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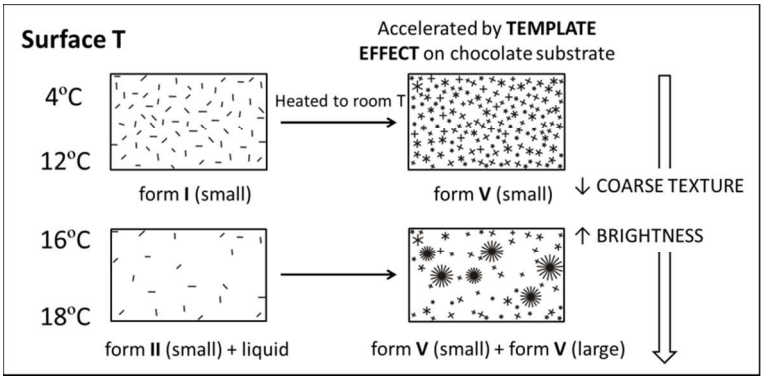

New types of chocolate textures with a soft mouth-feel can be formed by controlling the crystallization and polymorphic transformation of cocoa butter (CB) with thermal treatment and template effects. A quick spray of molten chocolate liquor on chilled substrates (normally formed chocolate or metal) caused the crystallization of meta-stable forms of CB, which transformed to a stable form during subsequent heating processes. We characterized the domain sizes of β_V for the CB crystals in velvet chocolate, which were much smaller and exhibited a lower melting temperature and softer mouth feeling than those in normally tempered chocolate. Polymorphic crystallization and transformation of CB were in-situ monitored by X-ray diffraction by changing the temperatures of the substrates. The velvet effect was induced solely by decreasing the temperature of the substrates below 16ºC, because crystallization of the metastable γ_I form and subsequent transformation to β_V of cocoa butter are prerequisites for forming velvet chocolate. The chocolate substrate was much more effective than the metal substrate in forming the velvet chocolate because of the template effect.

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ABSTRACT

We report new types of chocolate textures with a soft mouth-feel (velvet effect) formed by controlling the crystallization and polymorphic transformation of cocoa butter (CB) with thermal treatment and template effects. A quick spray of molten chocolate liquor on chilled substrates (normally formed chocolate or metal) caused the crystallization of meta-stable forms of CB, which transformed to a stable form during subsequent heating processes. Cryo-scanning electron microscopy and confocal interferometric scanning microscopy were employed to observe the surface structures of the velvet chocolate. We characterized the domain sizes of β_V for the CB

crystals in velvet chocolate, which were much smaller and exhibited a lower melting temperature and softer mouth feeling than those in normally tempered chocolate. Polymorphic crystallization and transformation of CB were in-situ monitored by X-ray diffraction by changing the temperatures of the substrates. It was obvious that the velvet effect was induced solely by decreasing the temperature of the substrates below 16ºC, because crystallization of the metastable γ_I form and subsequent transformation to β_V of cocoa butter are prerequisites for forming velvet chocolate. The chocolate substrate was much more effective than the metal substrate in forming the velvet chocolate because of the template effect.

INTRODUCTION

Chocolate is made up of cocoa butter crystals as a continuous body, in which tiny particles of sugar, cacao mass and other ingredients are dispersed. Sharp melting and quick release of flavor and sweetness/bitterness are determined by the melting behavior of cocoa butter (CB) crystals. CB is composed of three main triacylglycerols (TAGs), 1,3-dipalmitoyl-2-oleoyl-glycerol (POP), 1-3-distearoyl-2-oleoyl-glycerol (SOS), and rac-palmitoyl-stearoyl-2-oleoyl-glycerol (POS). Many studies have focused on the polymorphic behavior of CB[1] and its three main TAGs.[2-6] Cocoa butter exhibits six different polymorphic forms referred to as I through VI. Among them, form V is industrially promoted through tempering processes, as this polymorph provides the desired melting, textural, and mouth-feel characteristics of chocolate.[7]

Recently, we examined the influence of dynamic temperature variations on the polymorphic behavior of the principal TAGs of edible fats and oils.[8-10] The results indicated that, by tailoring specific cooling and heating rates, the polymorphic crystallization may be directed to obtain

desired polymorphic forms with expected physicochemical properties for pharmaceutical, cosmetic, and food applications. We observed that more stable forms were directly obtained by decreasing the rate of cooling, whereas less stable forms predominated at high cooling rates. Thermal treatment may also modify crystal sizes and their distributions as reported by Acevedo et al.,[11,12] who observed nanometer-scale fat crystals (nanoplatelets) by using cryogenic transmission electron microscopy (cryo-TEM) and determined that fast cooling rates and the application of shear significantly decreased platelet length, width, and thickness. Further investigation was performed by Maleky et al.,[13] who quantified the effects of applying laminar shear on crystalline orientation and nanostrstructure triglyceride crystal networks of cocoa butter.

In this paper, we focus on the use of specific thermal treatments for developing new textures of chocolate with a soft mouth-feel, called the "velvet effect" (Fig. 1).

Figure1. Velvet effect appearance on chocolate eggs.

Mainly used in *gourmet* chocolate products, the velvet effect was first developed in 1963 by Catalan chocolatiers[14] and the use of this texture has spread internationally. However, no precise

work has been reported to clarify the formation of the velvet effect; the present study is the first to do so.

The velvet effect is obtained when fluidized chocolate (a tempered mixture of chocolate and cocoa butter) is sprayed on a cold chocolate surface. This process enables the formation of thin layers of cocoa butter crystals with a lower melting point than that of normally tempered chocolate, leading to the creation of a soft mouth-feel. Its name (velvet) is due to its soft but rough appearance, obtained after cocoa butter crystallization.

In this study, we characterized the velvet effect and monitored the polymorphic crystallization and transformation that occur during rapid cooling and subsequent heating on the velvet effect production. From the results obtained, the experimental conditions to obtain the desired characteristics of an acceptable velvet effect could be optimized. The use of small droplets obtained after spraying may accelerate the crystallization and transformation processes as it offers very high cooling rates, both via large surface area-to-volume ratios and high rates of convective heat and mass transfer, according to previous studies on spray freezing methods applied to cocoa butter.[15-17] These researchers observed a polymorphic transformation similar to those expected in a bulk mass of cocoa butter, but which occurred significantly faster in droplets.

We also studied the effects of different supercooling on polymorphic crystallization in velvet preparation, and used two substrate materials (chocolate and metal) to analyze the template effect caused by a chocolate surface, as template effects on lipid crystallization have been demonstrated by previous work.[18-21]

EXPERIMENTAL SECTION

Materials

Velvet chocolate and normal chocolate samples were prepared by Enric Rovira, master chocolatier (Enric Rovira S.L., Castellbell i el Vilar, Spain). Normal chocolate samples consisted of 70% cocoa chocolate (60% cocoa paste, 30% sugar, 10% cocoa butter and less than 1% soy lecithin).

Sample preparation

To prepare the velvet chocolate, a mixture of 70% cocoa chocolate (Enric Rovira S.L.) and cocoa butter (Nederland S.A, Viladecans, Spain) was prepared in a ratio of 3:2 and tempered by completely melting the sample at 45ºC, cooling it at 28ºC and finally heating it at 32ºC. The tempered mixture (fluidized chocolate) was sprayed on a cold surface (metal or chocolate at different temperatures) to cause rapid crystallization of the chocolate droplets. Spraying was performed using a Sagola 3300G Pro spraying gun with a 1.2mm nozzle. In this text, the term *fluidized chocolate* will be used to designate the tempered mixture of 70% cocoa chocolate and cocoa butter (3:2) which is sprayed to create velvet chocolate. This term will be used to distinguish the chocolate before spraying from *velvet chocolate, which* was obtained after spraying the fluidized chocolate on the cold surface.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were conducted at atmospheric pressure using a PerkinElmer Diamond. Samples were weighed into 50µl aluminum pans, and covers were sealed into place. The instrument was calibrated with reference to the enthalpy and the melting points of indium (melting temperature 156.6ºC; ΔH 28.45J/g), and decane (melting

temperature -29.7ºC; ΔH 202.1J/g) standards. An empty pan was used for reference. Dry nitrogen was used as a purge gas in the DSC cell at 20cm^3/min. Thermograms were analyzed using Pyris Software to obtain the enthalpy (J/g, integration of the DSC signals) and peak top T, T_{onset}, and T_{end} of the transitions (ºC, intersections of the baseline and the initial and final tangents at the transition). Three independent measurements were made for each experiment (n=3). Random uncertainty was estimated with a 95% threshold of reliability using the Student's method.

Laboratory-scale X-ray diffraction

Laboratory-scale powder X-ray diffraction (XRD) allowed identifying, as a first stage, the crystal forms present in velvet chocolate and comparing them with those in normal chocolate. These initial measurements were performed using a PANalytical X'Pert Pro MPD powder diffractometer equipped with a Hybrid Monochromator and PIXcel Detector. The equipment also included an Oxford Cryostream Plus 220V (temperature 80 to 500K). This diffractometer operated with Debye-Scherrer transmission. Samples were introduced in a 1mm-diameter Lindemann glass capillary. The latter was rotated about its axis during the experiment to minimize preferential orientations of the crystallites. The step size was 0.026º from 1º to 40º 2θ, and the measuring time was 100 seconds per step.

Laboratory-scale powder XRD also enabled monitoring of the polymorphic transformations that occurred during velvet formation. The fluidized chocolate sample was directly sprayed either on a stainless steel metallic sample holder of maximum height of 4mm or on a chocolate surface placed on the sample holder, at different temperatures (4ºC, 12ºC, 16ºC and 18ºC). Each sample was subjected to XRD measurements taken during heating from chilled temperatures to

room temperature (approximately 20ºC). Temperatures were registered in a parallel experiment, in identically simulated conditions. These XRD measurements were carried out using the same powder diffractometer (PANalytical X'Pert Pro MPD) but using a convergent beam with a focalizing mirror in reflection geometry. The step size was 0.026º from 1º to 30º 2θ, and the measuring time was 10 seconds per step.

Synchrotron radiation X-ray diffraction

Synchrotron radiation X-ray diffraction (SR-XRD) experiments were conducted on beamline BL11-NCD at the synchrotron Alba (Cerdanyola del Vallès, Barcelona, Spain) at 12.4kEV. The sample-detector distance was 2.2m. X-ray scattering data were collected on a Quantum 210r ADSC detector with a pixel size of 102.4x102.4μm^2 for the SAXD data and on a LX255-HS Rayonix detector with a pixel size of 40x40mm^2 for the WAXD data. The exposure time was 20s. The temperature of the sample was controlled by a Linkam stage. SR-XRD patterns were acquired while the sample was heated from 5 to 40ºC at a controlled rate of 2ºC/min. The sample was placed in an aluminum sample cell with a Kapton film window. The q-axis calibration was obtained by measuring silver behenate[22] for SAXD and Cr_2O_3 for WAXD. The program pyFAI[23] was used to integrate the 2D WAXD into the 1D data; the SAXD data were processed with in-house software.

Cryo-Scanning electron microscopy

Scanning electron microscopy (SEM) on frozen samples was performed with a JEOL JSM-6510 scanning electron microscope equipped with an ALTO 1000 Cryotransfer System for SEM

(Gatan) and an evacuation chamber. Samples were coated with gold-palladium prior to examination.

Confocal Microscopy

A Leica DCM 3D (Leica Microsystems) confocal interferometric scanning microscope, with 10x, 20x, and 50x objectives, was used to capture images.

RESULTS AND DISCUSSION

Polymorphic and morphological characterization of velvet chocolate

Figure 2 shows the DSC heating curves of normal chocolate and velvet chocolate, obtained when the samples were heated from 5 to 50ºC at a rate of 2ºC/min.

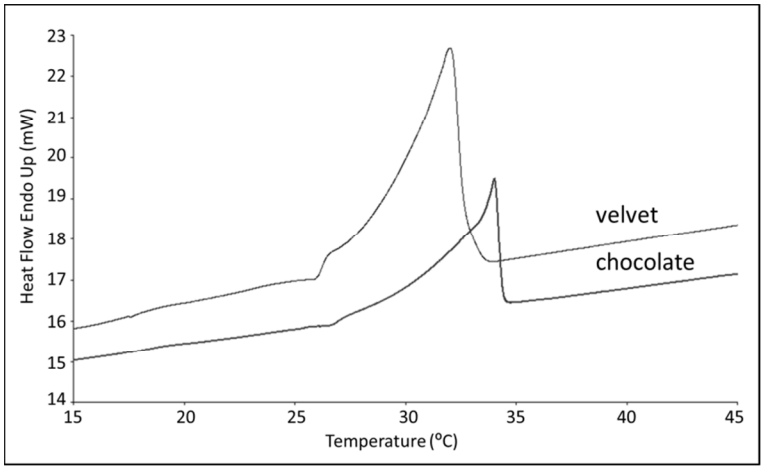

Figure 2. DSC melting curves of velvet and normal chocolate when heated from 5 to 50ºC at 2ºC/min

The melting peak of velvet chocolate occurred at a significantly lower temperature than that of normal chocolate. The onset, peak top, and end temperatures of the normal chocolate DSC peak were 27.9 ± 0.4ºC, 34.1 ± 0.3ºC, and 34.5 ± 0.4ºC, respectively, whereas the velvet DSC melting peak exhibited a T_{onset} of 26.8 ± 0.4ºC, peak top temperature of 32.1 ± 0.3ºC, and T_{end} of 32.7 ± 0.6ºC.

Figure 3 presents laboratory-scale XRD patterns of the polymorphic forms of the CB crystals present in the velvet samples taken at room temperature.

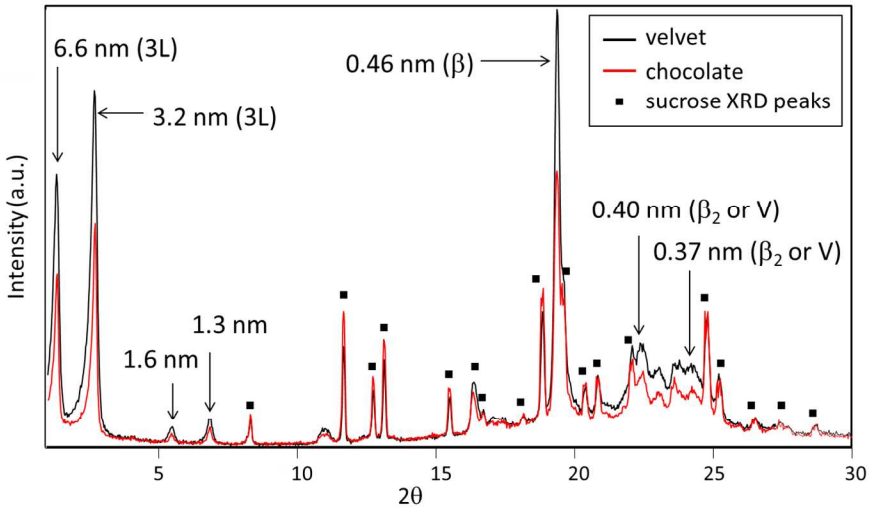

Figure 3. Laboratory-scale XRD of velvet and normal chocolate samples taken at room temperature.

The results showed identical XRD patterns for velvet and normal chocolates, revealing the presence of form V, with triple chain length structure XRD peaks at 6.6 and 3.2nm, and typical short spacing values of 0.46, 0.40, and 0.37nm. XRD peaks of the sucrose present in the samples are indicated by the symbol ■. Thus, the difference in the melting points of velvet and normal

chocolates was not due to the difference in the polymorphic forms of CB. However, the peaks of small-angle XRD patterns of the velvet chocolate were broader than those of normal chocolate. Broader diffraction peaks are related to smaller crystal size in a direction perpendicular to the scattering planes, through the Scherrer equation,[24] as discussed below.

The melting of form V CB crystals in the velvet chocolate was confirmed by SR-XRD with simultaneous SAXD/WAXD measurements (Fig. 4). The SR-XRD patterns were acquired while the sample was heated from 5 to 40ºC at a controlled rate of 2ºC/min, following the thermal treatment carried out by DSC.

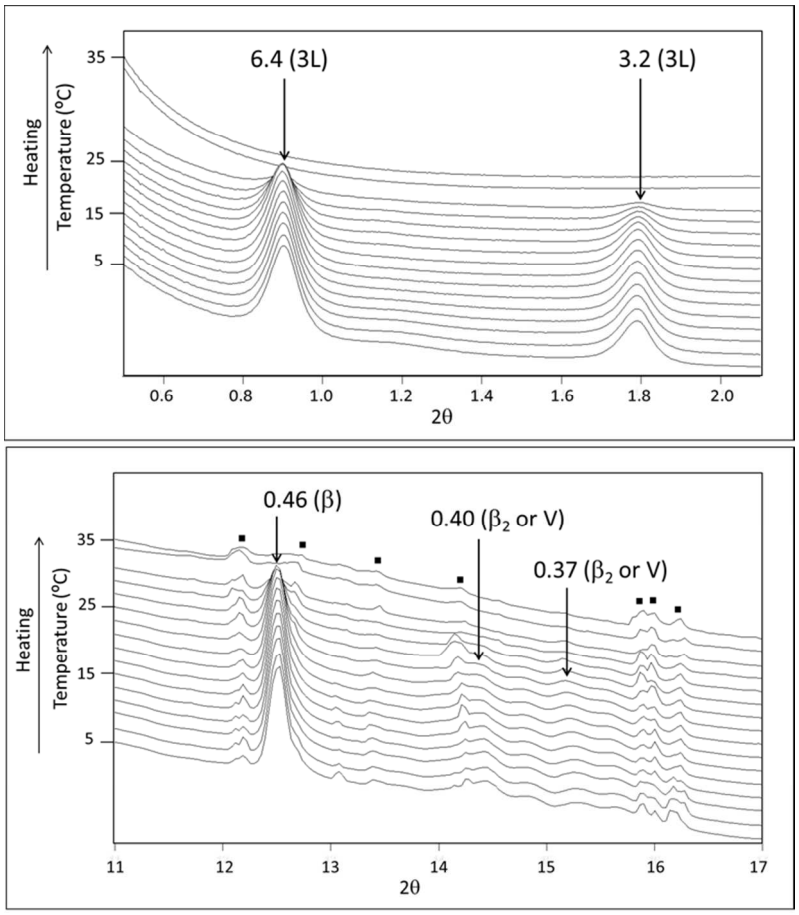

Figure 4. SR-SAXD (up) and SR-WAXD (bottom) patterns of velvet chocolate when heated from 5ºC to 40ºC at 2ºC/min.

The SAXD pattern revealed the presence of triple chain length structure peaks at 6.4 and 3.2nm, whereas form V cocoa butter in the velvet chocolate was confirmed by typical SR-WAXD peaks. Form V XRD peaks disappeared at around 33ºC due to melting of the cocoa butter crystals. The remaining SR-WAXD peaks were due to sucrose present in the sample (noted by the symbol ■) after the CB melting.

Cryo-scanning electron microscopy was also carried out in order to observe the velvet particle morphology. As depicted in Fig. 5, the velvet morphology consisted of aggregates of round particles of around 30-50μm diameter. The round morphology was due to the rapid cooling of the sprayed chocolate droplets on the cold surface.

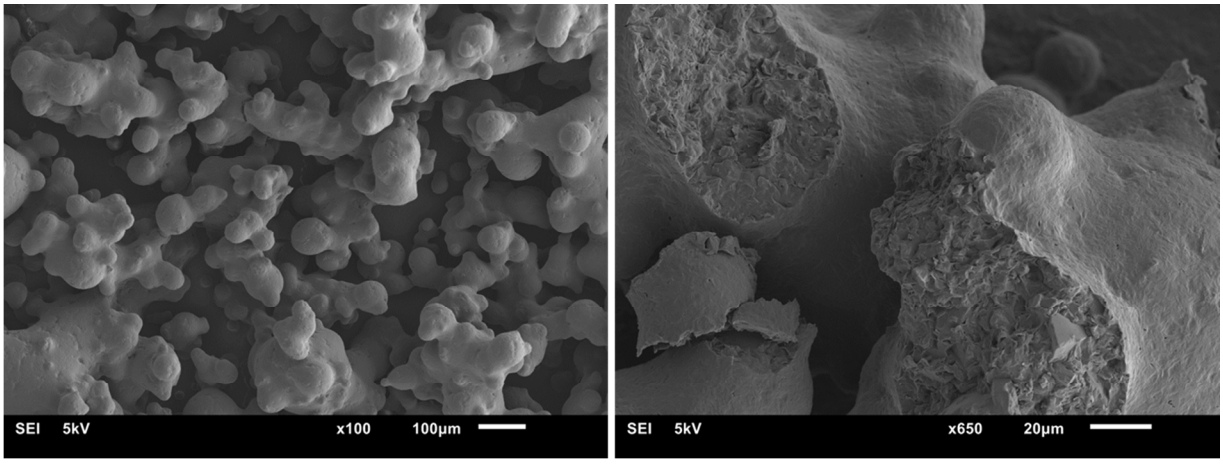

Figure 5. Cryo-SEM images of velvet chocolate

In Fig. 5 (right), one may also notice the presence of cocoa butter microstructure with embedded sugar crystals inside the aggregates of round particles.

Additional information on the morphological characterization of velvet was provided by confocal interferometric scanning microscopy. With this technique, the profile (peak-valley

heights) of one layer of round-particle aggregates could be determined (Fig. 6). Thus, several confocal microscopy images were taken in different areas of the velvet chocolate sample, and peak-to-valley distances were included in the range from 80 to 200μm.

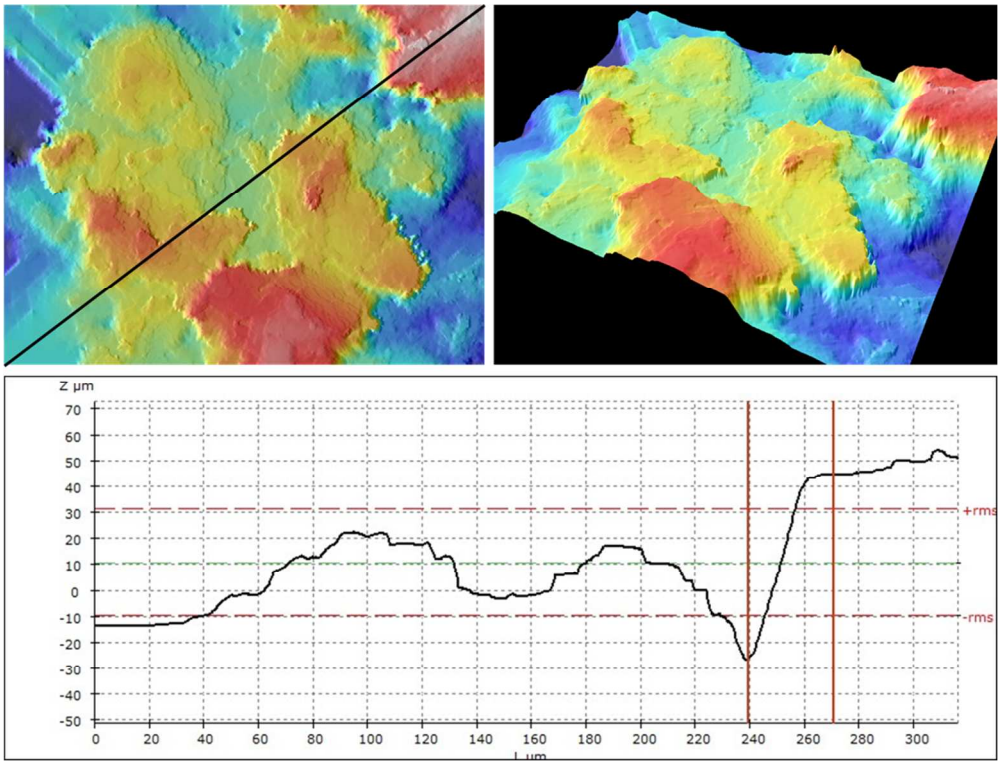

Figure 6. Confocal interferometric scanning microscopy image in 2D (top-left) and 3D (top-right), and profile of peak-to-valley heights (bottom). The profile depicted corresponds to the direction noted by a line in the 2D image.

Scherrer analysis

The Scherrer equation[24] was used to estimate the thickness of the primary cocoa butter crystals.

$$\tau = (K \cdot \lambda)/(\beta \cdot \cos \theta)$$

Here, λ is the wavelength (nm), θ is the Bragg angle at 2/3 of the height of the peak under study (rad), β describes the line broadening at half of the maximum intensity of the peak (FWHM, rad), and K is a dimensionless shape factor, that is close to unity and is related to the crystallite shape and to the way in which β and the thickness are defined. Scherrer analysis is an approximate method that assumes monodisperse crystals. This equation is only valid for crystallites smaller than 100nm and, as broadening increases with the diffraction angle, may be used for peaks in the small-angle region.

We used a K value of 0.9 to estimate the crystal thickness. This calculation is valid for well-defined, isolated, and symmetric peaks, so we selected the (005) diffraction peak (corresponding to a long-spacing value of 12.9Å, see Fig. 3) for the two samples. The FWHM of the peaks was estimated to be 0.21º 2θ for the velvet chocolate sample and 0.16º 2θ for normal chocolate, giving estimated crystal sizes of 37nm and 52nm, respectively.

Considering this estimated crystal size domain and the lamellar size, determined from the long-spacing value of the (001) reflection (65.7Å), we estimated the number of lamellae in a crystal domain, as described elsewhere.[25] The results obtained are presented in Table 1.

Table 1. Scherrer analysis data: crystal domain size and number of lamellae in a crystal domain in velvet and normal chocolate

	Velvet	Normal chocolate
Crystal domain (Å)	370	520
Lamellar size (long spacing value, Å)	65.7	65.7
Number of lamellae in a crystal domain	5.6	7.9

The difference in the XRD peak width between the velvet and normal chocolates indicated a smaller crystal size domain in the velvet, which could be estimated by Scherrer analysis. This smaller crystal size may be the reason for the lower melting temperature of form V velvet compared to that of normal chocolate.

Laboratory-scale XRD monitoring of chocolate velvet formation

Laboratory-scale XRD experiments were performed to monitor the formation of form V soon after spraying. Molten chocolate was sprayed on metal and chocolate surfaces at different temperatures in order to analyze the influence of the temperature and the kind of substrate (normal chocolate or metal) on the crystallization and transformation of CB crystals after spraying. Furthermore, as already stated, by following this procedure, the experimental conditions to obtain an acceptable velvet effect could also be determined.

Figure 7 presents laboratory-scale XRD data obtained when fluidized chocolate was sprayed on a metal surface at 4ºC, 12ºC, 16ºC, and 18ºC and heated to room temperature.

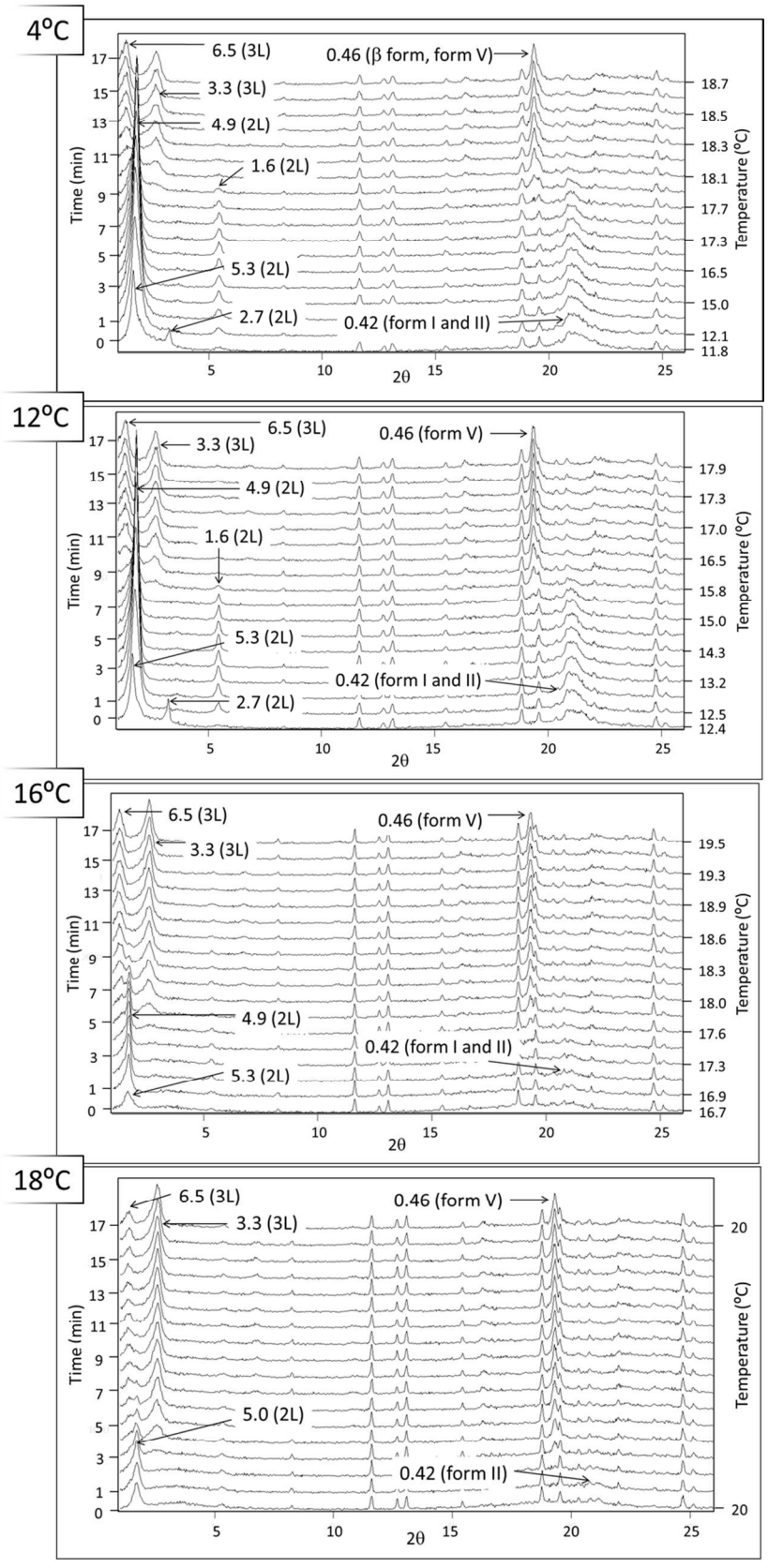
4°C
6.5 (3L)
0.46 (β form, form V)
3.3 (3L)
4.9 (2L)
1.6 (2L)
5.3 (2L)
2.7 (2L)
0.42 (form I and II)
Time (min)
Temperature (°C)
2θ
12°C
6.5 (3L)
0.46 (form V)
3.3 (3L)
4.9 (2L)
1.6 (2L)
5.3 (2L)
0.42 (form I and II)
2.7 (2L)
Time (min)
Temperature (°C)
2θ
16°C
6.5 (3L)
0.46 (form V)
3.3 (3L)
4.9 (2L)
0.42 (form I and II)
5.3 (2L)
Time (min)
Temperature (°C)
2θ
18°C
6.5 (3L)
0.46 (form V)
3.3 (3L)
5.0 (2L)
0.42 (form II)
Time (min)
Temperature (°C)
2θ

Figure 7. Laboratory-scale XRD patterns obtained when fluidized chocolate was sprayed on metal substrate at 4, 12, 16 and 18ºC, and heated to room temperature.

Soon after the fluidized chocolate was sprayed on the metal surface at 4ºC, initial form I developed and rapidly transformed to form II. A broad XRD peak at 0.42nm identifies both forms I and II. However, small-angle diffraction peaks became more suitable for distinguishing the two polymorphic forms, as there was no overlap with sucrose peaks at that 2θ range. Thus, peaks with long-spacing values of 5.3nm and 2.7nm correspond to the double chain length structure (2L) of form I, whereas the main 2L peak of form II appeared at 4.9nm. Ten minutes after spraying (when the sample reached a temperature around 18ºC), form V developed, as a typical main XRD peak of β form appeared at 0.46nm, accompanied by triple chain length diffraction peaks (3L) at 6.5 and 3.3nm. The form II → form V transformation ended at minute 13, in which the peak at 4.9nm disappeared.

The same sequence of transformation was observed when the metal temperature was 12ºC and 16ºC. However, in both results, the duration for the transformation to form V became shorter than that with a metal temperature of 4ºC. Specifically, the presence of form V was detected nine and (five) minutes after spraying when the metal temperature was 12ºC (16ºC). Slightly different behavior was observed when the metal temperature was 18ºC. In this case, form I did not develop, as droplets directly crystallized into form II, and form V was detected just three minutes after spraying. By comparing XRD data obtained at different temperatures of the metal surface, one may easily note that the intensity of the XRD peaks, especially small-angle diffraction peaks, of forms I and II decreased as the initial temperature of the metal increased from 4ºC to 18ºC.

The same experiments were carried out by spraying fluidized chocolate on a chocolate substrate (see laboratory-scale XRD patterns in Fig. 8).

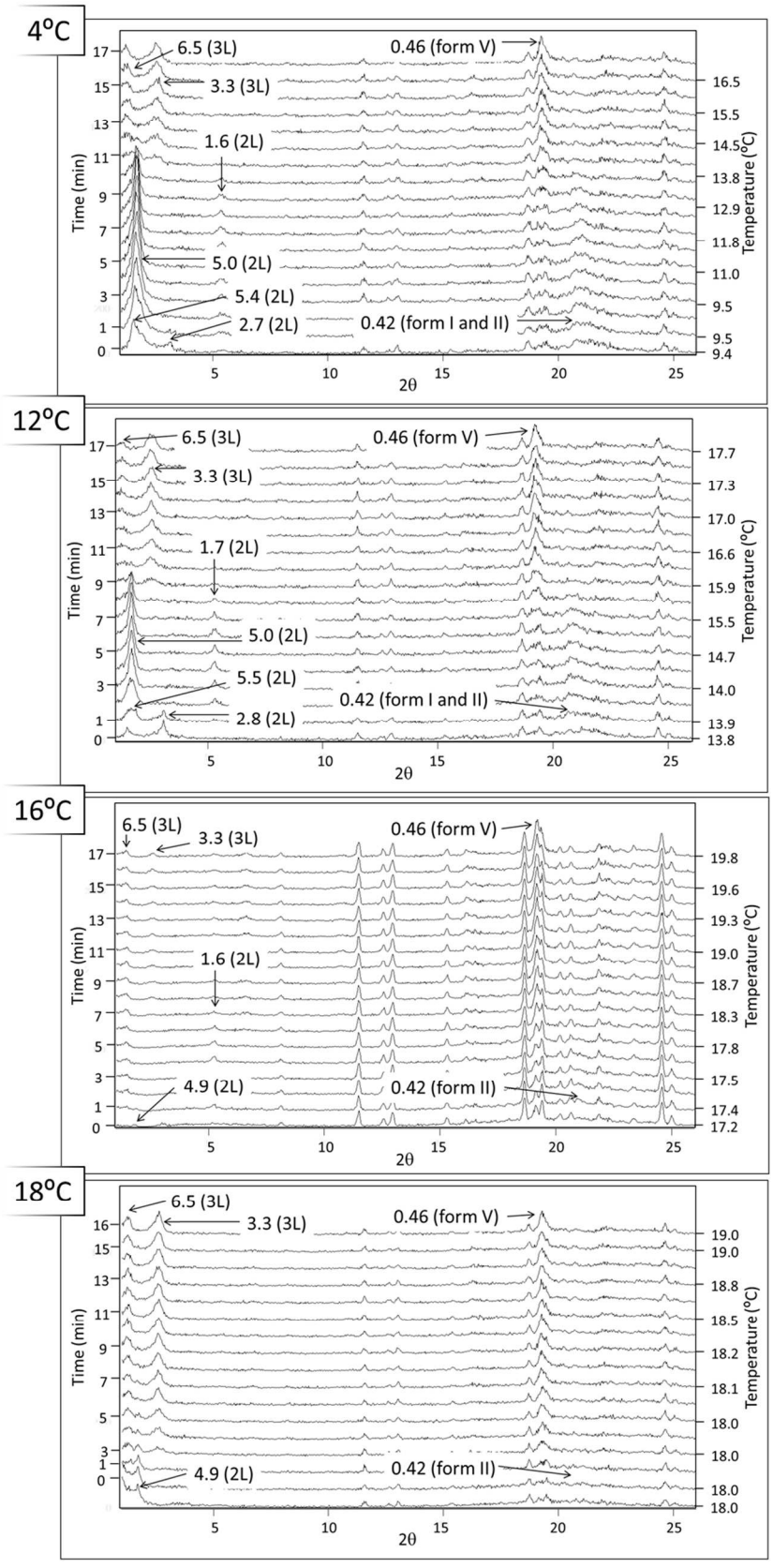
4°C
6.5 (3L)
3.3 (3L)
1.6 (2L)
5.0 (2L)
5.4 (2L)
2.7 (2L)
0.46 (form V)
0.42 (form I and II)
Time (min)
Temperature (°C)
2θ
12°C
6.5 (3L)
3.3 (3L)
1.7 (2L)
5.0 (2L)
5.5 (2L)
2.8 (2L)
0.46 (form V)
0.42 (form I and II)
Time (min)
Temperature (°C)
2θ
16°C
6.5 (3L)
3.3 (3L)
1.6 (2L)
4.9 (2L)
0.46 (form V)
0.42 (form II)
Time (min)
Temperature (°C)
2θ
18°C
6.5 (3L)
3.3 (3L)
4.9 (2L)
0.46 (form V)
0.42 (form II)
Time (min)
Temperature (°C)
2θ

Figure 8. Laboratory-scale XRD patterns obtained when fluidized chocolate was sprayed on chocolate substrate at 4, 12, 16 and 18ºC, and heated to room temperature.

The first occurring metastable form was form I with 2L structure peaks at 5.4nm and 2.7nm and a main short-spacing value of 0.42nm when the temperature of chocolate surface was 4ºC, quite similar to those using the metal substrate. This form quickly transformed into form II (with a 5.0nm main long-spacing peak) and, 11 minutes after spraying (at a temperature of 18.0ºC), the typical XRD peak of form V cocoa butter was detected at 0.46nm. 3L structure peaks at 6.5nm and 3.3nm also indicated form V occurrence. Compared to the metal substrate, the duration for the development of forms I and II became shorter as the initial temperature of the chocolate surface before spraying increased. Hence, form V appeared seven, three and two minutes after spraying when the chocolate surface temperature was 12ºC, 16ºC, and 18ºC, respectively. However, unlike the spraying experiment on a metal surface at 16ºC, when velvet was grown on a chocolate surface at the same temperature, form II was directly crystallized from the melt without the development of form I.

Table 2 summarizes the time and temperature at which form V developed when sprayed crystallization of chocolate was performed on both metal and chocolate substrates at 4ºC, 12ºC, 16ºC, and 18ºC. The initially formed metastable forms for each condition are also specified. Figure 9 indicates the durations necessary to complete the transformation from form II to form V CB crystals at the two surfaces with different substrate temperatures.

Table 2. Time and temperature for form V occurrence for experiments on metal and chocolate substrates at 4, 12, 16 and 18ºC. Metastable forms obtained soon after spraying are also specified at each condition.

		Metal	Chocolate
4ºC	t (min)	10	11
	T (ºC)	18.0	13.8
	Metastable forms	I + II	I + II
12ºC	t (min)	9	7
	T (ºC)	15.8	15.5
	Metastable forms	I + II	I + II
16ºC	t (min)	5	3
	T (ºC)	17.6	17.5
	Metastable forms	I + II	II
18ºC	t (min)	3	2
	T (ºC)	20	18
	Metastable forms	II	II

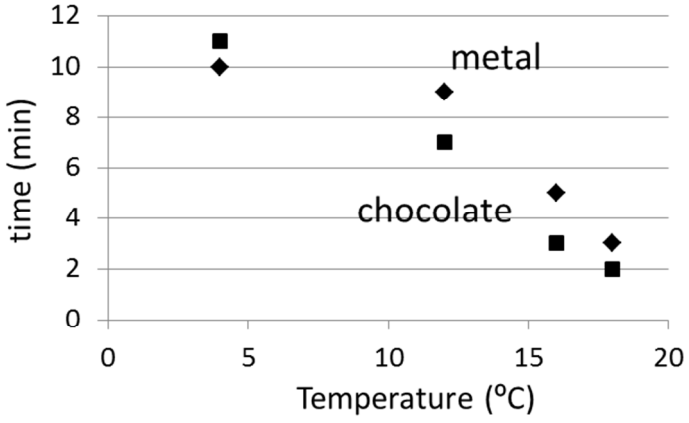

Figure 9. Duration for form V formation of CB crystals on metal and chocolate substrates at the different temperatures.

From these results, it is clear that form V cocoa butter developed more rapidly on the chocolate substrate than on the metal substrate. This fact may be related to the template effect on the rate of form II → form V transformation by the chocolate substrate.

However, when the spraying was performed at 4ºC, form V developed on the metal substrate one minute earlier than on the chocolate substrate. This may be explained by considering the different thermal conductivities of metal and chocolate. For all of the experiments, the velvet temperature was registered soon after spraying and was monitored until the end of the XRD measurements. Just after spraying chocolate on a surface to create velvet, the temperature increased due to the hot sprayed chocolate. More importantly, the temperature increased especially if the surface temperature was considerably below room temperature, as in the case of a surface temperature of 4ºC. By interpreting the data in Table 2, soon after spraying on the metal and chocolate substrates at 4ºC, the temperature of the velvet was considerably higher when sprayed on the metal (11.8ºC) than when sprayed on the chocolate (9.4ºC), due to the higher thermal conductivity of metal. The initial temperatures for the two different materials were therefore not comparable, and due to the higher thermal conductivity of metal, its velvet chocolate temperature reached room temperature more quickly. Although form V appeared one minute later on the chocolate substrate, it occurred at 13.8ºC (see Table 2), whereas form V was first detected at 18.0ºC when metal was used. Despite this one minute difference, the template effect may also exist in this case, as a difference of 4.2ºC was registered between the velvet

chocolates grown on the metal and chocolate substrates, and higher temperatures may accelerate the polymorphic transformation.

When the temperatures of the metal and chocolate surfaces were closer to room temperature (12ºC, 16ºC and 18ºC), no significant differences in the initial temperatures after spraying were observed when chocolate or metal were used as substrate material, as seen in Table 2.

The template effect caused by the chocolate surface was also confirmed by the metastable forms observed at the first stage of crystallization. For both metal and chocolate substrates, forms I and II were detected for surface temperatures of 4ºC and 12ºC. However, with an initial temperature of 16ºC, forms I and II were present when metal was used, whereas only the more stable form II was present at first when the chocolate substrate was sprayed.

In any case, the small crystallized droplets caused by spraying may result in a large contact surface, which may accelerate polymorphic crystallization and transformation, as previous studies reported.[15-17]

Figure 10 depicts the velvet grown on the chocolate surface at 4ºC, 12ºC, 16-18ºC, and 26ºC, several hours after spraying, so after polymorphic crystallization and transformation ceased. Enlarged images were taken for velvet chocolate grown at 4ºC and 26ºC.

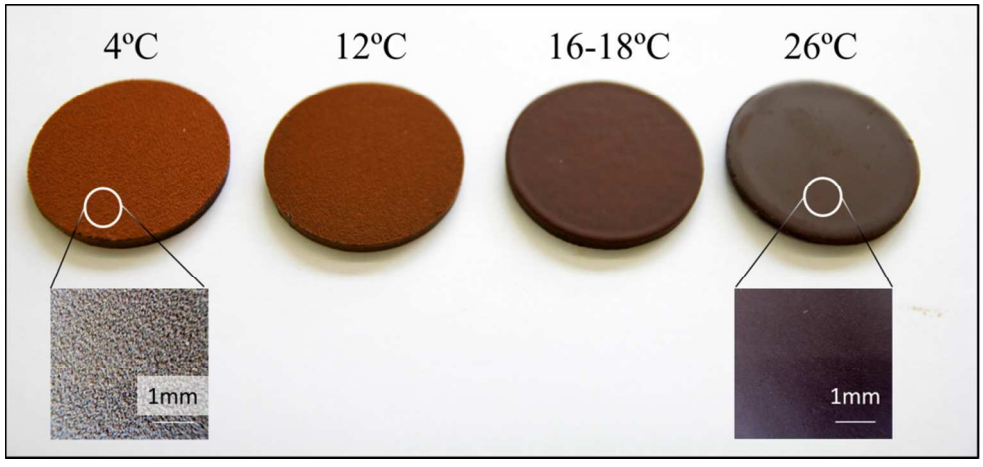

Figure 10. Appearance of velvet grown on chocolate surface at 4, 12, 16-18 and 26ºC.

The appearance of the velvet was the same at 16ºC and 18ºC. Velvet was also grown on chocolate at above room temperature (26ºC). One may appreciate the typical coarse texture of velvet at 4ºC and 12ºC. However, the fluidized chocolate sprayed on chocolate became softer and brighter as the substrate temperature increased, yielding a texture highly similar to that of normally tempered chocolate when the temperature was 26ºC, which cannot be considered a velvet effect. Also, the color of the velvet chocolate became darker as the chocolate surface temperature increased.

One may be able to define a critical temperature above which velvet cannot be properly formed. At 16ºC and above, the coarse texture of velvet is lost, so lower temperatures (preferably 4-12ºC) must be used in order to obtain the desired mouth-feel of velvet. The XRD data obtained during velvet formation at different temperatures (Figs. 7 and 8) indicated that the amount of metastable forms I and II decreased as the substrate temperature increased. Thus, the development of metastable forms may be the key factor for developing an acceptable velvet effect.

Figure 11 summarizes the results obtained when velvet was grown at different temperatures (different supercooling).

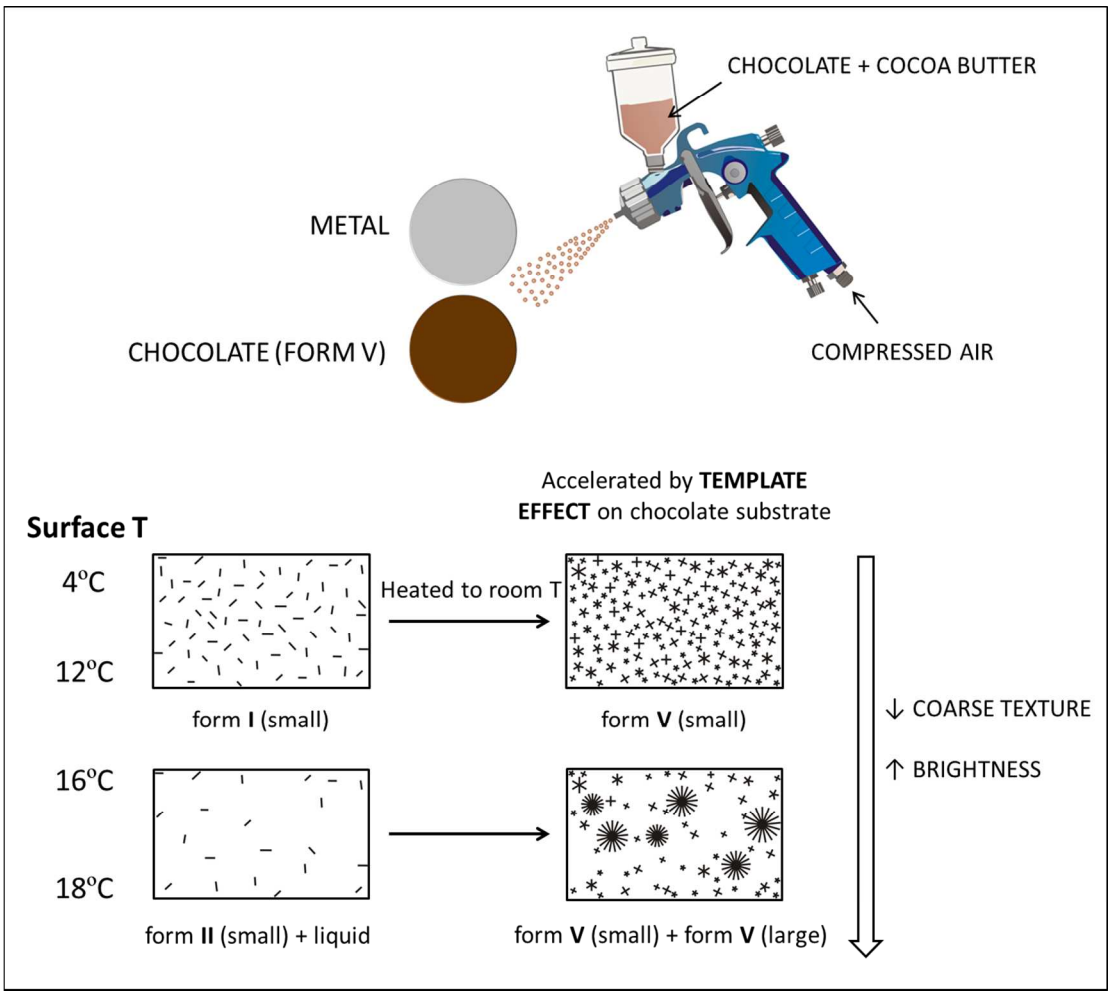

Figure 11. Models for describing the microstructure of velvet chocolate when grown at different surface temperatures on chocolate substrate.

When using a substrate temperature of 4ºC or 12ºC, metastable form I with small crystals developed and transformed to form V (through form II) as the sample reached room temperature. Form I then transformed to form V in the solid state, maintaining their small crystals. The thus-formed small form V crystals of CB in the velvet chocolate had a lower melting point than normally tempered chocolate, in which the form V crystals are larger. However, when fluidized chocolate was sprayed on the substrates at higher temperatures, the more stable form II was

directly crystallized. Under such conditions, not all of the cocoa butter may have crystallized, so form II coexisted with some amount of liquid, as XRD data demonstrated with the increase in background when the substrate temperature increased (Figs. 7 and 8). Hence, the initially developed form II may have transformed to form V while keeping small crystals, whereas the liquid present in the sample may have crystallized into form V with its larger crystals (more similar to normally tempered chocolate). The formation of larger crystals of form V may be responsible for the softer and brighter texture observed when higher substrate temperatures, such as 26ºC, were used (Fig. 10).

CONCLUSIONS

The present study demonstrated that thermal treatments may be applied to developing new chocolate textures, such as the velvet effect. This texture was defined as form V of cocoa butter, with a smaller crystal domain size, which led to a lower melting point and, therefore, to a soft mouth-feeling. By monitoring the velvet effect formation using laboratory-scale X-ray diffraction, we identified the first occurrence of form I, and subsequent polymorphic transformations I → II → V, upon heating. Precursor forms I and II may be key factors for obtaining form V, with smaller crystal size domains compared to normally tempered chocolate. This difference in crystal size domains was revealed by Scherrer analysis. These polymorphic transformations were accelerated by the template effect when chocolate substrate was used. The appearance of the velvet (e.g. roughness, color, brightness) largely depended on the supercooling (temperature of the substrate). Thus, the surface became coarser and duller as the supercooling increased. When the supercooling decreased (for substrate temperatures from 16 to 26ºC), the

appearance of the velvet became more similar to normally-tempered chocolate (softer and brighter), as shown in Figure 10.

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FOR TABLE OF CONTENTS USE ONLY

New textures of chocolate are formed by polymorphic crystallization and template effects: velvet chocolate

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b. Enric Rovira S. L., Castellbell i el Vilar, Spain

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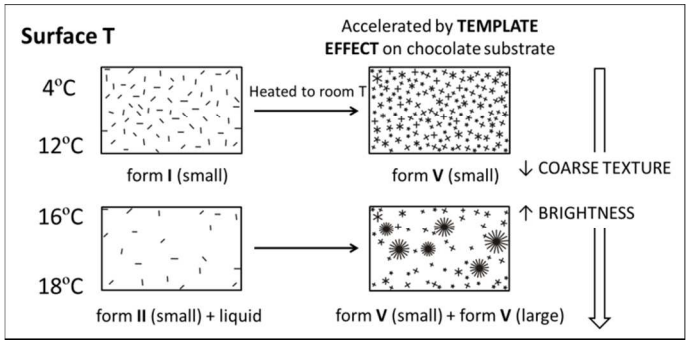
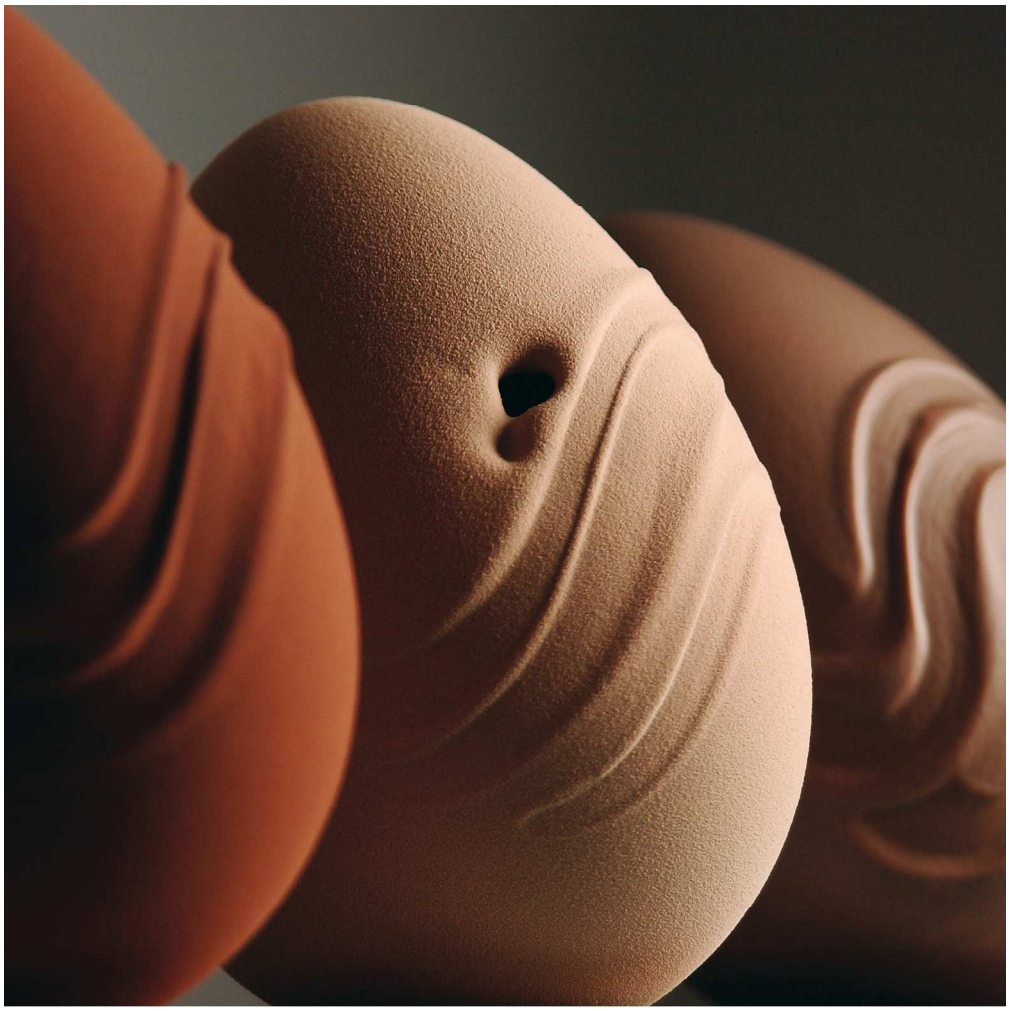
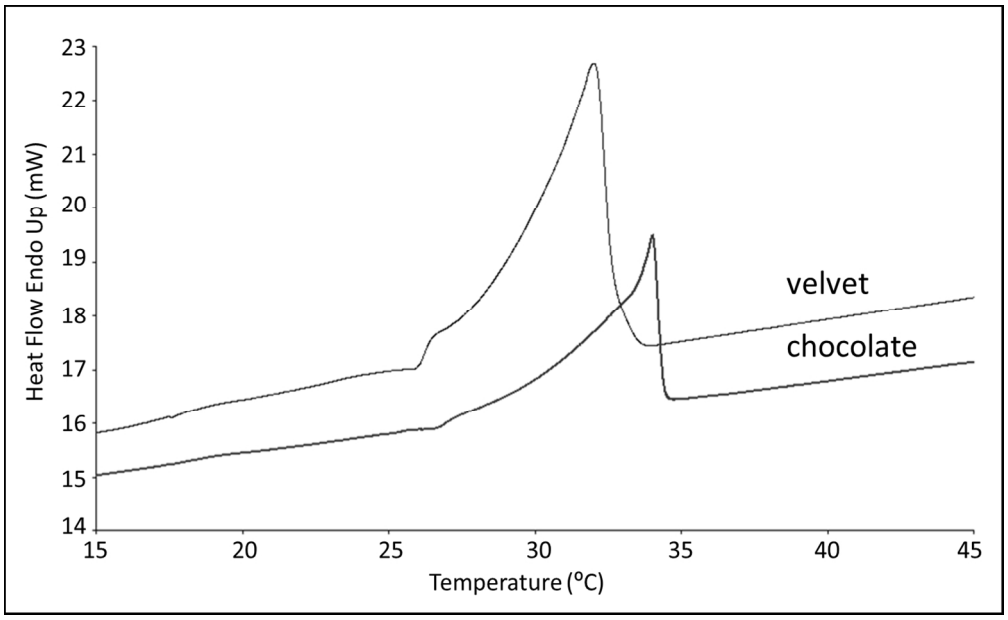


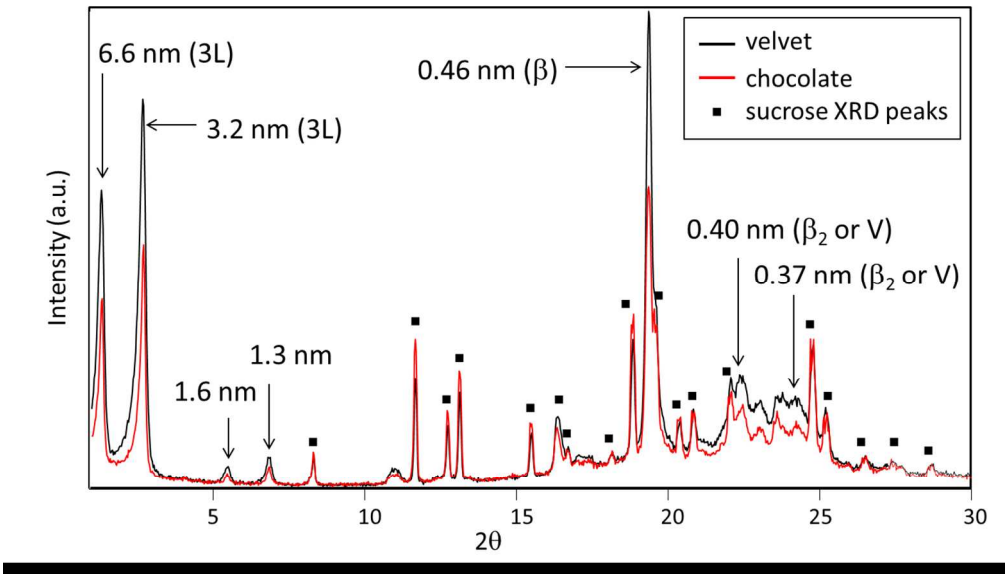
New types of chocolate textures with a soft mouth-feel can be formed by controlling the crystallization and polymorphic transformation of cocoa butter with thermal treatment and template effects.



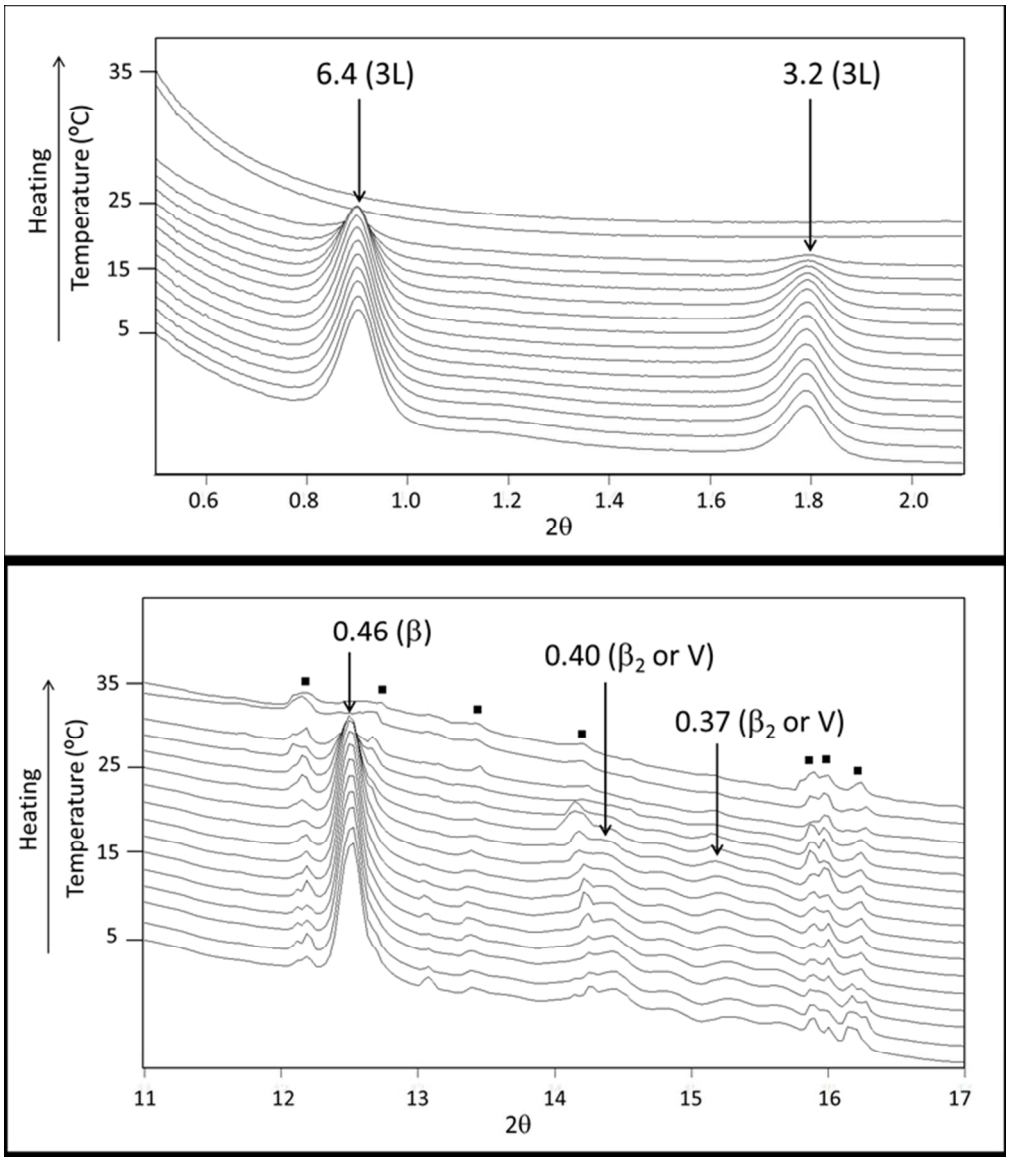
Velvet effect appearance on chocolate eggs.
161x161mm (300 x 300 DPI)



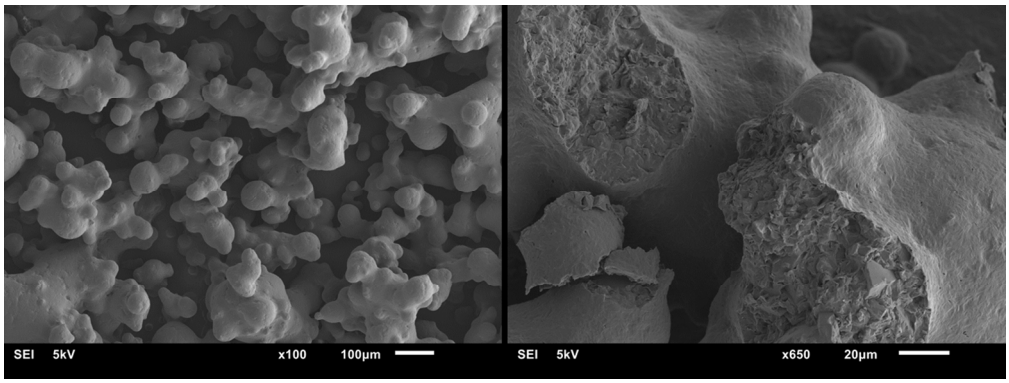
DSC melting curves of velvet and normal chocolate when heated from 5 to 50°C at 2°C/min.
252x153mm (150 x 150 DPI)



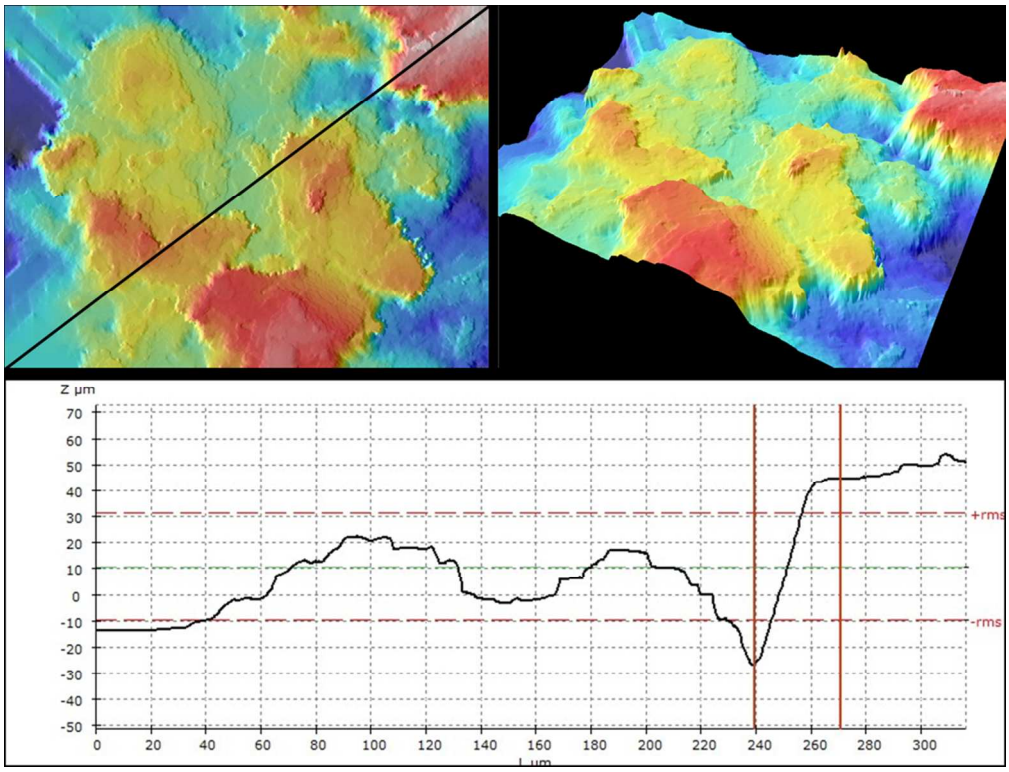
Laboratory-scale XRD of velvet and normal chocolate samples taken at room temperature.
238x139mm (150 x 150 DPI)



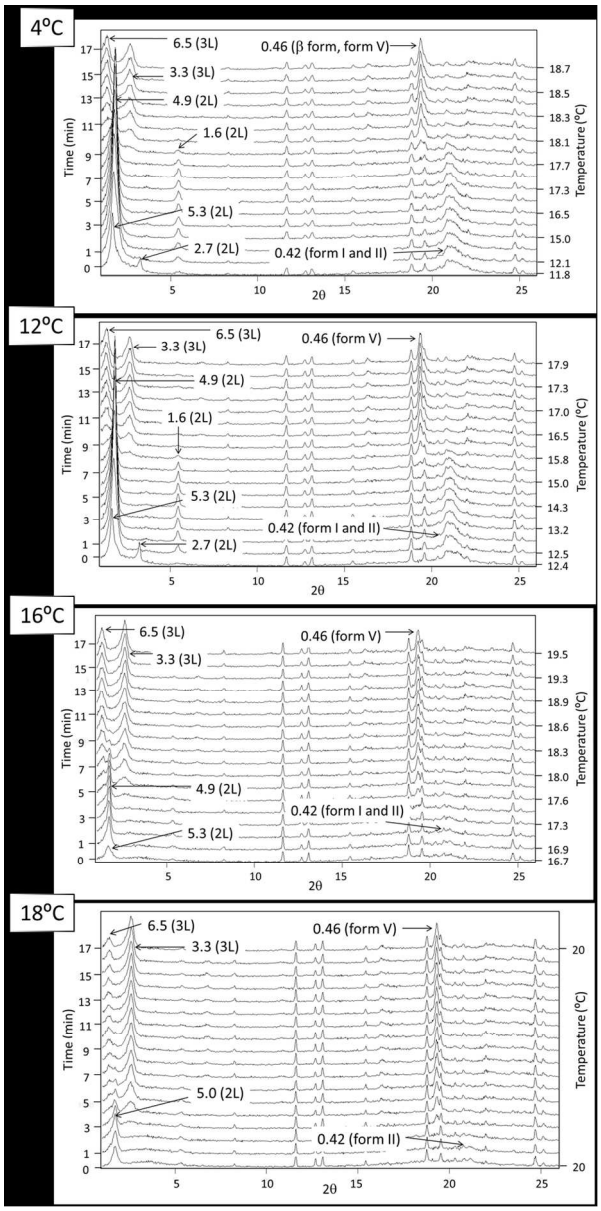
SR-SAXD (up) and SR-WAXD (bottom) patterns of velvet chocolate when heated from 5ºC to 40ºC at 2ºC/min.
129x149mm (150 x 150 DPI)



Cryo-SEM images of velvet chocolate
236x88mm (150 x 150 DPI)



Confocal interferometric scanning microscopy image in 2D (top-left) and 3D (top-right), and profile of peak-to-valley heights (bottom). The profile depicted corresponds to the direction noted by a line in the 2D image.
182x138mm (150 x 150 DPI)



Laboratory-scale XRD patterns obtained when fluidized chocolate was sprayed on metal substrate at 4, 12, 16 and 18ºC, and heated to room temperature.
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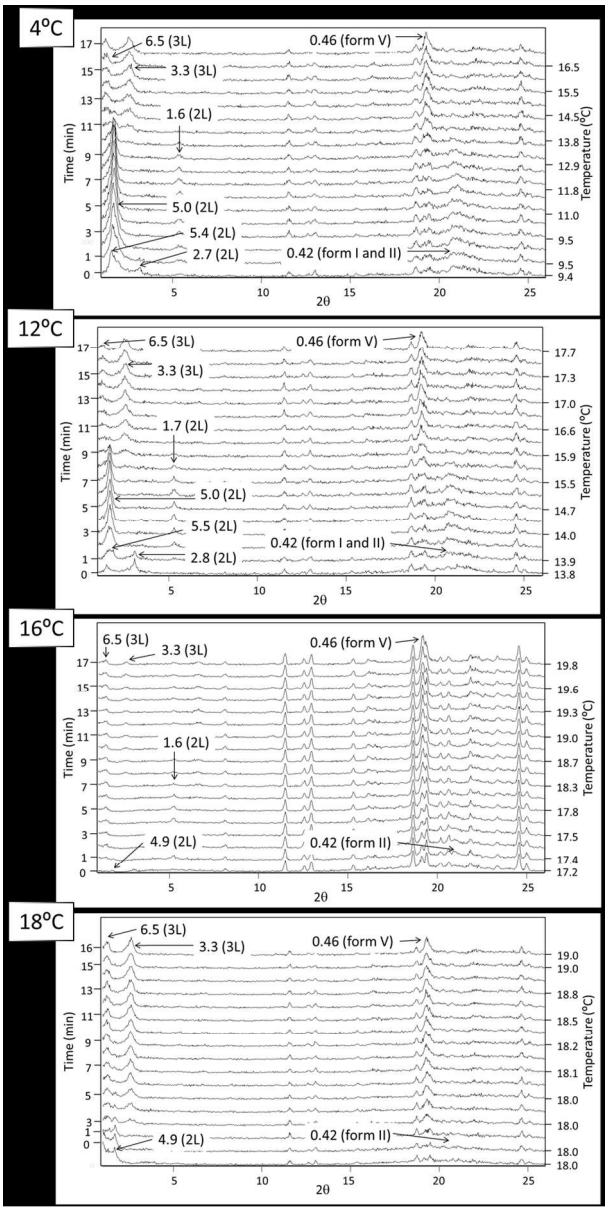
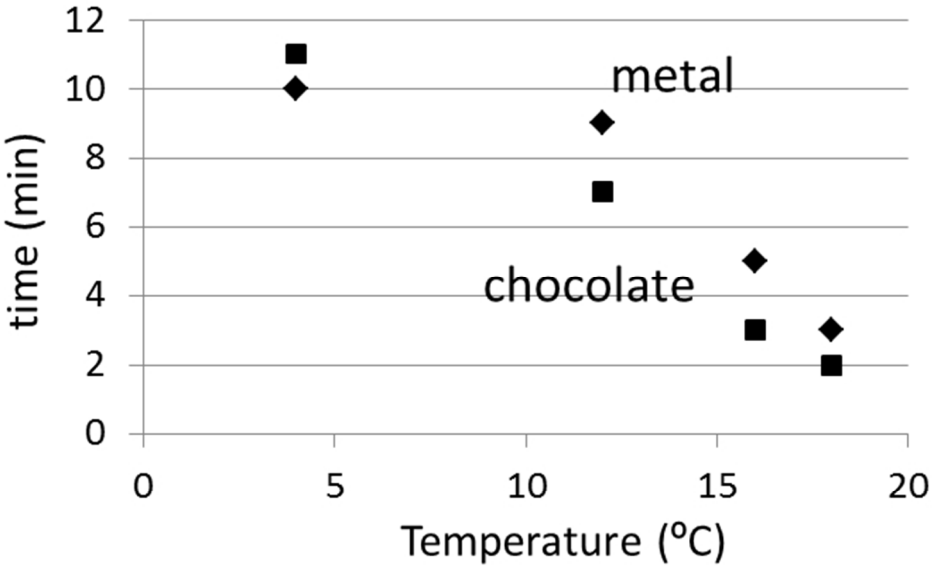
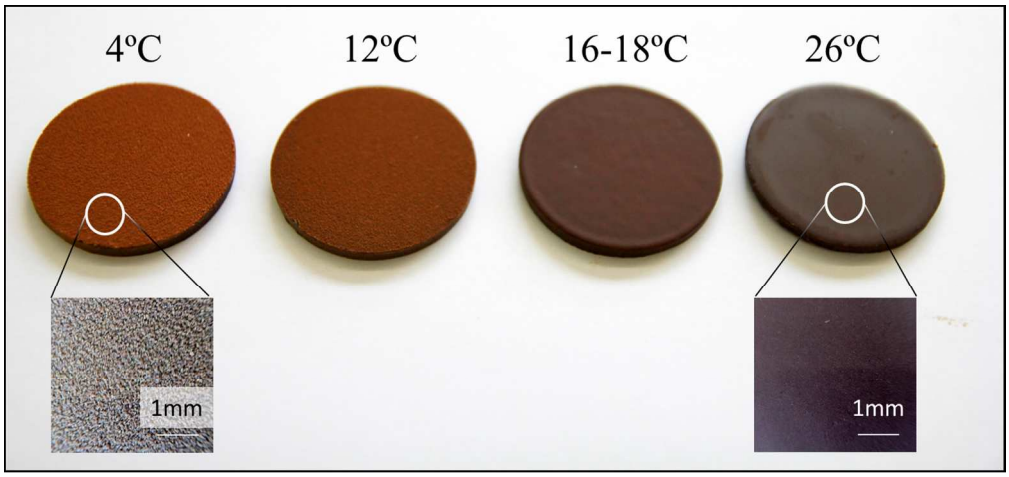


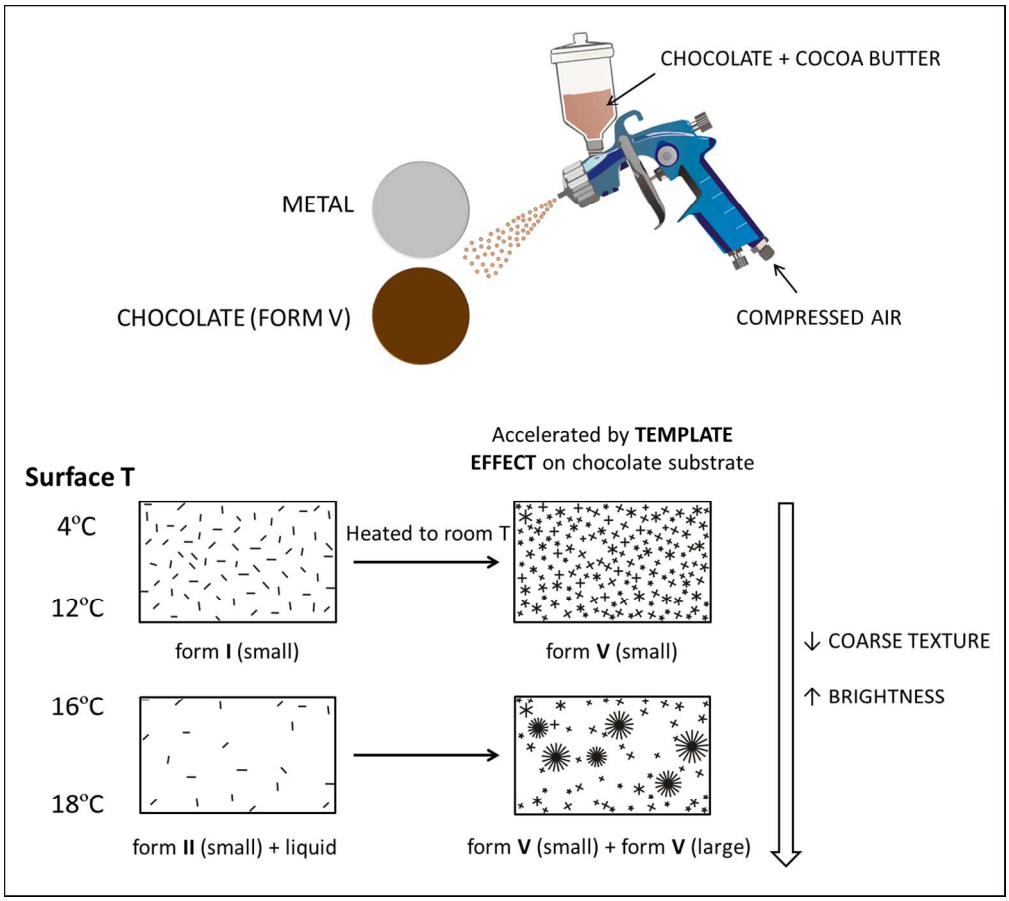
Laboratory-scale XRD patterns obtained when fluidized chocolate was sprayed on chocolate substrate at 4, 12, 16 and 18ºC, and heated to room temperature.
164x328mm (150 x 150 DPI)



Duration for form V formation of CB crystals on metal and chocolate substrates at the different temperatures.
120x77mm (150 x 150 DPI)



Appearance of velvet grown on chocolate surface at 4, 12, 16-18 and 26ºC.
255x118mm (150 x 150 DPI)



Models for describing the microstructure of velvet chocolate when grown at different surface temperatures on chocolate substrate.
245x218mm (150 x 150 DPI)