Polymorphic behavior of cocoa butter. Influence on chocolate tempering conditions

Introduction:

Cocoa butter is one of the main constituents of chocolate. It is composed of triglycerides (TG) formed mainly of Stearic, Palmitic and Oleic acids. Due to their nodal structure, TG can crystallize under different forms, leading to a polymorphic behavior. Six different polymorphic forms of cocoa butter are reported in literature [1,2], noted from I to VI, by order of stability (VI is the thermodynamically stable form).

Form V is the most desirable one in chocolate as it combines firmness, good snap, and a melting temperature close to body temperature. Form VI is to be avoided as its melting zone makes it harder to melt in the mouth, and the V to VI form transition leads to the unpleasant fat bloom effect. The purity of some of these forms is still debated, especially because of the diversity of TG contained in cocoa butter.

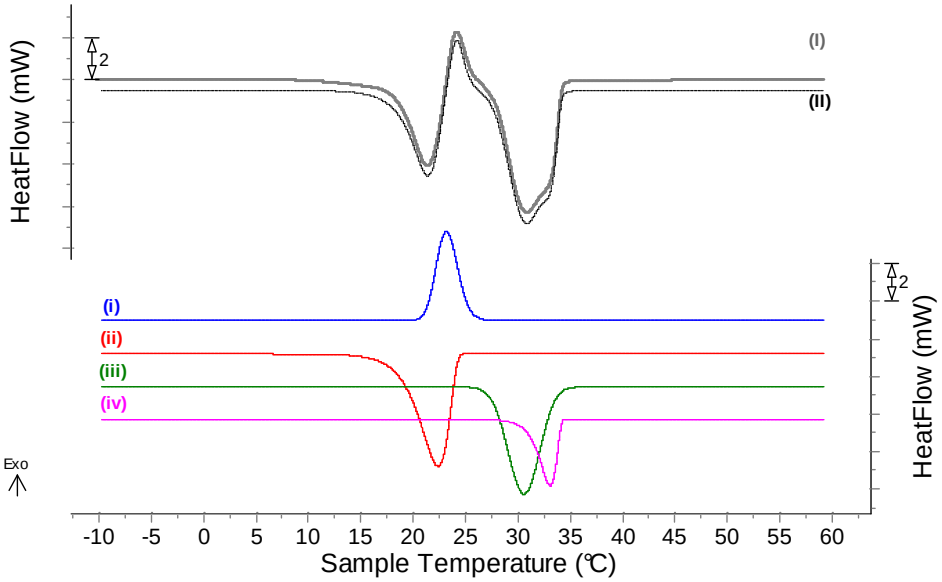

Figure 2 – Typical cocoa butter thermogram and associated peak separation

Notation	Melting	Cryst. subcell	Macros. Features
I	17	Sub-α	Soft, crumbly, melts too easily
II	23	α	Soft, crumbly, melts too easily
III	25	β'	Firm, poor snap, melts too easily
IV	27		Firm, good snap, melts too easily
V	34	β	Glossy, firm, best snap, melts near body temperature
VI	36		Hard

Table 1 – Possible conformations of cocoa butter Triglycerides (adapted from [1])

Cocoa Butter melting

Figure 2 represents a typical thermogram obtained after heating a 123.04mg cocoa butter sample between -10°C and 60°C at 0.2K.min^{-1} with a µDSC7Evo. (I) are the experimental data when (i), (ii), (iii), (iv) are the separated peaks using Calisto software, and (II) is the sum of the individual peaks.

Although the interpretation of these peaks can be more detailed when the triglyceride content of the tested cocoa butter is known, literature [3] suggests that (ii) corresponds to the melting of α phase (form II) immediately followed by its crystallization (i) into phases β and β' (partly form IV and partly form V). Then they melt at higher temperature, leading to a two-step endothermic peak, with (iii) linked to the melting of form IV and (iv) linked to the melting of form V.

Tempering process

In chocolate processing, the final step is called tempering. It consist of three phases:

1. First, chocolate is heated to 50°C to melt all forms of crystal germs.
2. Next, it is cooled down to a temperature between 26°C and 29°C which will allow crystal types IV and V to form. Then slow heating to 30°C-32°C allow melting undersized germs and thus creating a uniform population of germs of the targeted type V.
3. Finally, chocolate is slowly cooled down. Type V germs will then grow, together with the crystallization of a few type II germs. After a few days of storage, metastable type II crystal transform in type V.

This process is coherent with the previously displayed thermogram. It creates the most stable crystals so the texture and appearance will not degrade over time.

The thermograms below are obtained after successive heating of a 123.04mg cocoa butter sample between -10°C and 60°C at 0.2K.min^{-1} with a µDSC7Evo. Between every heating, cooling rate was controlled and equal to 2, 1.8, 1.6, 1.4, 1.2, 1, 0.8, and 0.6K/min.

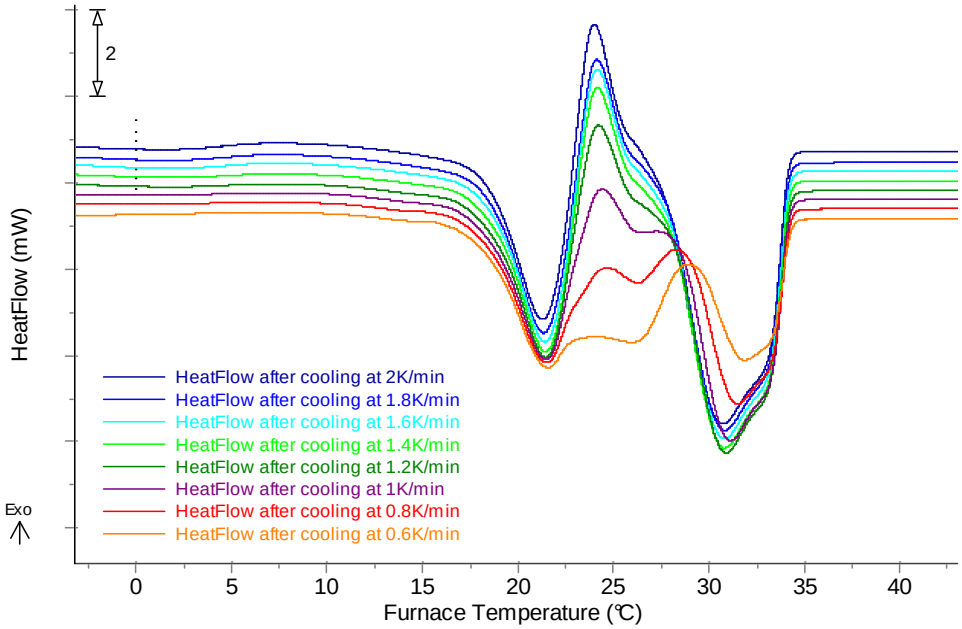

Figure 3 – Superposition of successive cocoa butter sample heating after different controlled cooling conditions

It is obvious that controlled cooling rate has a strong influence on the exothermic crystallization, slow cooling rates leading to less heat of crystallization. It can also be noticed that the intensity of higher temperature endotherm decreases with slower cooling rates, mainly due to the decrease of the form IV melting (referenced as (iii) in the previous page). This can be interpreted by the formation of smaller amounts of germs allowing the crystallization of form IV. It is then coherent with the fact that slow cooling rates during tempering operation leads to higher amounts of expected type V phase. µDSC technique combines good control of slow temperature scanning rates and high enough accuracy to detected heat effect under those conditions.

[1] Lopez, C., Kalnin, D.J.E., and Ollivon, M.R., "Coupling of Differential Scanning Calorimetry and X-ray Diffraction to Study the Crystallization Properties and Polymorphism of Triacylglycerols", Calorimetry in Food processing, Chapter 8, pp. 169 – 194, 2009.
[2] M. Bauer, Polymorphisme: conséquences en pharmacie, Techniques de l'Ingénieur, P 1 098, pp. 1 – 14
[3] Olivon, M.R. and al, Phase Transitions and Polymorphism of Cocoa Butter, JAOCS, Vol. 75, no. 4 (1998)