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ORIGINAL PAPER

A Method to Qualify and Quantify the Crystalline State of Cocoa Butter in Industrial Chocolate

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Abstract A range of methods, mainly X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC), have been used to characterise the polymorphism of fats in food products. As sugars present in chocolate have a significant XRD pattern, partially overlapping with the signal of cocoa butter, XRD cannot be applied directly to chocolate. In this paper, the XRD signal of a molten sample, similar to the one for pure sucrose, was subtracted from the signal of a solid sample of chocolate to remove the impact of the crystallised sugar. The XRD patterns obtained were compared with the pattern of cocoa butter cooled under the same conditions. Strong peaks were observed at similar inter lamellar d spacings showing that the polymorphic state of cocoa butter in processed chocolate could be obtained using this method. Numerical integration of the peaks also allowed quantification of the degree of crystallinity present in the system during a typical process. The accuracy of the method developed was found to be dependent on the (cocoa butter)/(sugar) ratio in the chocolate used.

Keywords Fat crystallisation · Polymorphism · Structural properties · Functional properties

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Introduction

Chocolate is a complex food product; it is the mixture of a dispersed hydrophilic phase made of sugar and cocoa solids in a continuous fat matrix rich in cocoa butter [1]. The fat crystal structure determines the macroscopic properties of chocolate [2–6] and sensory perception [7–9].

The different crystalline states of cocoa butter have been extensively studied and typically reported to exist as six [10] or five [11] different polymorphs. The different polymorphs can be identified using X-Ray Diffraction (XRD) [10, 12–15] and Differential Scanning Calorimetry (DSC) [16–18]. These different polymorphs can be summarised as follows:

- Form I (γ) is the most unstable polymorph and has a melting point of around 14 °C and the XRD pattern shows a very strong peak at 4.18 Å.
- Form II (α) melts at around 20 °C and the XRD pattern shows a very strong peak at 4.20 Å.
- Form III (β') is a polymorph thought to be a mixture of form II and IV [19, 20] and melts at around 22 °C. The XRD pattern shows a very strong peak at 4.20 Å.
- Form IV (β') melts at around 24 °C and the XRD pattern shows two strong peaks at 4.13 and 4.32 Å.
- Form V (β) melts at around 30 °C and the XRD pattern shows a very strong peak at 4.58 Å.
- Form VI (β) melts at around 32 °C and the XRD pattern shows a very strong peak at 4.59 Å, its pattern differs from form V only by the lack of a mid intensity peak at 3.75 Å.

After chocolate has been processed, it is desirable to obtain form V. Indeed, form V has the appropriate melting point to melt rapidly in the mouth, ensuring maximum consumer experience. Chocolate is usually seeded during

the tempering step with form V nuclei. If not, cocoa butter is then crystallised in a different form, more unstable, since form VI cannot be crystallised directly from the melt [21].

It is generally accepted that the main reason for the appearance of low melting point polymorphs (unstable) in tempered chocolate is a rapid cooling of the material [17]. The seed crystals then have little effect and most of the cocoa butter crystallises by spontaneous nucleation. The appearance of these crystals during the process should be avoided since one of the proposed blooming mechanisms for chocolate is growth of cocoa butter crystals during the polymorphous transitions of cocoa butter from β' to β crystals [22].

Several equipment manufacturers propose a rapid cooling apparatus for chocolate manufacturing that is likely to lead to the formation of unstable crystals and can increase the risks of bloomed chocolate [23]. An ability to quantify the relative amount of each of the unstable and stable family of crystals in solid chocolate therefore seems an attractive opportunity for the chocolate manufacturers.

A model able to predict the polymorphic state of cocoa butter in chocolate processed using such equipment has been recently published [24]. It would be valuable to measure the polymorphic state of chocolate during processing to validate the model.

DSC has been the method of choice for studying the crystallisation kinetics of fats in chocolate [17, 25]. One of the limitations of DSC is that it cannot provide direct structural information. There are only a limited number of studies on crystal polymorphism in chocolate using XRD. The main difficulty with using XRD is that only a small fraction of the signal can be attributed to the crystallised fats because the signal from sugar, whose XRD pattern shows strong peaks at 4.52 Å (overlapping with β crystals) and 4.71 Å [26], swamps the signal from the fats. Several workarounds to this problem have been published, such as glassifying the sugar [15] or removing it via a solid–liquid extraction technique. An XRD method was developed and applied to differentiate forms V and VI of cocoa butter in dark chocolate [12]. The method focusses on peaks that are not common to both sugar and cocoa butter, and is possible because the concentration of sugar in the dark chocolate used was low (<15%).

In our model for chocolate solidification [24, 27], for practical purposes, the polymorphs of cocoa butter have been classified into two categories, unstable crystals (forms I, II, III and IV melt at room temperature which will lead to bloom formation) and stable crystals (forms V and VI are solid at room temperature). Moreover, from the literature it can be seen that unstable crystals all have an XRD diffraction pattern presenting a strong peak around 4.20 Å while all stable crystals have a very strong peak at around 4.60 Å. The idea behind this simplification is that chocolate should leave the manufacturing site containing only cocoa butter crystallised in form V, in order to reach the consumer without bloom. Therefore, the unstable crystals have been lumped together and their presence was accessed by a strong peak at 4.20 Å while the stable crystals were represented by a strong peak at 4.60 Å.

It has been noted in the literature [13] that the proportionality coefficient between the mass and the area of the diffracted peaks for phase II and IV are different (1.7 and 3.2% SFC/nu, respectively) and therefore a global measurement of the unstable crystals concentration by this method is not completely accurate. However, from an engineering perspective and in order to simplify the modelling of the chocolate manufacturing process, such a simplification would be valuable. Furthermore, for similar experimental conditions, DSC measurements [24] show a single unstable crystals melting peak that leads the authors to assume that the different phases (γ, α and β') can indeed be grouped together.

Materials and Methods

Two different chocolate formulations were used for this study. One was a commercially available milk chocolate formulation from Barry Callebaut (Banbury, UK). The second one was a commercially available dark chocolate (Sainsbury's "Taste the difference"). The composition of both materials is presented in Table 1. None of these chocolate contained any vegetable fats except cocoa butter. The ratio (cocoa butter)/(sugar) (calculated from the specifications) for the two formulations was 0.35 for the milk chocolate and 2.68 for the dark chocolate. The cocoa butter used as a control was supplied by ADM Cocoa (Hull, UK).

A Revolation 2 bench-top temperer (Chocovision, UK) was used to temper the chocolate. The level of temper was validated using a bench-top tempermeter (Aasted, Denmark).

Data were collected at the EPRSC National Crystallography Centre using a Bruker-Nonius Kappa CCD diffractometer comprising an FR591 rotating anode and ApexII detector. The radiation used was produced by a

Table 1 Two recipes selected for the study

	Milk chocolate	Dark chocolate
Fat content/cocoa butter (%)	31.7/19.5	51.4/51.4
Moisture (%)	<1	<1
Energy per 100 g (kJ)	2,250	2,358
Proteins per 100 g (g)	6.1	8.8
Total carbohydrates per 100 g (g)	56.4	19.2

molybdenum (Mo) anode and focussed using 10-cm confocal Max Flux mirrors—the first design for a Mo source that produces a six-times increase in X-ray brilliance. Data were acquired using the COLLECT software package and preliminary integration of the Debye–Scherrer diffraction was performed using the Powderize module [28]. The concentrical rings were integrated from the center (0°) to the edge of the image (25°) to produce a powder-like (intensity vs. d) signal. The more intense the ring is in the picture, the stronger the peak will be in the 2D powder-like graph.

Samples of tempered chocolate and molten cocoa butter were crystallised at a cooling rate of 0.5 °C/min or by drops on an Aluminium plate kept in a freezer leading to a cooling rate of about 50 °C/min. X-ray diffraction patterns were recorded for the solid state at −30 °C and then for the liquid state at 40 °C. The data were then postprocessed using Powderize software (part of the COLLECT software package), To quantify the concentration of stable and unstable crystals, the 2D signal output from the Powderize software was postprocessed and the area of the peak in the signal proceeding from the subtraction was calculated using the trapezoidal rule. The amount of each of the phases was quantified using the area of the very strong peak representative of the phase.

Results and Discussion

Most of the data available on the crystal structure have been collected using copper radiation [10, 11] ($\lambda_{Cu} = 1.54$ Å), however, in this study the X-ray source used is molybdenum ($\lambda_{Mo} = 0.71$ Å) since it was readily available at the facility. Due to the lower wavelength, at a similar distance between the detector and the sample, the resolution of the images should be lower. However, the very high intensity of the setup allowed shorter exposure times resulting in a low signal to noise ratio. This was found to be a good compromise for obtaining quality data.

Using Bragg's law (Eq. 1), d spacings corresponding to the 2θ angle experimentally measured were calculated;

$$d = \frac{n\lambda}{2\sin(\theta)} \quad (1)$$

where λ is the wavelength of the source, d is the d-spacing and θ is the angle between the incident and the diffracted wave. The expected very strong peak associated d spacing for stable crystals is 4.60 Å whereas it is 4.20 Å for unstable crystals.

Typical data obtained from a milk chocolate system are presented in Fig. 1. In Fig. 1a, a typical XRD pattern for a solid chocolate sample at −30 °C is shown. The sample was solidified at a cooling rate of 0.5 °C/min and would be expected [17] to consist mainly of stable crystals, melting around 30 °C as pure cocoa butter or 27 °C when mixed with milk fat [18]. The top right quarter shows a magnification of the picture around the area of the expected peak for the stable crystals (4.60 Å). Two rings (4.56 and 4.71 Å) can be seen in this area, the outer (4.56 Å) one having a stronger intensity.

The sample was then melted at 40 °C in the diffractometer and a second scan was performed. The X-ray pattern obtained is presented in Fig. 1b. The two rings are still present but the outer ring (4.56 Å) is of similar intensity to the first ring (4.71 Å). Both of these rings correspond to the presence of crystalline sugar and are in agreement with published data [26].

Using the Powderize software, Fig. 2 was generated. Since the XRD signal intensity is proportional to the amount of crystals present in the system, the mass of the sample affects the intensity of the collected signal. This

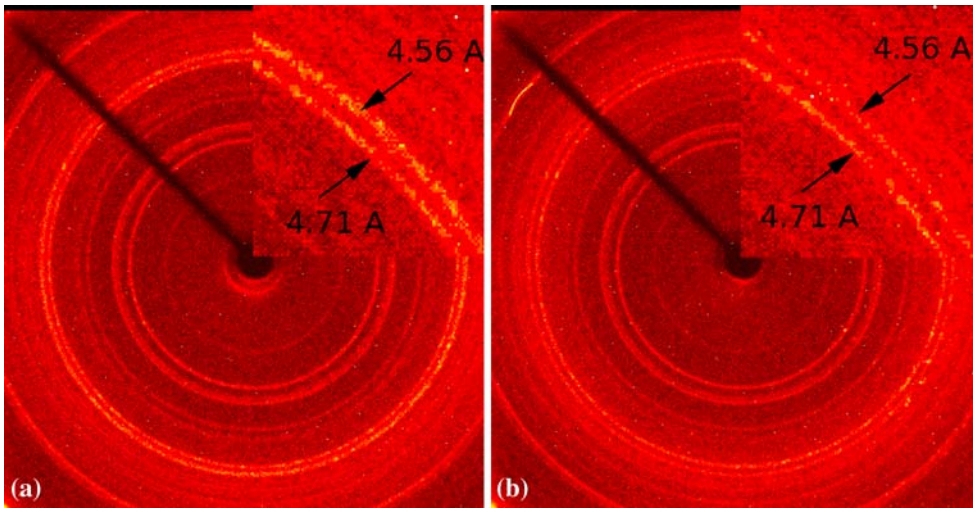

Fig. 1 Diffraction patterns for **a** solid milk chocolate (−30 °C) cooled at 0.5 °C/min and **b** liquid milk chocolate (40 °C)

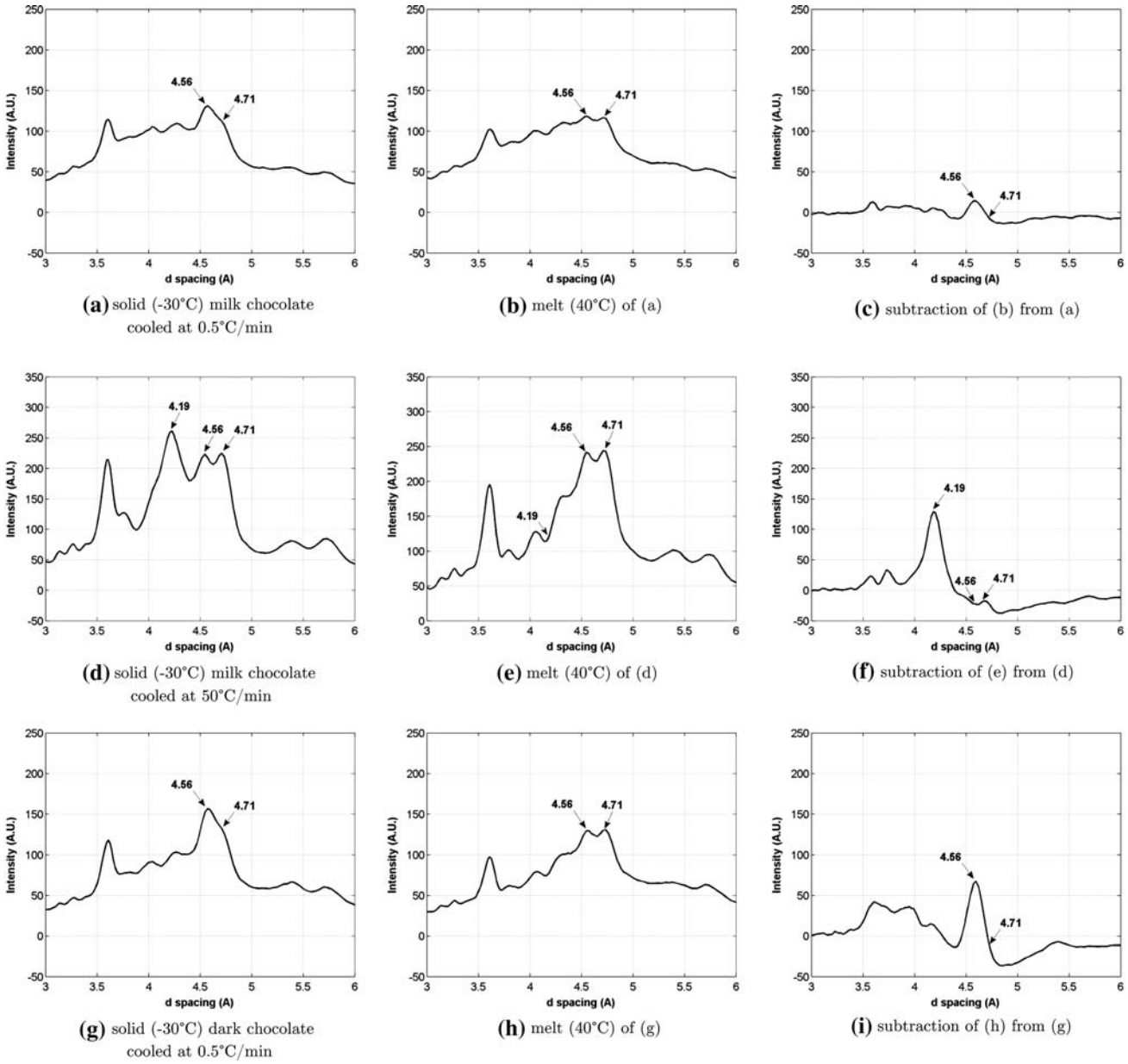

Fig. 2 Powder signal of solid (**a**) and liquid (**b**) milk chocolate cooled at a nominal rate of 0.5 °C/min. The subtraction of both signals is presented in (**c**). Powder signal of solid (**d**) and liquid (**e**) milk chocolate cooled at a nominal rate of 5 °C/min. The subtraction of both signals is presented in (**e**). Powder signal of solid (**g**) and liquid (**h**) dark chocolate cooled at a nominal rate of 0.5 °C/min. The subtraction of both signals is presented in (**i**)

explains the difference (due to sample mass variation) that can be observed between the different liquid samples (Fig. 2b, e, h), since data were not scaled (raw data).

In Fig. 2a, a peak can be observed at 4.56 Å which is characteristic of stable (forms V and VI) crystals [10]. A smaller peak at 4.71 Å can also be seen which corresponds to the sugar present in the formulation. When the sample is liquid (40 °C), the two consecutive peaks at 4.56 and 4.71 Å in Fig. 2b are still present but have a similar intensity as seen in Fig. 1b. This implies that both peaks are present because of the sugar diffraction pattern since only sucrose is crystalline at 40 °C. If the two diffractograms are subtracted from one another, the result is that a single sharp peak is obtained at 4.56 Å as presented in Fig. 2c. This peak is located at 4.56 Å, the same position than the peak presented in Fig. 2a and b. The residual intensity in this signal is due to the fat crystals present in the solid sample but absent in the liquid sample.

Similar analysis was conducted on the same milk chocolate cooled at 50 °C/min. Here the peak obtained

from the subtraction (Fig. 2f) of the solid (Fig. 2d) and the liquid (Fig. 2e) sample correspond to a different d spacing (4.19 Å) characteristic of unstable crystals [10]. This difference makes clear, as previously explained in the literature [17], that different cooling rates lead to different polymorphs in cocoa butter.

If dark chocolate first cooled at 0.5 °C/min is analysed, the peak resulting from the subtraction (Fig. 2i) corresponds to the same d spacing to the one measured in milk chocolate cooled under the same condition (4.56 Å) but with a higher intensity and a sharper shape, further explanations are given below.

Subtraction Method to Identify the Cocoa Butter State in Chocolate

Data obtained from the subtraction method were compared to the diffraction signal obtained from cocoa butter cooled under the same conditions.

Figure 3 shows triplicates of subtracted signals obtained for milk chocolate and pure cocoa butter cooled at 0.5 °C/min. Under these conditions one would expect stable crystals to be formed [17].

For all the pure cocoa butter samples the maximum peak recorded is at 4.56 Å, which is very close to the expected value according to the literature [10] for stable crystals (4.58 Å). A similar peak is recorded at 4.56 Å for a milk chocolate signal obtained using the subtraction method. Moreover the intensity of the peak is very similar for the three replicates of both cocoa butter and chocolate samples suggesting that the recorded data is reproducible.

During a second set of experiments, freshly tempered chocolate and molten cocoa butter were cooled using a

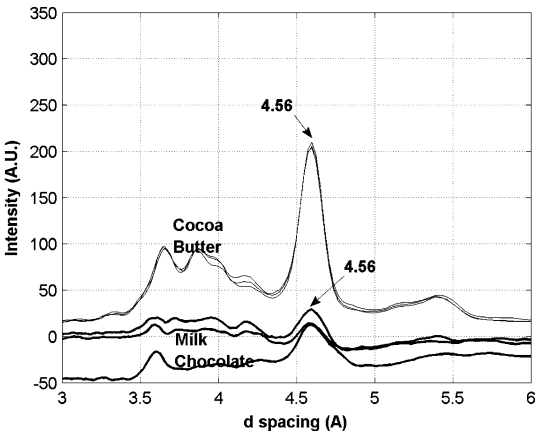

Fig. 3 Comparison between the XRD diffraction pattern of pure cocoa cooled slowly (0.5 °C/min), forming β crystals, and the XRD diffraction pattern from the subtraction method applied to milk chocolate cooled under the same conditions. Data are from three repeats of the experiments

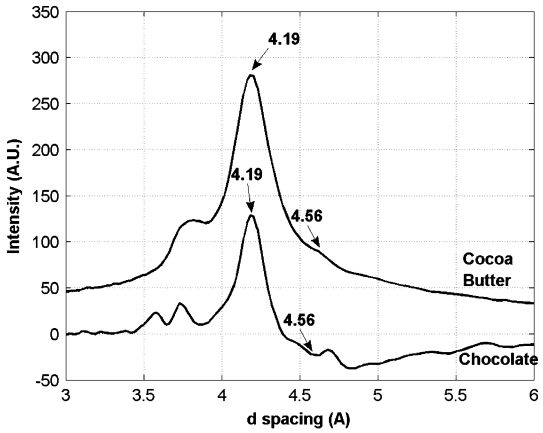

Fig. 4 Comparison between the XRD diffraction pattern of pure cocoa cooled rapidly (50 °C/min), forming β'crystals, and the XRD diffraction pattern proceeding from the subtraction method applied to milk chocolate cooled under the same conditions

cooling rate of about 50 °C/min. The subtracted signal of such chocolate is presented in Fig. 4 and is compared to the signal for pure cocoa butter cooled under the same conditions. Both pure cocoa butter and subtracted chocolate signal showed a maximum peak located at 4.19 Å which is very close to the theoretical value for forms I, II, III and IV which are clustered together as unstable crystals (4.20 Å) which are likely to form at high cooling rates [17].

Both the stable and unstable families of crystals can be qualitatively identified in commercial milk chocolate. As expected stable crystals are formed when using a slow cooling rate while a more rapid cooling rate leads to unstable crystals.

Unfortunately the subtraction method does not allow one to distinguish individual crystal forms but it is clear that one can distinguish between stable and unstable forms and be useful for comparing and validating the simplified model already developed by the authors [24].

A more quantitative approach was then implemented to follow unstable to stable polymorphous transitions.

Subtraction Method to Follow the Polymorphous Transitions of Cocoa Butter in Chocolate

During a typical rapid cooling process, chocolate is cooled very quickly (50 °C/min) to give a shape to the product and it is then solidified in a cooling tunnel. During the rapid cooling step, low melting point polymorphs (unstable) are likely to be formed, which are then likely to transform into stable crystals in the cooling tunnel. The subtraction method was applied at different temperatures to quantify the evolution of the crystalline state of cocoa butter during an industrial chocolate process.

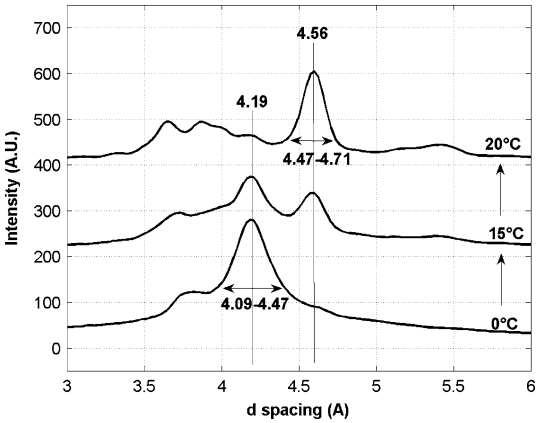

Fig. 5 Evolution of the polymorphism of cocoa butter rapidly cooled (50 °C/min) and then heated from 0 to 20 °C at 5 °C/min. The unstable β' crystals are gradually replaced by stable β crystals (the curves are separated by 200 units to allow better visualisation)

In Fig. 5 such a transition can be seen for pure cocoa butter. The cocoa butter was originally crystallised at a cooling rate of 50 °C/min down to 0 °C. A peak at 4.19 Å can be seen for the original sample at 0 °C. The sample was then heated up at 5 °C/min in the diffractometer to 15 °C and two peaks at 4.19 and 4.56 Å can be seen, indicating that unstable crystals have been gradually replaced by stable crystals. After further heating at 5 °C/min to 20 °C the cocoa butter has completely changed to the stable form showing only a peak at 4.56 Å.

The subtraction method was applied to solid milk chocolate samples in order to follow similar transitions of the cocoa butter crystalline state. The areas of typical peaks of stable (A_{stable}) and unstable (A_{unstable}) crystals were integrated to obtain quantitative information about the evolution of the concentration of both phases during reheating of quickly cooled chocolate.

The integration process required integration boundaries to be set. These are reported on Fig. 5; for the unstable peak around 4.19 Å, the integration limits were set as 4.09 Å for the lower bound and 4.47 Å for the higher bound. To determine the amount of stable crystals around 4.56 Å, we used 4.47 Å for the lower bound and 4.71 Å for the higher bound.

To minimise any variation in signal intensity due to the mass of the sample, signals were scaled so that a reference peak from sugar (4.71 Å), common to all milk chocolate samples, would have an intensity of 100 (arbitrary value). Integration results were also divided by the maximum value of the area under the appropriate peak reached during reheating, i.e. 10 °C for unstable $\left(A^{\max}_{\text{unstable}}\right)$ and 25 °C for stable $\left(A^{\max}_{\text{stable}}\right)$ in order to normalise the areas between 0 and 1. This was necessary to remove the effect of the difference in the proportionality coefficient of the different phases [13].

The method allows the quantification of the balance between stable and unstable crystals to be determined. Experiments were conducted in which chocolate was first cooled very quickly to 0 °C, after having been freshly tempered (50 °C/min). There, most of the cocoa butter is in the unstable state, as shown in Fig. 6a. XRD experiments were conducted in which the quenched sample was heated from 0 to 40 °C at 5 °C/min. The amount of cocoa butter in the unstable state decreases significantly between 10 and 20 °C, essentially to zero as presented in Fig. 6a. Reciprocally, the amount of cocoa butter in the stable state increases between 10 and 20 °C as can be seen in Fig. 6b. The cocoa butter in the unstable phase is gradually replaced by the stable phase as shown in Fig. 5 in the case of pure cocoa butter. Finally the stable crystals melt between 25 and 30 °C, creating a loss of signal. Each sample was measured in triplicate and the low standard deviation represented by the error bars in Fig. 6a and b indicates a good reproducibility of the method.

The temperatures obtained for the melting of the unstable crystals, recrystallisation (or polymorphous transition) and melting and the stable crystals are consistent with the temperatures obtained by DSC for the same milk chocolate [24] and published [18] for a mixture of cocoa butter form V and milk fats.

Increasing the Signal to Noise Ratio

When Fig. 2a–c is compared with Fig. 2g–i, the effect of the ratio (cocoa butter)/(sugar) can be seen. The cooling rate being the same, similar crystals are formed. However, the peak intensity in dark chocolate has a stronger intensity than the case in milk chocolate. The liquid chocolate data is very similar since, in this case, XRD detects the spectrum of the sugar present in both milk and dark chocolate. This translates into a better quality for the peak obtained by the subtraction method. Figure 7 presents the subtracted signal collected from slowly cooled (0.5 °C/min) tempered dark chocolate and the signal collected from pure cocoa butter and milk chocolate cooled under the same conditions.

The intensity of the recorded peak was highest for pure cocoa butter and smaller for dark chocolate and milk chocolate. The peak intensity is higher by a ratio of 4.7 (67 vs. 14) in dark compared to milk chocolate as expected since the (cocoa butter)/(sugar) ratio is higher by 4.66 (2.8 vs. 0.6). The relative abundance of cocoa butter in the dark chocolate formulation increases the sensitivity of the method and allows recording of low intensity peaks at 3.65 Å, typical of V and VI, and 3.98 Å, typical of V only [12, 15]. The crystalline state of cocoa butter in this case is confirmed to be of the stable form V.

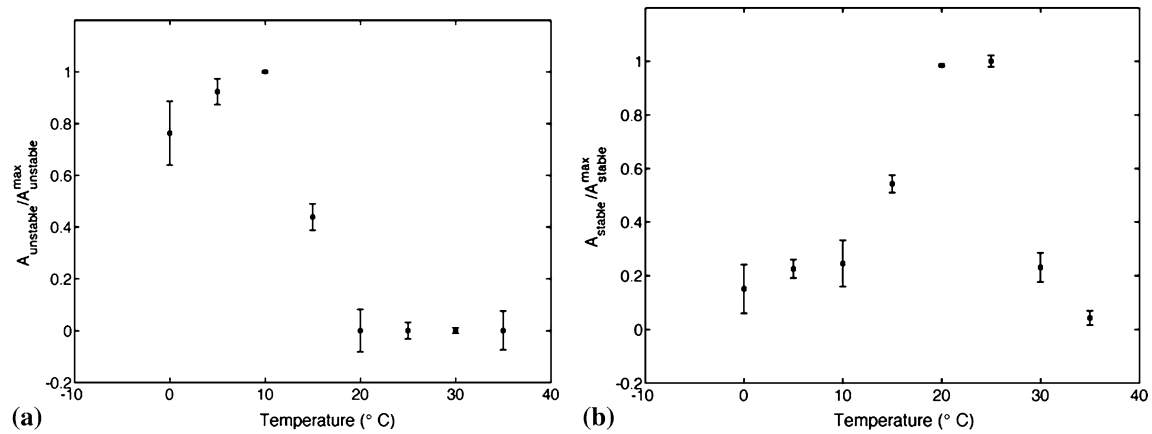

Fig. 6 Evolution of the integral of the peak for **a** unstable β' crystals (4.19 Å) and **b** stable β crystals (4.56 Å) to quantify the evolution of polymorphism in rapidly cooled (50 °C/min) milk chocolate heated at 5 °C/min

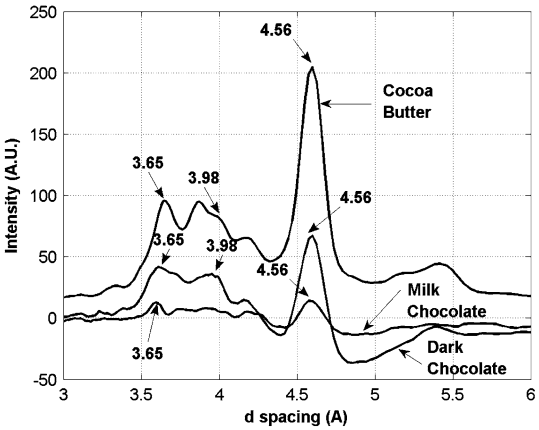

Fig. 7 Comparison between the XRD diffraction pattern of pure cocoa cooled slowly, leading to the formation of stable β crystals and the signal obtained from the subtraction of the XRD pattern of liquid dark (and milk) chocolate from the XRD pattern of solid dark (and milk) chocolate cooled using the same process as the cocoa butter

In Fig. 7, one can see that in the case of dark chocolate, the subtraction method has generated a small negative peak after the main cocoa butter peak (4.56 Å). The negative peak is inherent to the subtraction method where there are small errors due to over/under subtraction of the liquid sample compared to the solid sample.

Conclusions

XRD patterns were obtained from chocolate samples solidified using slow or fast cooling rates. Subtraction of the pattern of liquid chocolate from the pattern of the same sample analysed in a solid state proved to be an efficient method for identifying the crystalline state of cocoa butter. This was possible by clustering forms I, II, III and IV into an unstable group and V and VI into a stable group, since it does not appear feasible to distinguish individual polymorphs. The method is of value to industrial chocolate manufacturers as it enables measurements of the concentration of unstable crystals to avoid blooming problems related to the transition of unstable to stable crystals. The results of the method compared very well with analysis of the polymorphous state of pure cocoa butter cooled under the same conditions. Some quantitative information can be obtained by integrating the area under the peaks. The experiments were reproducible as assessed by the low dispersion of the quantitative analysis results. It was also found that, as expected, the formulation of the chocolate used had a great impact on the quality of the results, the higher the ratio of cocoa butter to sugar the better are the subtracted data.

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