 mg cocoa butter sample, according to DSC traces obtained at 2 K min<sup>-1</sup> heating rate (data not shown).



**Fig. 13** Fit of the experimental data relevant to the progress of the mass fractions of polymorphs IV (romps), V (full circles) and VI (squares) in pre-conditioned (see text) cocoa butter samples kept at 23, 25 and 27°C

Samples prepared in this way were annealed at three different temperatures (23, 25, 27°C) for various lapses of time. Annealed samples were investigated with a DSC run at 2 K min<sup>-1</sup> heating rate so as to calculate the mass fraction of each polymorph from the deconvolution of the relevant traces. The results are shown in Fig. 13 (experimental points). It has to be noticed that the three high melting polymorphs account for about 90% of the overall mass of the sample.

In order to define a quantitative description of these changes, the three consecutive steps model assessed above was tentatively interpreted assuming simple first order kinetics for each step:



where *A* stands for a mixture of amorphous and low melting forms. This choice requires integration of the following system of differential equations:

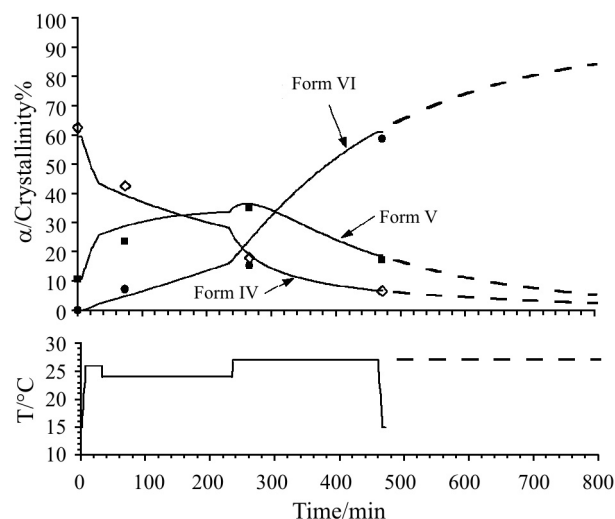
$$\frac{d(A)}{dt} = -k_1(A)$$

$$\frac{d(IV)}{dt} = k_1(A) - k_2(IV)$$

$$\frac{d(V)}{dt} = k_2(IV) - k_3(V)$$

$$\frac{d(VI)}{dt} = k_3(V)$$

where (*A*), (*IV*), (*V*), (*VI*) are the relevant mass fractions and *t* is the time.



**Fig. 14** Predicted trends (lines) of the mass fractions of polymorphs IV, V and VI in pre-conditioned (see text) cocoa butter samples that undergo a selected thermal history (lower part). The experimental data are the result of the deconvolution of the DSC traces obtained from different samples that actually underwent the selected thermal history

The  $k_j$ 's stand for effective kinetic constants that were used as fitting parameters in the integration routine (analytical solution can be easily achieved) aimed at the best fit of the  $\alpha_i$  - vs. -  $t$  trends drawn from DSC data.

Fitting trials with this model were unsatisfactory and suggested that the second step of the above scheme could not be described with a simple first order kinetics, as  $k_2$  seemed dependent on IV.

The simplest way to simulate such a behavior was to assume for  $k_2$  a linear expression, like

$$k_2 = a(IV) + b$$

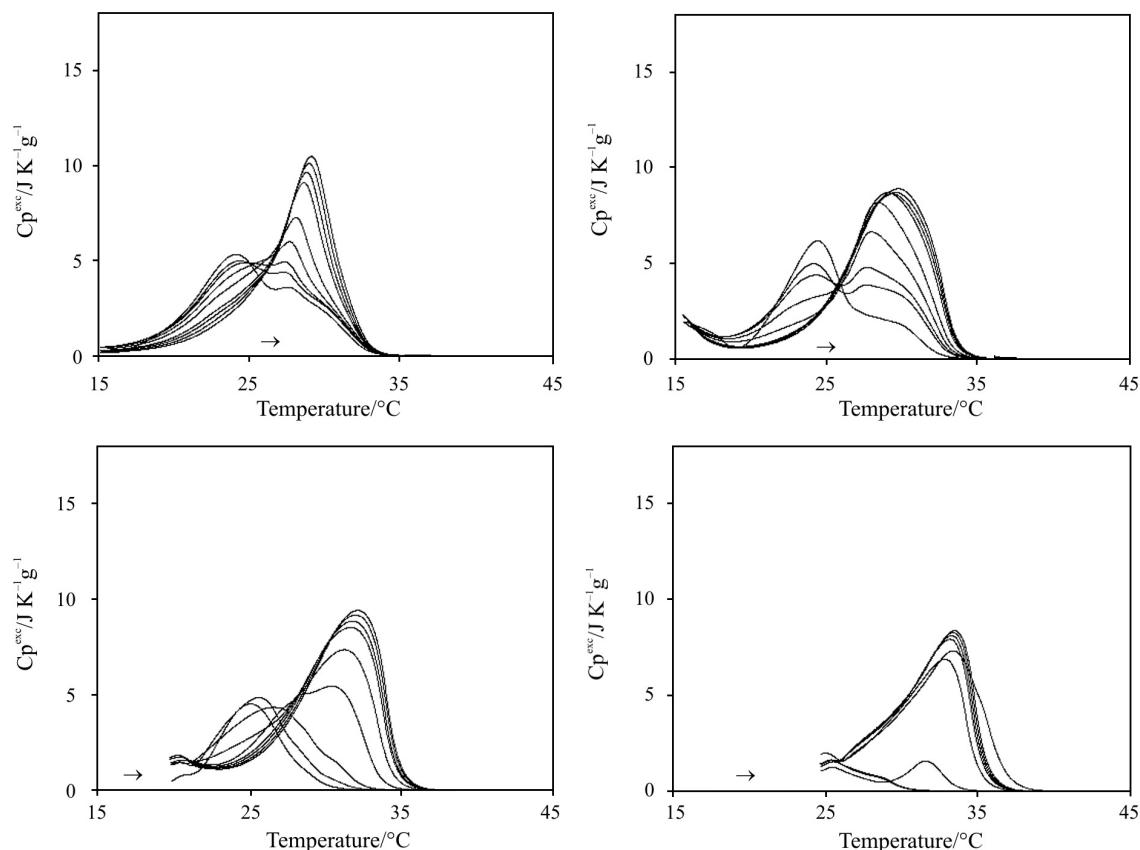
where  $a$  and  $b$  became the new fitting parameters to be determined in the integration routine.

This adjustment led to a substantial improvement of the fit as shown in Fig. 13 (fitting lines), that reports the results of these calculations for the three annealing temperatures. In this representation the very fast decay of the starting fraction of amorphous + low melting polymorphs (mainly III), has been omitted for the sake of clarity.

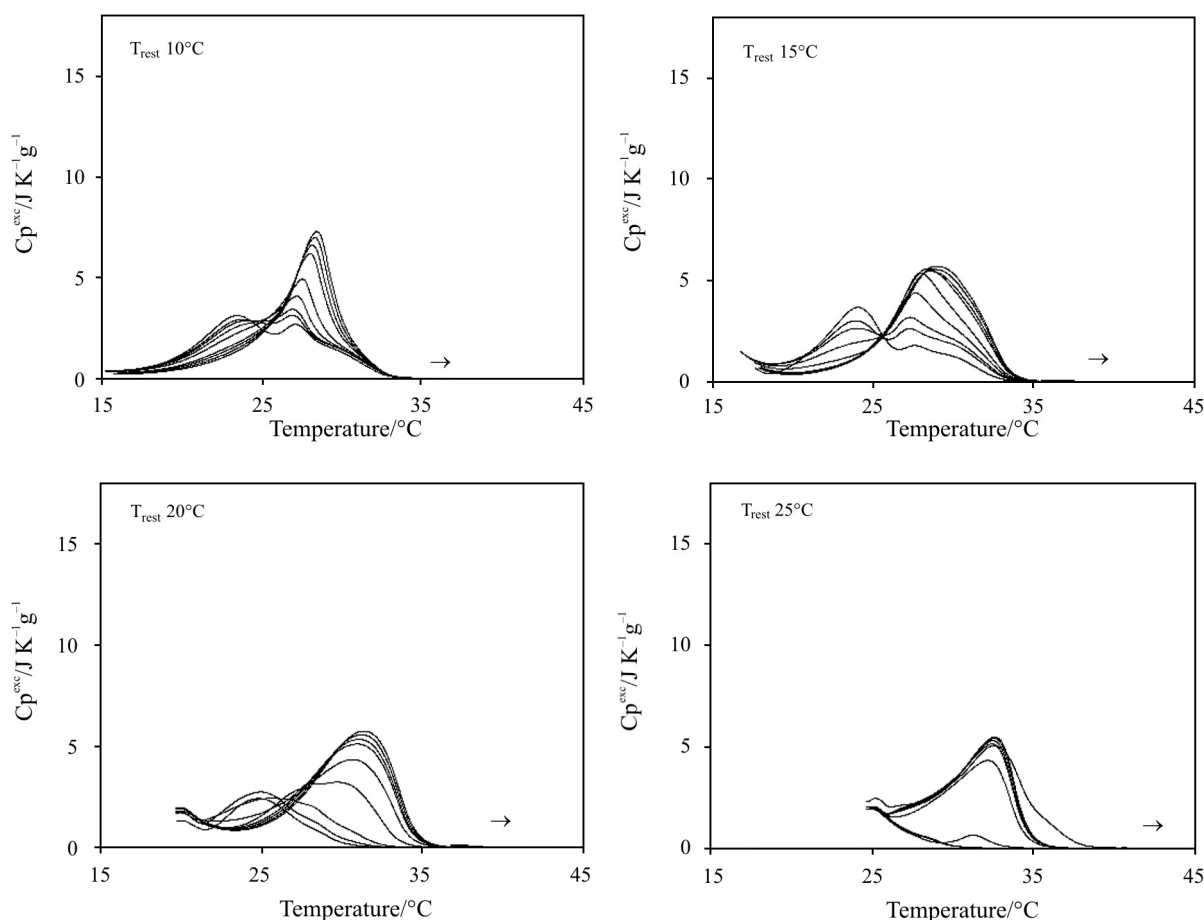
The effect of temperature on  $k_1$ ,  $k_2$  and  $k_3$  was accounted for using a fitting empirical expression for the calculated  $k$ 's at the three temperatures. A dedicate software was accordingly designed to predict the

three mass fractions, IV, V and VI, at any moment of a given thermal history. The details of this part of the work and the values of the  $k$ 's are still reserved and therefore may not be reported in this paper, but they are not crucial for a thorough understanding. It has to be stressed that the 'predicted' trends reflect an adequately tailored phenomenological scheme, which may not be referred to as the real mechanism of these polymorphous transitions at the molecular level. They are instead useful tools for technological applications. To exemplify the use of this model, the progress of the mass fraction during a given thermal history (see Fig. 14, lower part) was calculated (Fig. 14, upper part) starting from the same initial conditions ( $IV_0$ ,  $V_0$  and  $VI_0$ ) as those assessed for pre-treated samples (see above, Fig. 13). The reliability of this prediction was experimentally checked on pre-treated cocoa butter samples that experienced (within the calorimetric cell) the selected thermal history to different extents. The samples were eventually tested with a DSC run at  $2 \text{ K min}^{-1}$  and the relevant traces were deconvoluted as described above to evaluate the mass fractions of IV, V and VI (Fig. 14 experimental points).

This phenomenological description was extended to analogous investigations (Figs 15 and 16)



**Fig. 15** DSC traces (heating run at  $2 \text{ K min}^{-1}$ ) of cocoa liquor samples cooled from the molten state ( $50^\circ\text{C}$ ) at  $10 \text{ K min}^{-1}$  and kept at rest for various lapses of time (5, 10, 15, 30, 60 min, 3, 5, 10, 20 h) at four different resting temperatures  $T_{\text{rest}}$  (10, 15, 20 and  $25^\circ\text{C}$ )

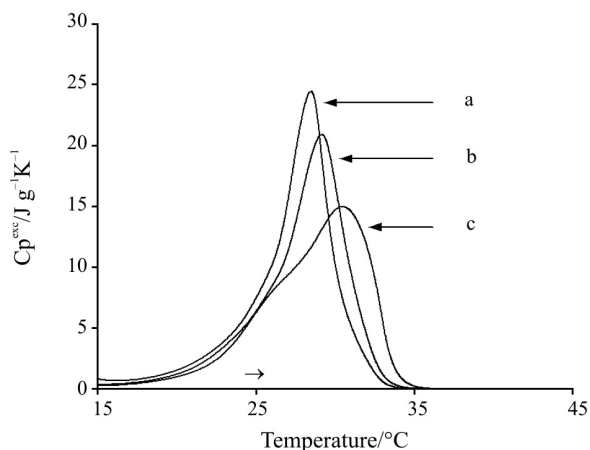


**Fig. 16** DSC traces (heating run at  $2 \text{ K min}^{-1}$ ) of dark chocolate samples cooled from the molten state ( $50^\circ\text{C}$ ) at  $10 \text{ K min}^{-1}$  and kept at rest for various lapses of time (5, 10, 15, 30, 60 min, 3, 5, 10, 20 h) at four different resting temperatures  $T_{\text{rest}}$  ( $10, 15, 20$  and  $25^\circ\text{C}$ )

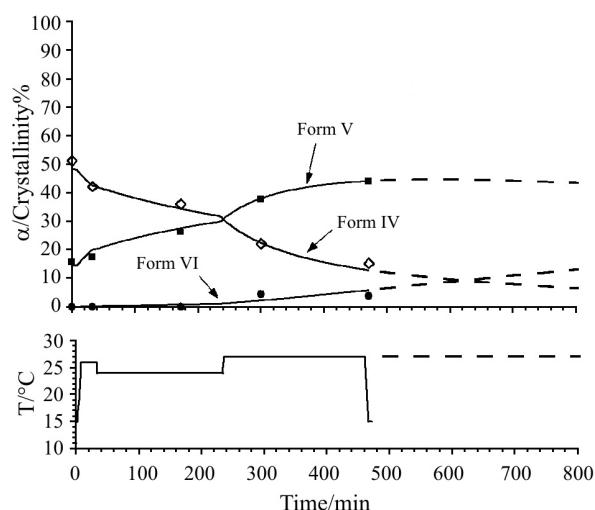
on cocoa liquor and whole dark chocolate to collect evidence of the role of other components on the TAG polymorphous transitions.

Despite the smaller thermal effects (namely, enthalpy values), which were expected because of the smaller TAG mass fraction, these data suggest that the non-TAG ingredients simply delay the progress of the transitions without affecting their phenomenal mechanism. A direct comparison of the behavior of cocoa liquor and whole chocolate with respect to that of pure cocoa butter is reported in Fig. 17, where the signals have been normalized to the cocoa butter content (see section Material and Methods).

These findings support the expectation that a formal kinetic model for TAG transitions in cocoa butter holds also in the presence of the other chocolate ingredients. In order to confirm the above statement, the experimental and calculation procedures assessed for the cocoa butter was followed to evaluate  $k_1$ ,  $k_2$ ,  $k_3$  for chocolate samples. The predicted trends of the mass fractions of cocoa butter polymorphs in the chocolate bulk and the relevant experimental check (data collected as in the case of cocoa butter) are reported in Fig. 18.



**Fig. 17** DSC traces (heating run at  $2 \text{ K min}^{-1}$ ) of a – cocoa butter, b – cocoa liquor and c – dark chocolate samples cooled from the molten state ( $50^\circ\text{C}$ ) at  $10 \text{ K min}^{-1}$  at kept at rest for 20 h at  $25^\circ\text{C}$ . Signals were normalized with respect to the actual content of cocoa butter



**Fig. 18** Predicted trends (lines) of the mass fractions of polymorphs IV, V and VI in pre-conditioned (see text) chocolate samples that undergo a selected thermal history (lower part). The experimental data are the result of the deconvolution of the DSC traces obtained from different samples that actually underwent the selected thermal history

## Conclusions

A very large number of DSC thermograms were collected to investigate the TAG polymorphous transitions that take place in cocoa butter, cocoa liquor and dark chocolate with a given thermal history. A quantitative picture of the TAG polymorphous transitions was assessed for thermal histories not far from those of the industrial practice.

The results reported allow to single out many factors that can affect the progress of TAG crystallization and may therefore be of interest in planning the annealing treatment of chocolate. However, to scale these results up to the industrial level, other important factors have to be accounted for, namely, heat diffusion during cooling, mechanical stirring, and viscosity range compatible with the annealing plant used, mainly because of the much larger mass of material considered in the industrial practice. Another main aspect of technological interest is that the polymorphous transitions may not be the only reason for the

chocolate blooming [11, 12] which still demands further investigations [13], including those relevant to the effects produced by other ingredients usually added in the industrial product, like sugars, milk fats, etc. and by the dynamic treatment of the product in the industrial practice [14]. For this reason, this paper will be followed by another one related to assess the formal kinetic parameterization of the transitions between cocoa butter TAG polymorphs in various kinds of chocolate, where other ingredients, like milk fat, are present, and to find possible correlations with the chocolate blooming.

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DOI: 10.1007/s10973-005-6934-y