CHOCOLATE: A USEFUL MODEL FOR TEACHING BASIC TERMS ON CRYSTALLOGRAPHY AND THERMODYNAMICS

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Abstract

By using a simple, attractive and sweet model, as chocolate is, many scientific concepts related to different disciplines, which are often understood as complex and dull by most students, may be introduced. In particular, the student may be able to develop crystallographic concepts and methodologies combined with some thermodynamic aspects, which have been historically known as complex and arduous disciplines. Hence, the student may enjoyably assimilate complicated concepts such as polymorphism, mixing behavior, crystal morphology, crystal size or thermodynamic stability, and may also be capable of understanding their application to daily life. These concepts may be applicable to any kind of material and can be more deeply developed depending on the level required.

Keywords: science teaching, easy learning, Crystallography, phase behavior

1 INTRODUCTION

Crystallography is defined as an interdisciplinary branch of science with far-reaching applications in Mineralogy, Chemistry, Physics, Mathematics, Biology and Materials Science. According to the International Union of Crystallography (IUCr), a material is a crystal if it has essentially a sharp diffraction pattern,[1] but it may be also understood as an ordered solid material in which atoms and molecules occupy specific positions giving rise to a symmetric and periodic structure. Crystallography, together with Thermodynamics, is understood as a complex and arduous discipline by most of students. As an example, when students are initially introduced in the crystallographic understanding, they should develop three-dimensional vision and assimilate new and basic concepts, such as *order*, *symmetry* and *periodicity*, which often mean high difficulties for students. In order to focus on the development of such fundamental concepts, combined with related experimental methods for the materials characterization, we chose a daily and attractive product, as chocolate is.

Although most people are aware of the satisfaction felt when eating a piece of chocolate, most people are not aware of the rich science that lies behind this desired food product. Chocolate is mainly composed by cocoa mass (which basically consists of cocoa powder and cocoa butter), sugar and other additives (milk powder, vanilla, etc.). Among these components, cocoa butter becomes a key constituent of chocolate and responsible for many of its sensory attributes. Physical properties of chocolate, such as melting, rheology and texture, mainly depend on the crystal (polymorphic) forms present in cocoa butter[2]. Polymorphism (Greek: *poly* = many, *morph* = form) was defined by McCrone[3] as “a solid crystalline phase of a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state”. These different arrangements of the molecules involve different states of matter with different properties. Many crystals exhibit polymorphism, in which structural determination and thermodynamic stabilization of the polymorphic modifications are of primary significance to determine the overall polymorphic nature of every substance.[4] In addition, the kinetic properties of crystallization and structural transformation are important, particularly for the application of polymorphic crystal systems in pharmaceutical, biomedical, food technology and other applications.

Cocoa butter, composed by three basic triacylglycerols, exhibits six different polymorphic forms referred to as I through VI. Among them, form V is the desired polymorphic form and industrially promoted, as it provides the desired melting, textural and mouth-feel characteristics of chocolate. Thus, controlling the crystal forms present during the chocolate manufacturing and storage becomes necessary in order to obtain the desired characteristics of the end food product.

With this work, we show some general guidelines to clarify complicated crystallographic concepts, like polymorphism, among others, and connect them with a thermodynamic basis. Depending on the level required by students, these concepts may be focused and developed in a simpler or deeper way.

2 METHODOLOGY

2.1 Basic concepts to be absorbed by students

Chocolate becomes an attractive model for students, but they should be aware of its complex composition and microstructure. Triacylglycerols are the main components of solid lipids employed in spreads, creams and confections. These compounds exhibit a complicated crystallization behavior and polymorphic transformation pathways, in which the three most commonly encountered polymorphic forms ordered by increasing thermodynamic stability are: α (least stable polymorphic form having the lowest melting temperature), β', and β (most stable and with highest melting temperature). However, additional polymorphic forms can occur depending on the chemical nature of the triacylglycerol molecule, so that the complexity of the polymorphic behavior can significantly increase. In order to obtain the desired end product characteristics, some parameters are determining for the selection of the adequate polymorphic form, such as the melting point, the crystal morphology or the crystal size.

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. Cocoa butter is mainly composed by three triacylglycerols and becomes the responsible for many of the desirable and unique sensory attributes of chocolate. Cocoa butter exhibits six different polymorphic forms, which are named by two different nomenclatures: form I (γ), form II (α), form III (β'_2), form IV (β'_1), form V (β_2) and form VI (β_1). Among them, form V is industrially promoted through tempering processes (temperature variations), as this polymorph provides the desired pleasing appearance of chocolate with shiny surface, and characteristic melting, textural and mouthfeel properties.[5] The melting temperatures of polymorphic forms of cocoa butter are shown in Table 1.

Table 1. Melting points of polymorphic forms of cocoa butter

Polymorphic form	I	II	III	IV	V	VI
Melting temperature (ºC)	17	23	25	27	33	36

At this point, students may notice that the melting point of the preferred form V is 33ºC, which is the temperature of humans' mouth, so as soon as they introduce a piece of chocolate, it immediately melts (due to its sharp melting profile) providing a fresh sensation. However, this form V is not the most thermodynamically stable polymorphic form. Most stable form of cocoa butter is form VI, having the highest melting point, which will be discussed further on. Some thermodynamic concepts may be introduced to the student, such as the Gibbs Free Energy functions and the Burger-Ramberger rules.

In order to characterize the polymorphic behavior of any kind of material, the most commonly used experimental techniques are the differential scanning calorimetry (DSC), X-ray diffraction (with both laboratory-scale and synchrotron radiation source), microscopy (electron microscopy, optical polarized microscopy, thermo-optical microscopy, atomic force microscopy, etc.) and spectroscopic techniques (FT-IR, Raman). The characterization of a chocolate sample by using different experimental techniques may introduce the student to (apart from the fundamental physics lying behind each apparatus) interpreting data with a well-defined objective and application.

As an example, Fig. 1 depicts an example of the DSC melting curve of tempered chocolate (up) and the corresponding laboratory-scale X-ray diffraction pattern at room temperature (bottom).

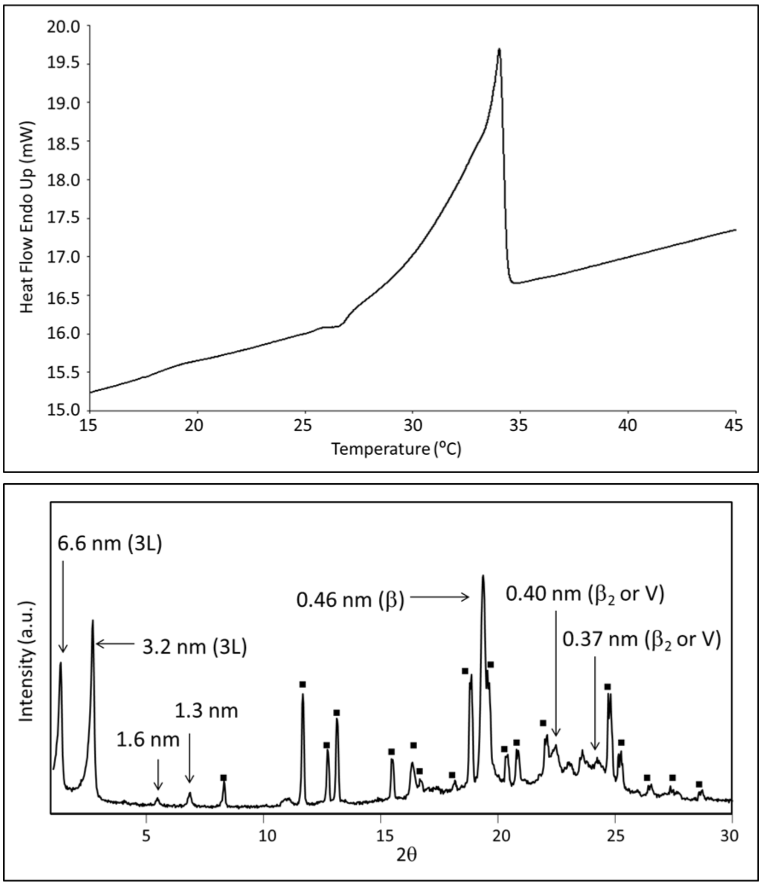

Fig. 1. DSC melting curve (up) and laboratory-scale X-ray diffraction pattern (bottom) of normally tempered chocolate.

The DSC melting curve shows the melting profile of the cocoa butter contained in the chocolate sample. Thus, the melting process started at around 27.9ºC (onset temperature, corresponding to the intersection of the baseline and the initial tangent at the melting peak), revealed its maximum at 34.0ºC (peak top temperature) and finished at 34.4ºC (end temperature, intersection of the baseline and final tangent of the peak). By considering the data given in Table 1, one may expect that the polymorphic form of cocoa butter in the chocolate sample under study may be form V. However, laboratory-scale X-ray diffraction data (Fig.1 bottom) may be used for confirming the presence of this form V. In a simple manner, we can define the diffraction phenomenon as produced when a crystalline substance is irradiated with a radiation having a wavelength similar to the interatomic distances. Then, constructive interferences between the diffracted beams are produced at specific directions, depending on the crystalline structure. Each crystalline polymorph has its own diffraction pattern. Thus, characteristic X-ray diffraction peaks of form V with typical short spacing values of 0.46, 0.40, and 0.37nm were detected. The long spacing values at 6.6 and 3.2 nm were indicative of the packing of triacylglycerol molecules, indicating a trilayer structure (3L). X-ray diffraction peaks of the sucrose crystals present in the chocolate sample are indicated by the symbol ■.

For chocolate industry, it is important to ensure shelf-life of chocolate products. In other words, the optimal state of form V crystals of cocoa butter, which provide the unique properties of chocolate, may be maintained during storage in order to satisfy consumers' expectations. If not cooled properly or if it is not stored for long periods of time and/or under fluctuating temperatures, the physical structure of chocolate will change and impart an unppealing "bloom" on the chocolate's surface.[5] Such undesirable conditions of storage at high temperatures and/or fluctuating temperatures involve the melting of some fractions of cocoa butter crystals, accompanied by complex processes of oil diffusion and dissolution, which result in the polymorphic re-crystallization and transformation into most stable polymorphic form VI of cocoa butter. Furthermore, long periods of storage cause the polymorphic transformation of form V to form VI, as the latter becomes the thermodynamically most stable form. The formation of form VI crystals in chocolate products results in the occurrence of a whitish layer on the chocolate surface and additional unpleasant sensory characteristics for the consumer. Thus, the larger crystal size and higher melting temperature of form VI crystals (see Table 1), compared to those of form V, lead to a rougher texture and the loss of the unique sharp melting profile of form V. Many research work have been conducted to find a solution to inhibit the Fat Bloom phenomenon or, at least, its retardation. However, the complex physical changes, polymorphic behavior, crystal growth and the interaction of cocoa butter with other ingredients are still not completely understood.

2.2 Case study: monitoring of Fat Bloom formation

Here we propose a simple case study for students to monitor the polymorphic transformation of form V of cocoa butter to the undesired form VI (Fat Bloom) by using different experimental techniques.

In order to force the Fat Bloom occurrence, chocolate samples may be subjected to higher temperatures than those adequate for ensuring shelf-life of chocolate (above 23ºC) and/or temperature fluctuations. The present case study was developed by subjecting a set of chocolate samples at a constant temperature of 26ºC. Samples were analyzed before (day 0), and at concrete stages of the thermal treatment (day 1, day 2, day 4, day 8, day 16, day 32 and day 64) by using DSC, laboratory-scale X-ray diffraction and scanning electron microscopy (SEM).

Fig. 2 shows the DSC melting profiles (up) and X-ray diffraction patterns (bottom) of chocolate samples obtained at different stages during the thermal treatment process.

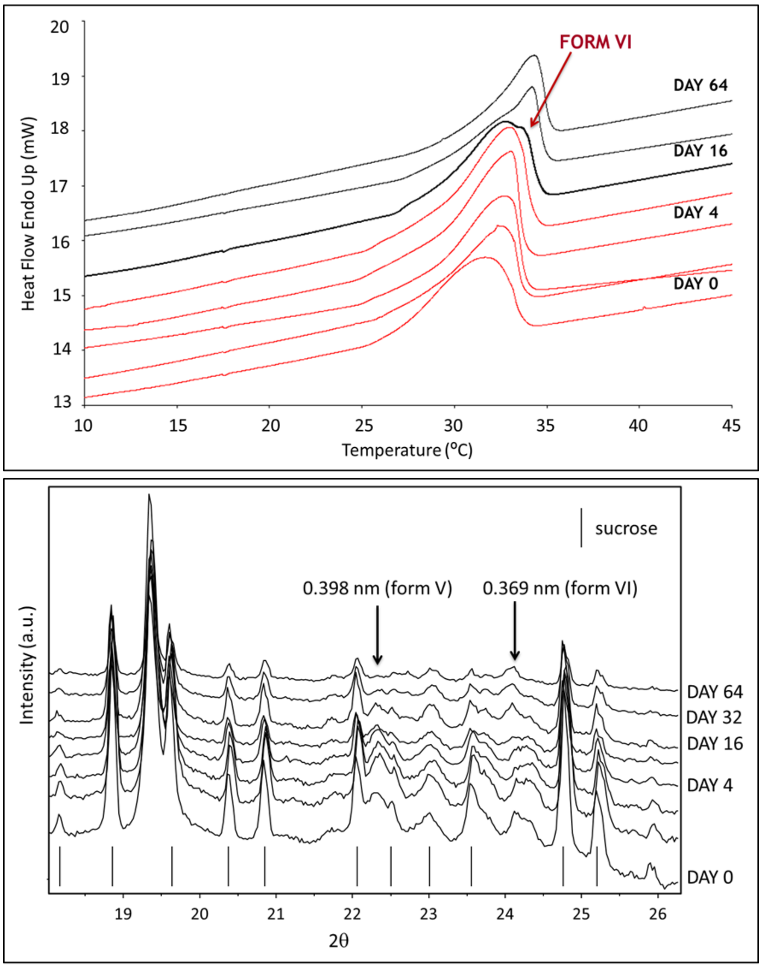

Fig. 2. DSC melting curve (up) and laboratory-scale X-ray diffraction pattern (bottom) of chocolate samples subjected to isothermal process at 26ºC for 64 days.

The melting peak corresponding to the cocoa butter of chocolate samples remained constant from day 0 to day 8, having peak top temperature at around 32ºC. However, the DSC melting curves of chocolate samples subjected to isothermal process at 26ºC for 16 days revealed the occurrence of an additional melting peak with peak top temperature at almost 35ºC, which progressively increased in intensity for analysis taken at day 32 and day 64.

Laboratory-scale X-ray diffraction revealed the evolution of the polymorphic forms of the cocoa butter contained in the chocolate samples. The results confirmed the occurrence of form VI through its characteristic diffraction peak with short-spacing value at 0.369 nm in samples of day 16, and its intensity increased for samples of day 32 and 64, at the expense of typical peak of form V at 0.398 nm.

For students may also be interesting to monitor the changes in crystal morphology of chocolate samples during the Fat Bloom formation. In Fig. 3, SEM images of the surface of chocolate samples are shown.

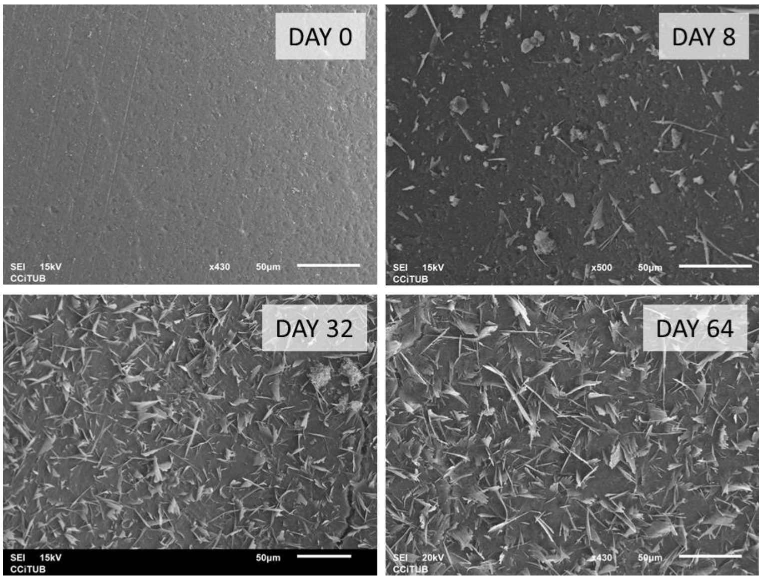

Fig. 3. SEM images of chocolate samples subjected to isothermal process at 26ºC for 64 days.

Students may note the regular, soft and flat surface of the chocolate sample before subjected to isothermal process (day 0). However, on day 8, needle-shaped crystals of 30-50 μm, corresponding to the polymorphic form VI of cocoa butter, were firstly detected on the chocolate surface. These crystals became more abundant and larger as the storage time of the samples at 26ºC increased. At this point, students may be capable of stablishing connections between the crystal morphology and crystal size observed through microscopic techniques and the sensory properties caused by chocolate with Fat Bloom on the surface. By analyzing the shape (needle-like) and size (larger than 50 μm in some cases) it is easy to understand the rough texture felt when eating a piece of chocolate with Fat Bloom.

In case that the techniques described in this paper are not available for students, similar methodology may be carried out by using less sophisticated equipment. Simpler microscopic techniques, like optical microscopy also become adequate for the observation and monitoring of the Fat Bloom occurrence.

Our experience in using chocolate as a model for teaching basic concepts on polymorphism and its applications revealed that students become more receptive and they more easily absorb such complex crystallographic and thermodynamic concepts. The guidelines exposed can be more deeply developed depending on the level required by the student.

3 CONCLUSIONS

Chocolate was proposed as a model to teach fundamental aspects on Crystallography and Thermodynamics, such as polymorphism, crystal morphology, crystal size and thermodynamic stability. The guidelines proposed combine both theoretical with experimental aspects, which may be complemented by sensorial properties. The study of the microstructure, melting characteristics and polymorphic characterization of tempered chocolate and the occurrence of Fat Bloom on its surface provide adequate tools to make the student assimilate complicated concepts in an enjoyable manner and understand its application to daily life. These concepts are applicable to any kind of material and may be focused in a deeper way depending on the level required by the student.

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