Food Structure

Volume 4 | Number 2 Article 9

1985

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FOOD MICROSTRUCTURE, Vol. 4 (1985), pp. 249-265
SEM Inc., AMF O'Hare (Chicago), IL 60666-0507 U.S.A.

0730-5419/85$1.00+.05

# CRYSTAL MORPHOLOGY OF COCOA BUTTER

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## Abstract

The multiple melting points of triglycerides have been known and studied for more than a century by numerous workers. The ability of fat to undergo polymorphic changes is important mainly due to its effect on product texture and appearance. Polymorphic resolidification during storage of cocoa butter into higher melting forms can destroy the smooth glossy appearance of a confectionery product. This manuscript will review the polymorphic characteristics and composition of cocoa butter from Theobroma cacao. A discussion of common fat behavior relative to tempering and bloom formation will be included. Scanning electron microscopy and polarized light microscopy aided in visually defining the crystalline forms of cocoa butter during crystallization. Thermal and compositional properties of cocoa butter during crystallization indicates that a high-melting crystal seed forms which promotes the solidification of additional quantities of less stable triglycerides.

Initial paper received January 27 1985
Manuscript received June 09 1985
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KEY WORDS: cocoa butter, scanning electron microscopy, polarized light microscopy, differential scanning calorimetry, tempering, fat bloom, crystal seed.

## Introduction

Theobroma cacao is the source of the cocoa bean. Cacao beans are cultivated from the tropical regions of Western Africa, Brazil, and many other locations within 20° latitude of the equator. The fermented dried cocoa beans entering the US and Europe are processed into various products. To assure cleanliness and quality, the beans are placed through air lifts, screens, and magnetic separators to remove fiber, stones, and immature small beans. Once the beans are cleaned, roasting is carried out to develop flavor and aroma. Roasting facilitates the removal of the shell during winnowing and also reduces the moisture content of the bean. The beans are then passed through breakers and winnowing machines which operate by cracking the shell and bean into large pieces. The fractured shell and bean fragments are separated by sieving and air elutriation. This separation process is dependent on a difference in density between the bean cotyledon fragments and the shell. The cotyledon fragments, called nibs, are converted into a fluid paste known as chocolate liquor. In the production of chocolate, the addition of sugar, milk solids (in the case of milk chocolate), and additional cocoa butter are added to the liquor prior to refining. After a small particle size (<25μm) has been established in the refiners, the chocolate blend is conched. Along with producing the desired flavor, conching promotes a continuous fat phase that evenly coats the sugar and cocoa solids thus producing a flowable liquid.

The final processing steps are tempering and solidification of the confectionery product. Immediately after tempering, the chocolate is molded and cooled to approximately 16°C for proper contraction. If the chocolate is shock cooled or if the cooling time is too short, product quality may be affected. A problem associated with poor tempering is the formation of fat bloom which visually appears as gray swirls or as large white circular fat crystals on the surface. Thus the snap, gloss, proper melting point, contraction, and other attributes are dictated by the fat crystalline forms present (Musser, 1973). Taste, smell, mouthfeel, hearing, and especially sight are involved in the total perception of a

food product. If the cocoa butter crystals present in a chocolate product are not in a stable form, mouthfeel, hearing, and sight are adversely affected.

Clearly defining the mechanisms involved in cocoa butter crystallization remains an interesting but controversial area of confection science. The following includes research efforts aimed at defining the compositional and thermal characteristics of cocoa butter crystals formed during crystallization. A discussion based on thermal and compositional data will shed new insight on the mechanisms of cocoa butter crystallization. There still may be art involved in cocoa butter crystallization and tempering but scientific studies are increasingly providing new answers.

## Polymorphism and Molecular Packing

In order to understand the mechanism of fat crystallization it is first necessary to understand how triglycerides crystallize at the molecular level. The phenomenon of triglyceride polymorphism has been known for over 100 years (Duffy, 1852). Throughout recent history numerous scientists have conducted research to demonstrate that the basis for multiple melting points of triglycerides was polymorphism (Clarkson and Malkin, 1934; Lutton, 1945). Nearly all fats exhibit polymorphism in a monotropic manner, in that transformations take place from less stable, lower melting forms to more stable, higher melting forms.

Fatty acids and glycerides have been observed to exist in at least two crystalline forms and some have as many as three or four (Bailey, 1950). When a transition occurs the molecular packing of the triglycerides shift to confer greater stability to the crystal. Clarkson and Malkin (1934) were the first to clearly demonstrate triglyceride polymorphism with X-ray diffraction analysis. It is known that if tristearin is melted and suddenly cooled, it first melts at 55°C, then solidifies again and melts at 71°C. The hypothesis to explain the different crystal stabilities was polymorphism.

The crystallization mechanism of monoacid saturated triglycerides is related to the packing of the hydrocarbon chains. Triglycerides in the liquid state present an X-ray diffraction pattern similar to liquid monoglycerides. Due to similar diffraction patterns, Larsson (1972) believed that liquid triglycerides exist in tuning fork conformations at temperatures above the melting point. It was believed that the triglycerides laterally interlock and possibly form a lamellar-like structure. Particular long spacing diffraction lines exhibited the same intensity distribution whether the triglycerides were liquid or crystalline. It was accepted that tristearin and other monoacid saturated triglycerides existed in three different polymorphic crystalline forms called alpha ($\alpha$), beta prime ($\beta'$), and beta ($\beta$), the latter being the most stable. The data obtained from X-ray diffraction analyses of triglycerides can be separated into two groups: long and short spacings. The long spacings are related to the distance between the planes formed by the terminal methyl groups of the fatty acids. The interpretation of the short spacings are related to the cross-sectional arrangement of the fatty acids on the triglyceride molecules (Chapman, 1962). For tristearin, as the melting point increases, the long spacings decrease as shown in Table 1. Thus the long spacing recorded for tristearin and most other saturated monoacid triglycerides is dictated primarily by the geometry of the triglycerides upon crystallization. For most saturated monoacid triglycerides the structure formed will be the double chain length structure. Larsson, (1964) altered the conventional tuning fork structure to a modified tuning fork configuration. This is believed to be the more correct arrangement, where the central and one of the alkyl groups are aligned along the same axis.

Table 1

Comparison of the melting points and long spacings for the three crystalline states of tristearin (Chapman, 1962).

| Crystalline state | Melting point (°C) | Long spacing (Å) |
|---|---|---|
| $\alpha$ | 54.0 | 50.6 |
| $\beta'$ | 64.0 | 47.2 |
| $\beta$ | 73.1 | 45.0 |

The unstable $\alpha$ form of tristearin is a vertically oriented (zero tilt) structure (Fig. 1$\alpha$) and the molecules are loosely packed in an inefficient manner. The uneven alignment of the terminal methyl plane complicates the packing of one bilayer in relation to adjacent layers. If the crystal of tristearin undergoes resolidification into the $\beta'$ or $\beta$ form, the long spacing decreases from 50.6 Å to 47.2 Å and 45.0 Å, respectively. The triglycerides in the $\beta'$ and $\beta$ forms are thought to tilt with respect to the methyl plane (Fig. 1$\beta'$,$\beta$). As the angle between the triglyceride and methyl plane decreases, a closer chain packing is adopted and the plane between adjacent bilayers is more even. Close chain packing produces a more dense structure with a higher melting point. It is believed that the terminal methyl groups in a $\beta$ crystal are located in one plane. The packing of the bimolecular layers is complicated if the chains from one bilayer penetrate neighboring bilayers (Larsson, 1982).

As the triglyceride becomes more complex in its fatty acid composition, a change from the double chain length structure occurs. If fatty acid chain lengths on a triglyceride differ by four or more carbons, triple chain length structures may form (Lutton, 1948). In this case, the alignment of glyceride fatty acids is dictated by sorting of short chain from long chain acids.

The last case to be discussed is the unsaturated glycerides which more closely resemble the composition of cocoa butter. The majority of the triglycerides present in cocoa butter are the 2-monounsaturated type such as POP, POS, and SOS where S = stearic acid, P = palmitic acid, and O = oleic acid. Mixed oleic-saturated glycerides

tend to form triple chain length structures. X-ray analyses reveal the long spacings for the β form of SOS to be ≅64 Å which corresponds to a triple chain length structure. Lutton (1972) has illustrated the conventional tuning fork packing for a 2-monounsaturated triglyceride, while Larsson (1972) has illustrated the triple chain length structure in the modified tuning fork (Fig. 2A,B).

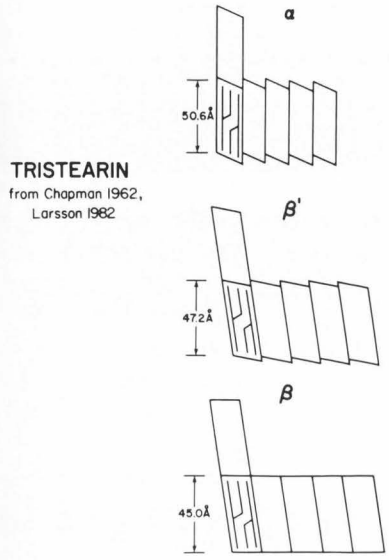



Fig. 1. Diagrams of saturated triglyceride dimers in a crystalline lattice: proposed triglyceride structure for the α form; proposed triglyceride structure for the β' form; proposed triglyceride structure for the β form (Larsson, 1982). Long spacings illustrate the α, β', and β crystals for tristearin (Chapman, 1962).

## Polymorph Classification

Since the discovery of polymorphism, numerous scientists have reported different numbers of polymorphs and conflicting melting points for the various crystalline forms found in cocoa butter. In general, the various nomenclatures assigned to each classification has compounded the problem due to a lack of consistency (Table 2). In 1951, four crystalline forms with

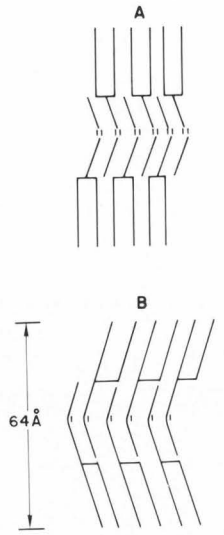



Fig. 2. Illustration of the arrangements of 2-monounsaturated triglycerides: conventional tuning fork packing (A) (Lutton, 1972); modified tuning fork packing (B) (Larsson, 1972).

different melting points were observed and labelled gamma (γ), alpha (α), beta double prime (β"), and (β) (Vaeck, 1951). Nine years later, Vaeck (1960) again examined cocoa butter and concluded four polymorphic forms, but melting points were slightly different, than previously reported. In 1964, a fifth polymorphic form was observed and recorded as β' (Duck, 1964). Two years later, six polymorphic forms were observed; however, the nomenclature denoting the various crystalline forms was changed to Roman numerals (Wille and Lutton, 1966). The most recent work of Lovegren et al. (1976) revealed six polymorphic forms, but in this case the nomenclature was exactly opposite that proposed by Wille and Lutton.

A technique commonly used to thermally analyze the polymorphic crystalline forms of cocoa butter is differential scanning calorimetry (DSC). Huyghebaert and Hendrickx (1971) recorded six polymorphic crystalline forms of cocoa butter using the DSC. A heating rate of 4°C/min with a 2 mcal/sec range produced six endotherms that varied in melting point from 14.9° to 34.9°C. More recent experimentation with the DSC resulted in the reconfirmation of only four polymorphic

Table 2. Classification and temperature (°C) of cocoa butter crystalline forms.

| Vaeck (1951) | Vaeck (1960) | Duck (1964) | Wille & Lutton (1966) | Chapman et al. (1971) | Lovegren et al. (1976) |
|---|---|---|---|---|---|
| γ 18.0 | γ 17 | γ 18.0 | I 17.3 | I | VI 13.0 |
| α 23.5 | α 21-24 | α 23.5 | II 23.3 | II | V 20.0 |
| | | | III 25.5 | III | IV 23.0 |
| β" 28.0 | β' 28 | β" 28.0 | IV 27.5 | IV 25.6 | III 25.0 |
| β 34.5 | β 34-35 | β' 33.0 | V 33.8 | V 30.8 | II 30.0 |
| | | β 34.4 | VI 36.3 | VI 32.2 | I 33.5 |

forms of cocoa butter (Merken and Vaeck, 1980). Therefore Forms V and VI may be phases differing in composition rather than existing as a distinct polymorphic form.

The problem existing by the presents of numerous polymorphic forms is identifying exactly which form or crystallite is desired at the completion of tempering in chocolate production. The ability to clearly define the origin of the desired stable crystal has not yet been resolved. However, the data obtained with X-ray analysis, DSC, dilatometry, and microscopy have increased our understanding of the mechanisms involved in cocoa butter crystallization.

## Tempering

Formulated chocolate is essentially composed of cocoa, sugar, milk solids (milk chocolate), vanillin, and lecithin, all of which are suspended in a crystalline matrix of cocoa butter. Chocolate with crystals in the less stable form has a tendency to be soft and also undergoes crystal transitions which could adversely affect product appearance. In order to ensure that the final chocolate product is in the proper crystalline form a process termed "tempering" is undertaken. Tempering is the controlled formation of a sufficient number of stable seed crystals. The conventional process of tempering involves cooling chocolate from 50°C to 32°C with constant agitation. Once 32°C is reached the temperature is then decreased to 28°C to produce stable cocoa butter seed crystals. After seed formation, the temperature is increased to between 30° and 32°C depending on the chocolate formulation (Kleinert, 1970). The chocolate is poured into molds, vibrated to remove air, and cooled to approximately 16°C. Cooling removes the latent heat of crystallization to ensure the formation of the largest number of small stable crystals. During cooling, contraction occurs which is an indication of proper temper. Exactly which crystal form is desired at the completion of tempering is still speculative. Vaeck (1960) believes that $\beta'$ or $\beta$ crystals are present in the final tempered product, while Wille and Lutton (1966) believe Form V is the crystal desired in the final product.

Fat crystals should be small for visual appearances, but also for texture and mouthfeel reasons (Musser, 1973). Problems may occur during tempering for numerous reasons. The presence of unstable crystals after tempering may cause production problems due to the absence of contraction upon cooling. The amount of stable seed formed and the manner in which the product is cooled has a large effect on product quality. Insufficient cooling may lead to large crystal formations and fat bloom (see below). The addition of foreign fat in confectionery products may affect the tempering procedure and product appearance. For example, addition of milkfat to a milk chocolate requires the reduction of the tempering temperature by approximately 1°C (Koch, 1956). During tempering there should be adequate agitation to assure proper heat transfer between the chocolate product and the cooling medium. Mechanical agitation usually involves a narrow working area which constantly fractures fat crystals which in turn become optimum seed. It is possible to temper cocoa butter through a mechanical process that influences polymorphic transition (Feuge et al., 1962). The procedure consisted of mechanically working triglycerides by extrusion under pressure to physically manipulate the crystals.

## Bloom Formation

The crystalline problem associated with the storage of chocolate is called bloom. Bloom can be of two distinct types, one being sugar bloom and the other fat bloom. Sugar bloom is characterized by a sandy, gritty texture and consists of sugar crystals that have accumulated on the surface of the bar. Fat bloom is a problem that causes the glossy surface of chocolate to become dull and covered with a grey film. This discoloration resembles the bloom on grapes thus it is termed bloom (Cerbulis et al., 1957). It is known that bloom on the surface of chocolate is definitely crystalline in structure (Neville et al., 1950). Whymper (1933) originally proposed that cooling produced an unstable solution in which the individual fat components separate. The higher melting fractions aggregate and separate away from the lower melting fractions thus producing fat bloom. Becker (1958) proposed a theory involving phase diagrams of various cocoa butter components and stated that the fractionation of triglycerides ultimately leads to bloom formation. Vaeck (1960) proposed a theory in which bloom is caused by a transition from an unstable crystal form into the stable form. During this change the crystal volume decreases allowing air to penetrate into the mass producing an opaque reflection. At elevated temperatures the cocoa butter melts and resolidifies into large high melting crystal formations. An example of bloomed and unbloomed chocolate is illustrated in Figure 3.

The crystalline triglycerides present in fat bloom have lower iodine values and higher melting points than those triglycerides dispersed throughout the chocolate mass. The composition of bloomed fat is rich in the triglycerides POS and SOS (Steiner and Bonar, 1961). The polymorphic crystalline form of bloomed fat is thought to be $\beta$. In most cases the crystals present after tempering are believed to be $\beta'$ (Giddey and Clerc, 1961). Jewell (1972) indicated that bloom formation is not solely a surface phenomena, but can be found permeating throughout the chocolate mass.

Most investigations aimed at preventing fat bloom employed food additives. The addition of butterfat or a mixture of sorbitan monostearate 60 and polysorbate 60 has been used extensively in the past to control fat bloom (Musser, 1980). Milkfat was thought to be a good selection because it is already used in the manufacture of milk chocolate. Campbell et al. (1969) reported bloom inhibition two to four times longer with the addition of 2.5% hydrogenated milkfat as compared to an equal addition of unhydrogenated milkfat.

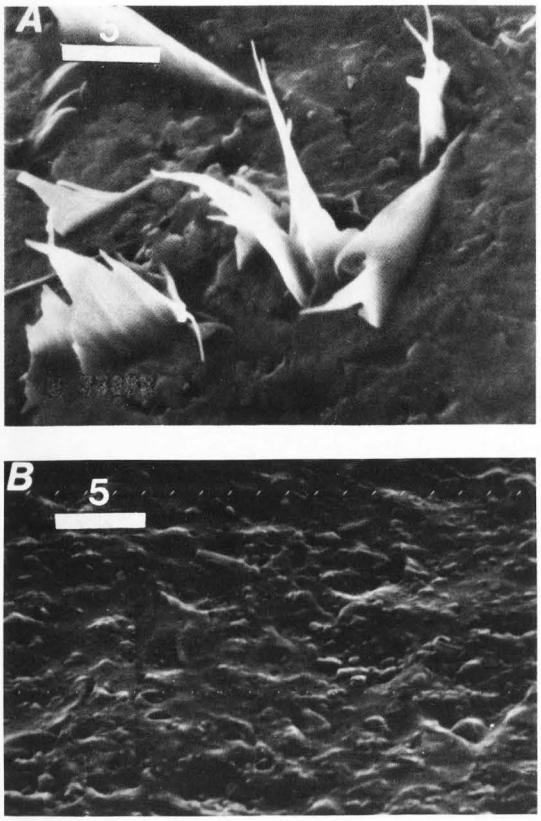



Fig. 3. SEM surface view of bloomed (A) and properly tempered (B) semi-sweet dark chocolate. **Scale bars in μm for all figures.**

The bloom problem is very complex and the cause may be a combination of factors instead of one single factor. Above all, the formation of bloom is affected by the way in which the chocolate is handled in the factory and in the marketplace.

## Polarized Light and Scanning Electron Microscopy Studies

The primary objectives of this section are to discuss the use of polarized light microscopy (PLM) and scanning electron microscopy (SEM) to characterize the crystalline structures of cocoa butter. Ivory Coast cocoa butter was utilized for these studies and had been isolated using the following processing conditions: 218°C air temperature of roaster; 36°C temperature of beans out of roaster; 82°C liquor temperature; 96°C liquor temperature filling presser; 71°C #1 press; 67°C #2 express cocoa butter temperature.

Microscopic techniques employed included the use of the Bristoline Bristolscope that utilizes polarized light. In conjunction with the polarized light microscope, a Leitz temperature variation stage was used to control the sample temperature. Along with polarized light microscopy (PLM), the International Scientific Instruments (ISI) Model-60 scanning electron microscope (SEM) was used in the comparative study.

For polarized light and scanning electron

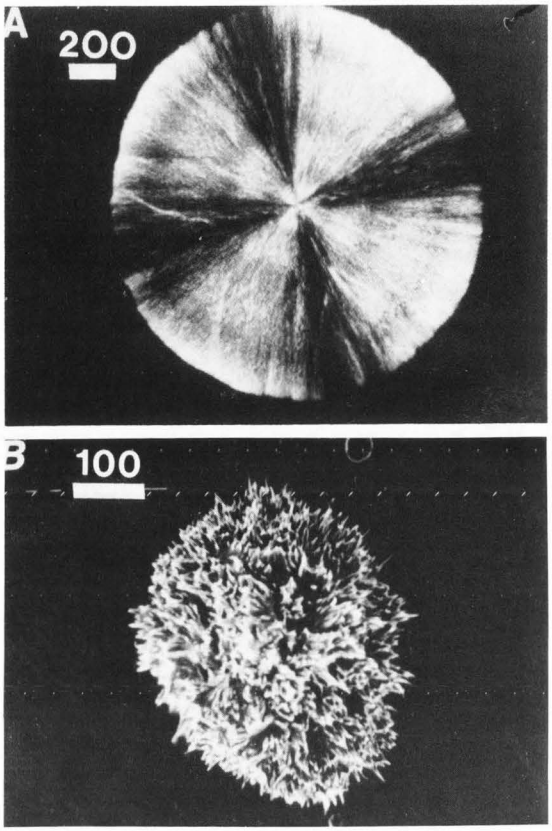



Fig. 4. Cross-sectional view of a 30°C cocoa butter crystal utilizing polarized light microscopy (A); and a micrograph of a similar 30°C crystal visualized by scanning electron microscopy (B).

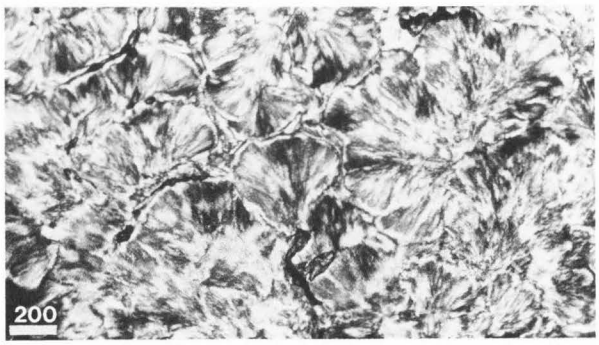



Fig. 5. Polarized light pattern produced after compressing numerous free growing cocoa butter crystals.

microscopy, cocoa butter was heated to 60°C for at least 6 hr. The aliquots for PLM were removed from the liquid butter and placed on glass slides equilibrated to the preset incubation temperature. A cover slip was placed on the sample and the slides were incubated at prescribed temperatures in a Precision Scientific Model 808, a Shel-Lab Model 35960-054, and a Precision Scientific Freas 815. For SEM, the stubs were

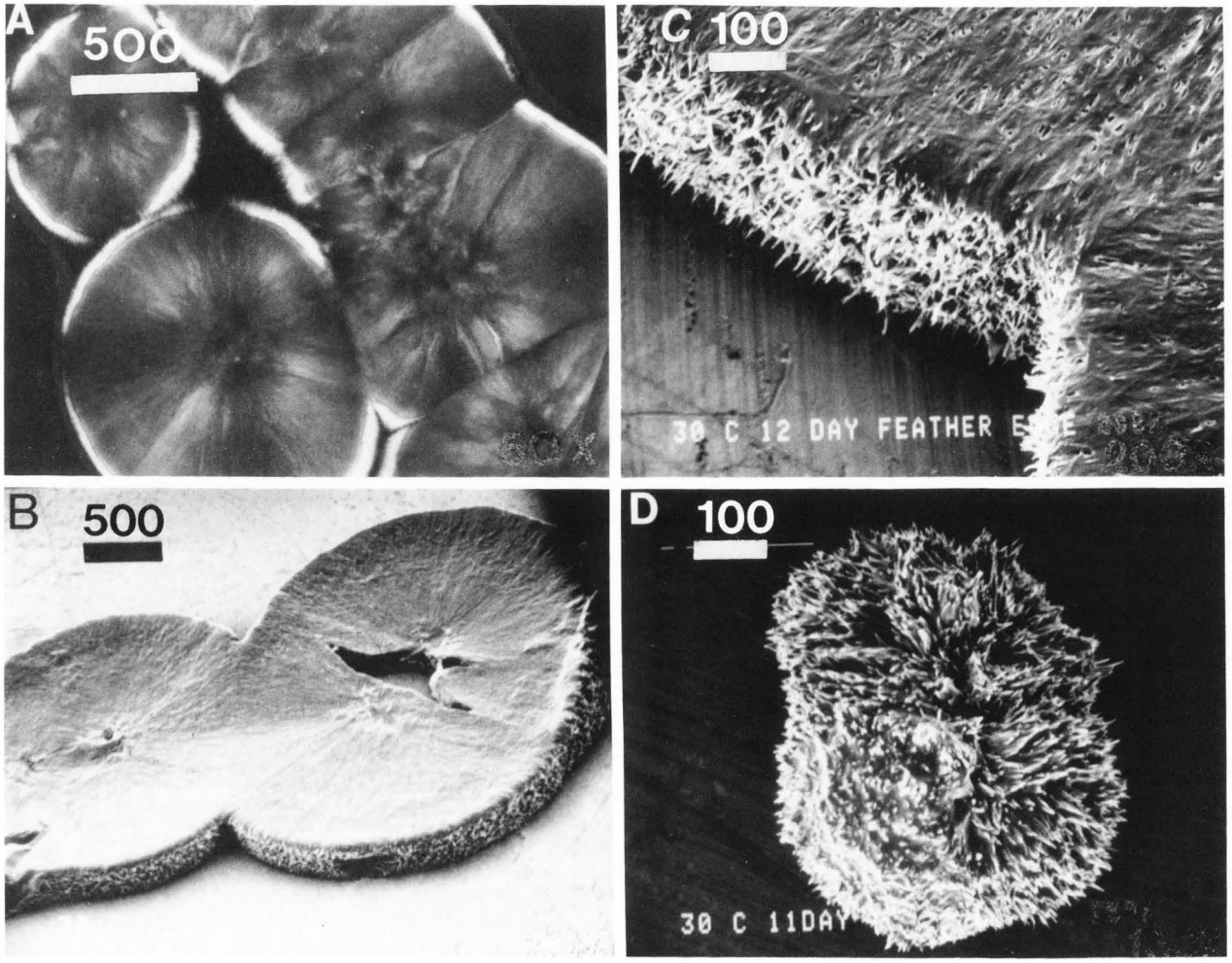



Fig. 6. Cross-sectional view of thick cocoa butter crystals utilizing polarized light (A); identical crystals from (A) viewed by SEM (B); SEM enlargement of peripheral edge of crystal (C) and SEM of free growing crystal (D).

tempered to the desired incubation temperature and approximately 50µl cocoa butter were placed on the stub surface. A blank stub was placed against the sample stub, rotated, and then removed. This action produced a thin film of cocoa butter on each stub, thus, upon crystallization small groups of crystals or even individual crystals could be visualized with the SEM. After incubation, the stubs were placed in the ISI PS-2 coating unit, cooled for 5 min at approximately 0-5°C and then gold coated (280Å) at 1.4 kV, and 10 mA for 4 min. Cooling conditions in the present studies did not alter the original crystals formed during incubation. The stubs were then placed in the SEM and viewed at an accelerating voltage of 10 kV and working distance of 8 mm.

The procedure to determine crystalline melting points utilized the Brabender Pressure Circulator, Leitz stage, and the Bristoline Bristolscope. The pressure circulator pumped temperature-controlled water through a network in the Leitz stage, thus maintaining a specific constant stage temperature. Prior to determining melting points the Leitz stage was allowed to equilibrate at the predetermined temperature for 15 min. After stage equilibration a sample was removed from the incubator after approximately 2 wk and placed directly upon the stage. The melt was then viewed with the PLM. This method was used rather than an increasing temperature-time gradient due to the fact that crystalline transition could occur making melting point data less precise.

The photographs obtained from each of the two microscopic methods demonstrate a dramatic difference in visual appearance of cocoa butter crystals. The PLM photographs represent a cross-sectional or internal structure view (Fig. 4A) while in SEM a surface reflection view resulted (Fig. 4B). When cocoa butter was placed on a slide with a cover slip and incubated, crystal growth was physically restricted, but without a cover slip crystals grew multidirectionally. To substantiate this physical phenomenon a free growing crystal was compressed to reveal the smooth feather-like internal structure (Fig. 5) which correlated well with Fig. 4A. When viewing thick crystals with polarized light the centers

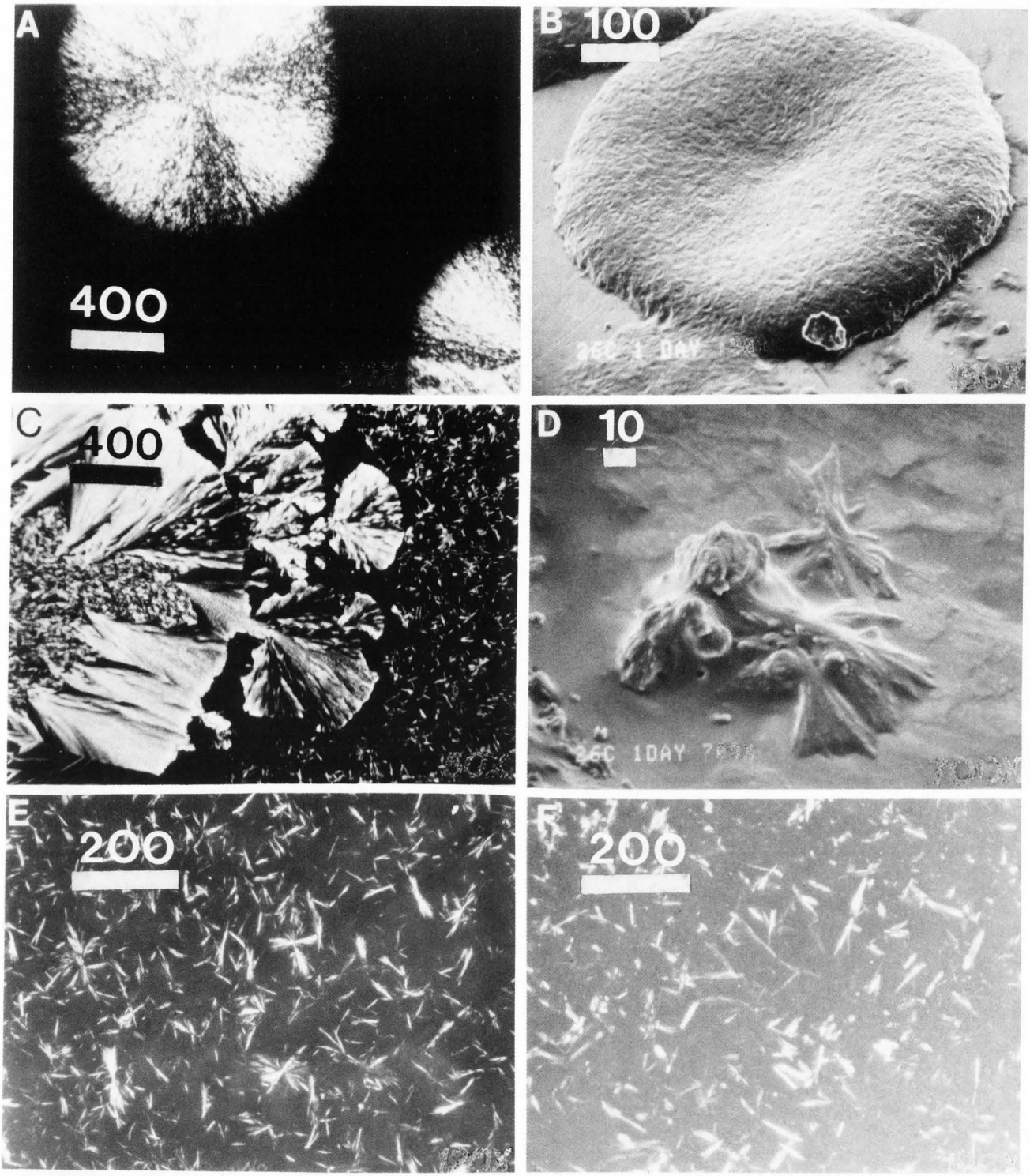



Fig. 7. At 26°C the tempered (mesh) crystal is observed utilizing PLM (A); a similar tempered crystal viewed with SEM (B); PLM of 'feather' crystals with 'individual' crystals on right (C); individual crystals viewed by SEM (D); individual crystals viewed by PLM (E) and 'opaque blade'crystals by PLM (F).

Scale bars in μm for all figures.

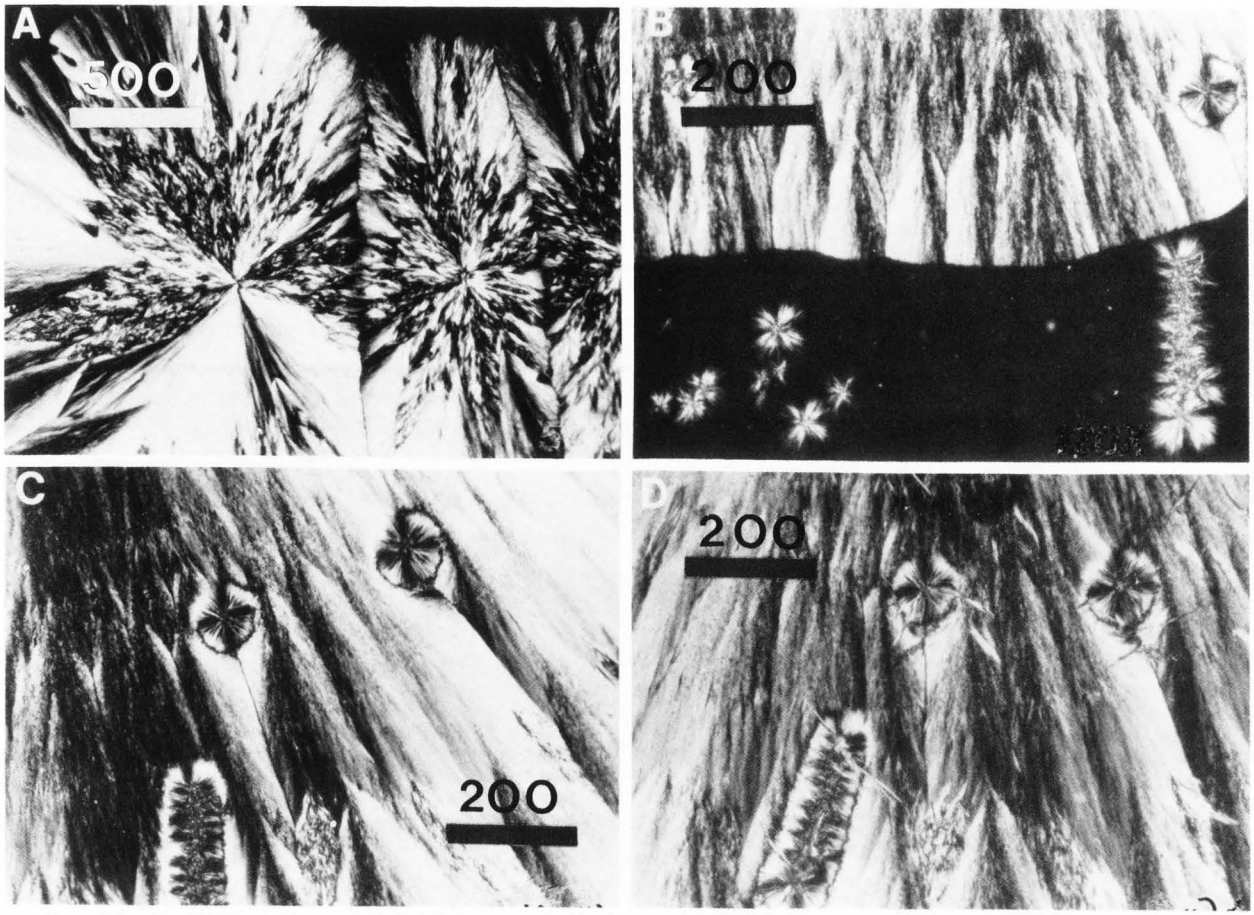


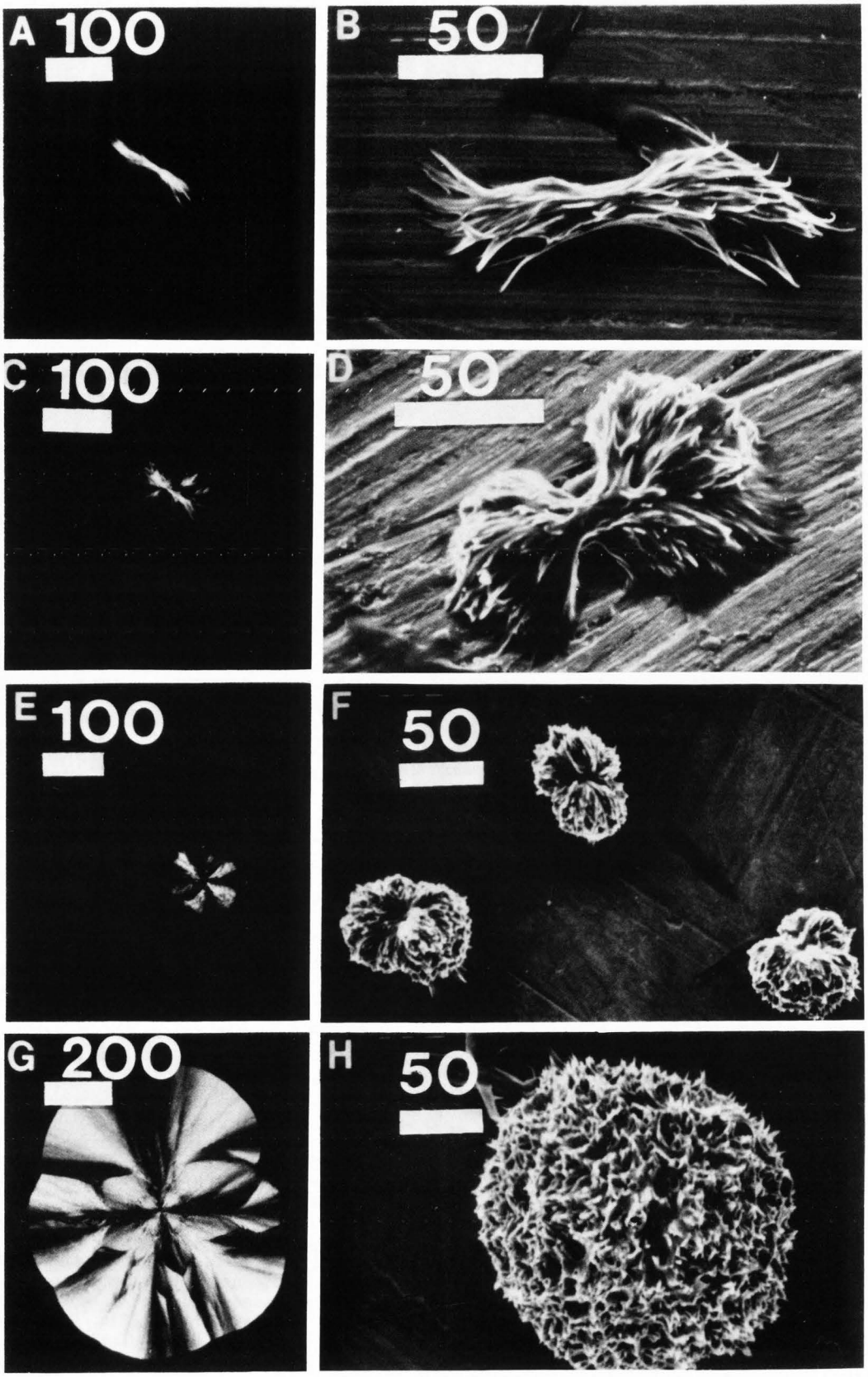

Fig. 8. Cross-sectional view of the 'ordered' (tempered) central area of a 28°C crystal with the predominant feather occurring on the periphery (A); 'feather' crystal growth engulfing the smaller 'spiney' crystals (B,C) and 'needle' type crystals forming in 'spiney' crystal matrix (D).

appeared dark due to less light transmittance while the periphery appeared lighter (Fig. 6A). The same crystals were then removed from the slide and placed on a SEM stub, gold coated, and viewed (Fig. 6B). Upon close examination an irregular peripheral edge (Fig. 6C) was visible which closely resembles the surface seen with the SEM surface reflection view of an unrestricted crystal (Fig. 6D). This was evidence that the two visualizations observed by different techniques were truly the same crystal structure. It was evident that the PLM technique visualized a cross-sectioned view of the crystal while the SEM micrographs visualize the actual unrestricted free growing crystal.

Crystal formation temperatures were pre-established and ranged from 26° to 34°C. In order to follow the natural order of transition from the less stable to the more stable form, the 26°C crystals will be discussed first. The first sign of crystal growth during incubation at 26°C occurred after approximately 2 hr. At 3 hr a non-distinct crystalline mesh was observed in areas throughout the liquid sample. At first this mesh lacks any obvious crystalline form, but as time elapsed a few circular forms begin to show a rosette pattern (Fig. 7A) and a uniform round shape as illustrated by SEM (Fig. 7B). After this center crystalline mesh has formed there appears on the periphery distinct 'feather' crystal growth (Fig. 7C). Also, during the same time interval, other smaller yet distinct crystals were observed (PLM) throughout the sample (Fig. 7C) and also by SEM in Figure 7D. As the 26°C crystals mature after 2 to 3 days there were two major distinct crystalline changes. The most dominant was the extension of 'feather' crystalline form (Fig. 7C) and, with time, these crystals predominated throughout the sample.

The less common crystallization change at 26°C involved the small 'individual' crystals in proximity with the feather type. In this case, if there was no visible growth in 'feather' crystals at 26°C, the smaller 'individual' crystals did not melt and thus did not contribute to the larger 'feather' structure. As time evolves these 'individual' crystals visualized with SEM (Fig. 7D) and PLM (Fig. 7E) slowly melted within approximately 30 days and another less distinct crystal type developed which was blade-like in appearance (Fig. 7F). In most

Fig. 9. PLM micrographs of the stepwise crystal growth from the 'bow-tie' seed to the 'feather' crystals (A,C,E,G,); the stepwise crystal growth visualized by SEM (B,D,F,H).


A 100
B 50
C 100
D 50
E 100
F 50
G 200
H 50

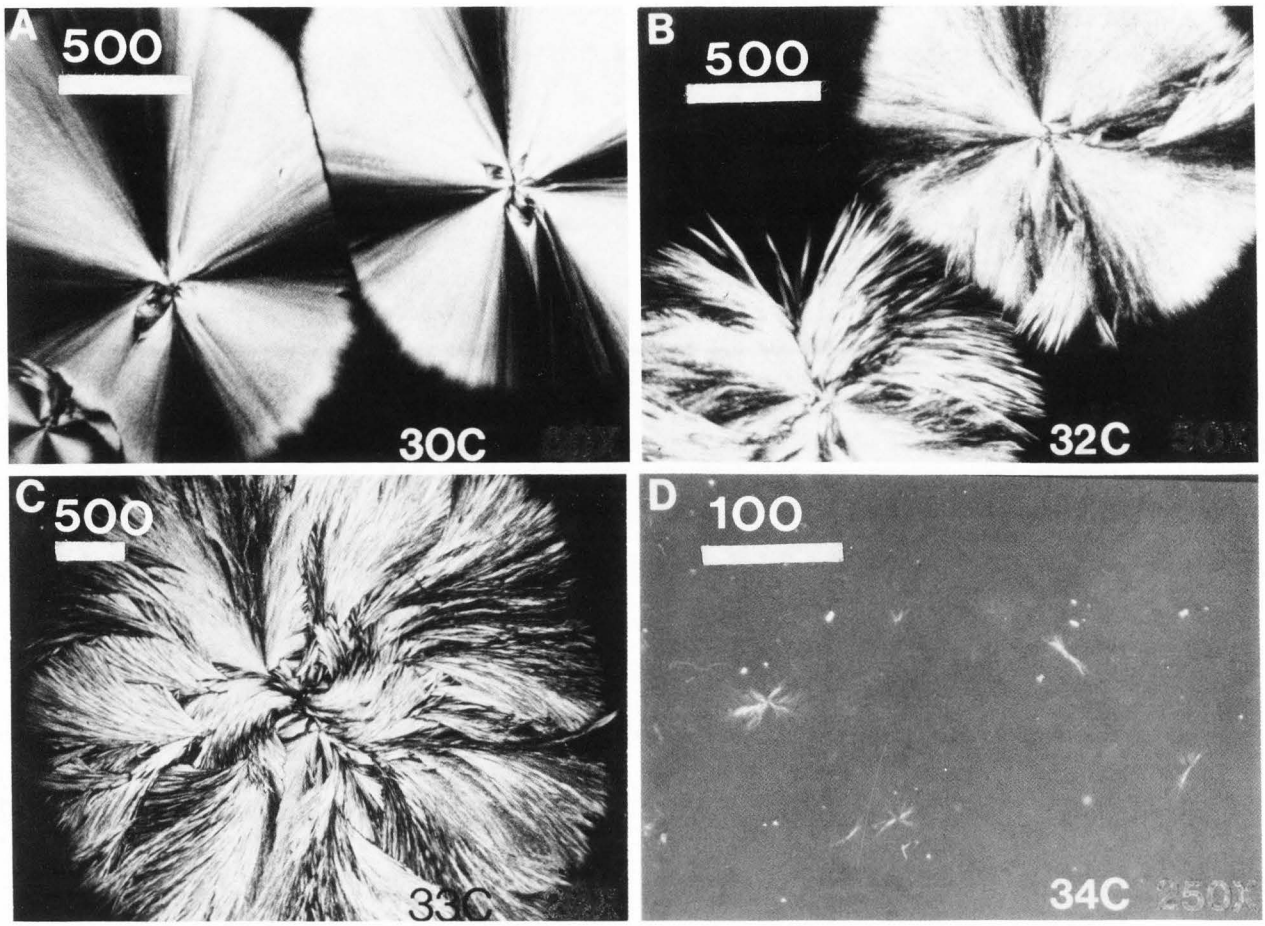



Fig. 10. PLM micrographs of cocoa butter crystals formed at 30°C (A); 32°C (B); 33°C (C) and 34°C (D).

cases these 'blade' crystals had a life of at least 60 days when the temperature was held constant at 26°C. Usually with extended time these crystals were engulfed by and blend with the 'feather' crystals thus losing their identity. However, there were instances when the opaque blades were not obscured by the 'feather' crystals. At this time a possible transition occurred from the 'opaque blade' to the slender 'needle' crystal (Fig. 7F).

At 28°C the crystalline 'mesh' was first observed, however, this area was more ordered in its appearance than that observed at 26°C. The difference between the mesh area of the two crystals was that at the higher temperature (28°C) the crystalline form appeared more feather-like in structure. After approximately 2-3 days the 'feather' crystal predominated and continued growing in this form (Fig. 8A). Concurrent with 'feather' crystal growth, smaller crystalline forms were developing. These crystalline forms were stable in that they were not melted during the growth of the large 'feather' crystal (Fig. 8B). Eventually these smaller crystals were entrapped by the 'feather' crystal networks (Fig. 8C). It is speculated that at 28°C the heat of crystallization was insufficient to melt these smaller 'spiney' crystals, thus it is thought that they have greater stability than the 'individual' crystal observed at 26°C. As time elapsed at 28°C the 'feather' crystals enlarged and spread as long as there was liquid cocoa butter available to supply the growing crystals. The small entrapped crystals remained intact within the 'feather' crystal structure but after approximately 3-4 wk these small crystals underwent a transition to a form characterized by slender 'needle' projections that occurred singly or in orderly bunches (Fig. 8D). It appeared this transition occurred more rapidly when the small 'spiney' rosettes are engulfed within the 'feather' crystals.

At the 30°C incubation a dramatic change was visualized in the initial crystal form. Crystallization first occurred (3-4 hr) in the form of a 'bow-tie' shape (Fig. 9A,B). The term 'bow-tie' is descriptive in that it depicts the crystal form that has a constriction in the center from which crystal growth fans out in opposite directions. As time passes (5-6 hr) the 'bow-tie' form enlarged primarily in the distal areas while the medial or central area of the crystal remained in a constricted form (Fig. 9C,D). As time progressed the crystals spread and began to show a circular pattern (Fig. 9E,F) and eventually became smooth and had a distinct rigid pattern which is characteristic of 30°C crystals (Fig. 9G,H).

As the temperature was increased above 30°C, PLM was utilized more extensively due to a decrease in the amount of actual crystal formation and growth (Fig. 10A). At the temperature of 32°C the crystals viewed were similar to those found at 30°C except they tended to be more irregular from the onset of crystallization (Fig. 10B). When the temperature was increased to 33°C the crystal was predominately the 'irregular' form. As pointed out previously, these higher melting point crystals originally formed from a 'bow-tie' like seed crystal. In the center of the 33°C crystal a 'bow-tie' configuration was readily visible (Fig. 10C). At a temperature of 34°C the only crystals produced were very similar to the'bow-tie' form. This trend indicated that the 'bow-tie' may act as a seed for 'feather crystal' formation. The fact that the 'bow-tie' crystals were formed in a short incubation time (4 hr) and were also present at extremely high temperatures indicated that they may be composed of more saturated triglycerides. Fatty acid and glyceride composition data were needed to fully characterize crystal structure and behavior.

Crystal melting points are related to their formation temperature in that basically the higher the temperature of formation the higher the melting point range. The results obtained by past investigators state only two or maybe three polymorphic forms with melting points above 28°C. The results presented here show numerous crystals with melting points at 28°C and above (Table 3). The lowest melting point crystals observed were the 'individual' crystals formed at 26°C. A low melting point (29°C) gives the crystals poor stability compared to the other crystals. The life of this crystal was approximately 30 days. All other crystals formed in this study melted between 32-39°C. The 'tempered' crystals which form first at 26°C possessed a melting point at 33°C. The 'feather' crystals commonly form on the edges of the 'tempered' crystals and these crystals have been implicated in bloom formation. These crystals being the most common high melting point crystals can produce a white circular pattern common in untempered or heavily bloomed chocolate. The last high melting point crystals formed at 26°C are the 'opaque blade' crystals which formed after approximately 20 days of incubation. The 'opaque blades' were not as common as the 'feather' crystals but also may be a cause of bloom formation due to its 'blade' appearance. The 'opaque blade' has a melting point of approximately 34-36°C.

During crystal formation at 28°C the inner 'ordered' area which corresponds to the 'tempered' crystal area observed at 26°C temperature has a melting point between 33-36°C. Again the 'feather' crystals formed at the edges of the inner 'ordered' area and predominate during further crystallization. Also the 'feather' crystals produced at 28°C have slightly higher melting points than those formed at 26°C. This was thought to be due to the increased energy input (heat) which allows the triglycerides to align themselves in a more stable manner. The third crystal observed at 28°C was the 'spiney' crystal which has a high melting point of 37-38°C. At 30°C, the 'feather' crystals have a melting point of 33-36.5°C while the 'spiney' crystals

Table 3
Melting points of cocoa butter crystal forms.

| Formation temperature (°C) | Crystal description[a] | Melting point range (°C) |
|---|---|---|
| 26 | Individual | 28-29 |
| | Mesh (tempered) | 32-34 |
| | Feather | 32-34.5 |
| | Blade | 34-36 |
| 28 | Ordered (tempered) | 33-36 |
| | Feather | 33-36 |
| | Spiney | 37-38 |
| | Needle | 36-37 |
| 30 | Feather | 33-36.5 |
| | Spiney | 37-39 |
| 32 | Irregular | 35-37.5 |
| | Spiney | > 40 |

[a]Descriptive term established by authors to denote the various crystals (See text).

melt at 37-39°C. The 32°C crystals melted at 35.0-37.5°C whereas the small 'spiney' crystals melted at a temperature greater than 40°C.

Based on these data, the melting points of the numerous crystals found would fall in the β and β' form classification. One must realize then that the polymorphic forms are very diverse in visual structure and crystal appearance.

An investigation of crystallization in cocoa butter compared with that of semi-sweet dark chocolate was undertaken. The chocolate was incubated under the same conditions as the pure cocoa butter and examined by SEM. The crystals appeared very similar to those found in pure cocoa butter (Fig. 11).

The changes during cocoa butter crystallization are subtle and variable. A one-degree change in incubation temperature can permanently alter crystal formation. Also the consistency of crystallization with time is variable in that one sample may solidify in 3 days while an identically handled sample may take 3 wk. The procedures and methods undertaken in this investigation have shown trends in overall crystalline change. In the past most literature dealing with cocoa butter crystallization was based solely on melting point characteristics. Melting points of particular crystals are important but just as significant are the formation temperatures these crystals require. By controlling the temperatures which crystals form we can indirectly control their melting points along with other important characteristics.

## Thermal and Compositional Properties During Dynamic Crystallization

Ivory Coast cocoa butter and a semi-sweet chocolate were utilized in these crystallization studies. A Brabender viscometer and pressure circulator were used to induce and control crystallization. All samples were heated to 60°C for 6 h prior to experimentation to assure that all crystal structures were liquified. After

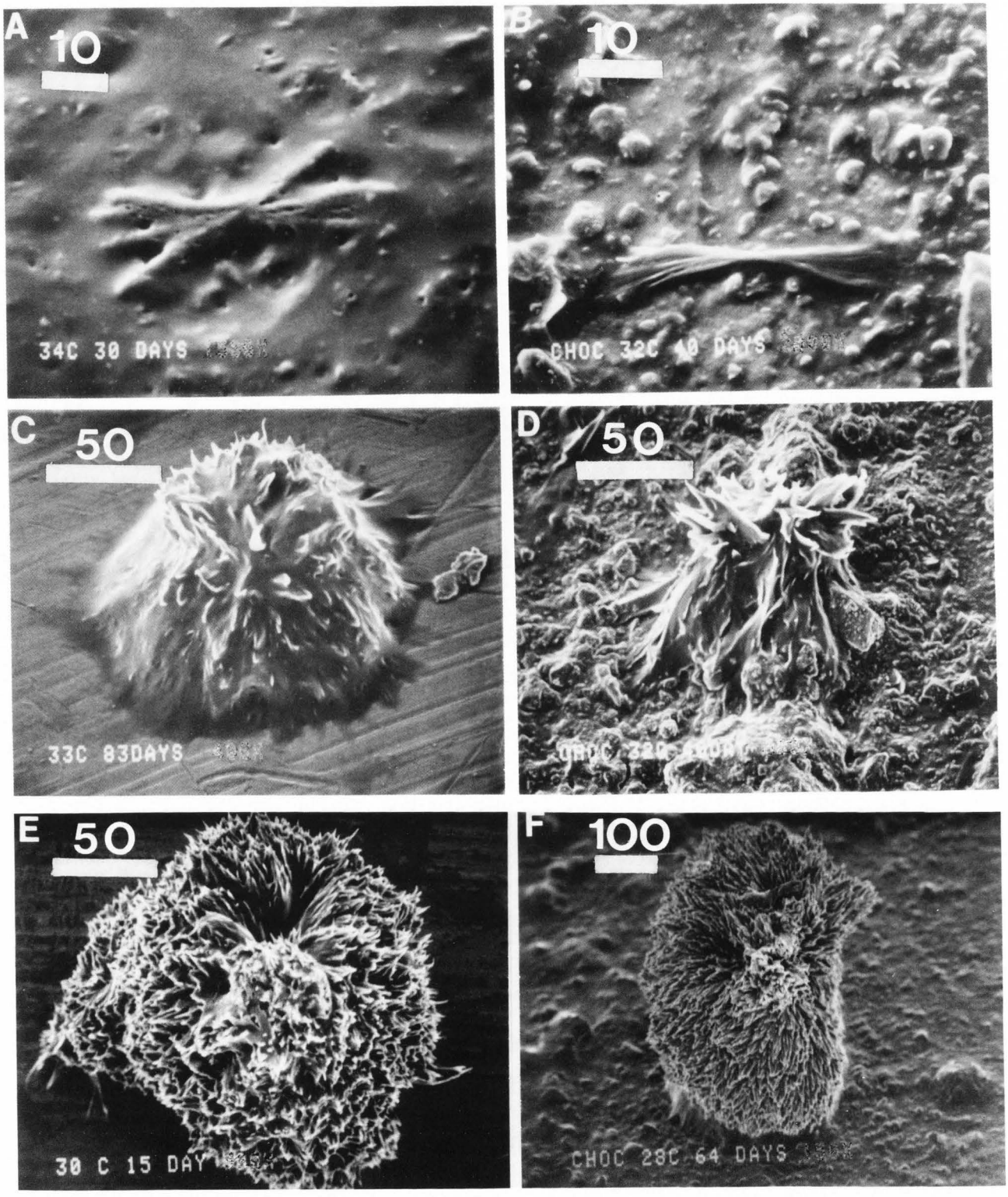



Fig. 11. SEM micrographs of Ivory Coast cocoa butter (A,C,E,) and semi-sweet dark chocolate (B,D,F).

Scale bars in μm for all figures.

heating, 50 g Celite was slowly added to the Brabender cup (45 rpm) which contained 165 g cocoa butter. The Celite addition to the butter produced a crystallization in a shorter period of time when compared to pure cocoa butter. The temperature cycles evaluated were 32.5° - 28.0° - 32.5°C and 32.5° - 30.0° - 32.5°C for both the cocoa butter and chocolate tempering studies. Samples were removed for analysis based on Brabender viscosity readings. Discussion of all the data would be rather lengthy, therefore only two trials will be discussed. A complete treatment of these data can be found elsewhere (Manning, 1984).

A Perkin Elmer DSC-2 was used to monitor crystalline melting points. A small spatula was used to obtain and transfer samples from the revolving Brabender cup to the DSC sample pan. Once the sample was in the pan, a lid was immediately placed on the sample to gently spread it over the bottom of the pan. The pan was immediately placed in the calorimeter for sample assay at 20°C/min over a temperature range of 15° to 45°C. Parameters used to characterize the thermal analysis of cocoa butter using DSC have been reported (Manning and Dimick, 1983).

It was found that the small cocoa butter crystals forming during tempering in the cup could not be isolated and analyzed, thus a method was developed to separate the liquid butter from the solid crystalline butter. At various viscosity levels, a 5 ml sample was removed from the Brabender cup and immediately placed into a filtering centrifuge tube (Fig. 12) which was in a temperature controlled Sorval GLC-1 centrifuge.


Fig. 12. Diagram of the centrifuge tube used to separate the liquid from the crystalline cocoa butter.

The cocoa butter-Celite samples were centrifuged at 800 rpm (107 x g) for 55s to separate a small amount of liquid cocoa butter from the crystalline slurry. The temperature of the centrifuge was held at the same temperature as the sample. The semi-sweet chocolate was handled in a similar manner except centrifugation was at 1000 rpm (168 x g) for 75s. The liquid filtrates from the cocoa butter-Celite and semi-sweet chocolate trials were solubilized in chloroform and filtered with a 0.45 Millipore type HA filter.

Triglyceride determinations were conducted using a Waters Associates HPLC pump and a Waters differential refractometer (Model 401). An acetonitrile-chloroform 6:4 (v/v) mobile phase was pumped at 0.7 ml/min through an Alltech Associates C-18, 5μm reversed phase column. The column was 25 cm in length with an internal diameter of 4.6 mm. Commercial triglycerides (Supelco, Inc.) POO, SOO, POP, POS and SOS were used as qualitative and quantitative standards. Triglycerides for which standards were not available (PLiP, SLiS, and SOA, where Li = linoleic acid and A = arachidic acid) were identified by retention volume data and also by interpreting chromatographic data from Shuklu et al. (1983). In order to determine the weight percent of PLiP, PLiS, SLiS, and SOA in each sample, the standard with the closest retention time was used.

Figure 13 illustrates a pure cocoa butter Brabender viscosity curve and the times when samples were removed and placed on a 16°C sample head for thermal assay. At 26°C, 2 h elapsed before crystals could be observed in the sample cup. After initial seed formation, a high rate of crystallization was observed as evident by a sharp increase in viscosity. Following this initial crystallization at 26°C, the resulting crystals exhibited a 30.8°C melting point. When the viscosity began to increase rapidly, the temperature of the butter was increased to 32.5°C to prevent solidification of the entire mass. After this temperature increase, a shift in the melting point of the crystals was observed. The melting point gradually increased after 7 min at 32°C and two endotherms were recorded on the thermogram. The melting point continued to increase to approximately 34°C and endotherms representing two crystal types were clearly evident in the last three samplings (Fig. 13C,D,E).

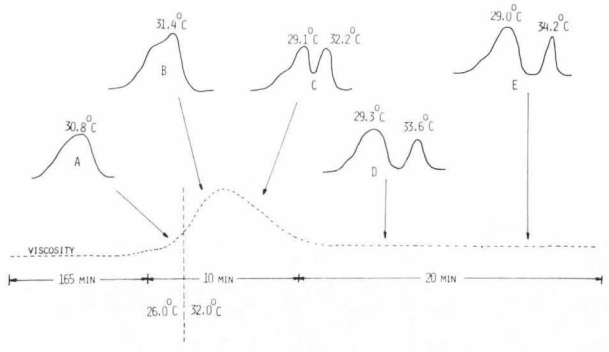



Fig. 13. An illustration of dynamic crystallization of cocoa butter occurring over time with changes in temperature.

Interestingly, the lower melting point endotherm (≅29°C) was not originally present in the Brabender cup and was an artifact as a result of the procedure. It must be remembered that the sample removed from the Brabender cup was a mixture of liquid and crystalline cocoa butter and the 29°C crystals originated from the liquid portion. To demonstrate this, and to prove that liquid cocoa butter was solidifying on the DSC head, a sample was rapidly cooled to 5°C to solidify the liquid fraction into low melting, unstable polymorphs. When the sample reached the temperature range at which the 29°C melting point crystal could form, an exotherm was observed indicating that the heat of crystallization was being released. An exotherm prior to the formation of the 29.3°C endotherm signaled that crystallization was occurring on the DSC sample head and was not representative of the original solid butter crystals in the Brabender cup (Manning and Dimick, 1983).

Semi-sweet chocolate also was studied with the Brabender viscometer and DSC to study cocoa butter seed formation in a formulated product. The viscosity of chocolate was much greater than pure cocoa butter due to the solids present. Small changes in crystallinity of the cocoa butter in chocolate produced large fluctuations in viscosity which were easily monitored. Seed formation in semi-sweet chocolate during a 32.5°C - 28.0°C - 32.5°C tempering cycle was a slow gradual process. After approximately 100 min at 28.0°C, seed formation commenced resulting in a small amount of 33.8°C melting point crystal (Fig. 14A). After approximately 135 min at 28.0°C, the stable seed concentration increased slightly which helped to form low melting point crystals when the liquid and solid sample was momentarily cooled to 15°C on the DSC head prior to analysis (Fig. 14B). After 165 min at 28.0°C, the viscosity began to increase rapidly due to increased amounts of crystals being formed from the stable seed. Figure 14C illustrates an increase in the amount of crystals present in the Brabender cup and also a decrease in overall melting point at 32.4°C. The dashed endotherm in Figure 14C illustrates the stable seed superimposed under the newly formed less stable 32.4°C crystal.

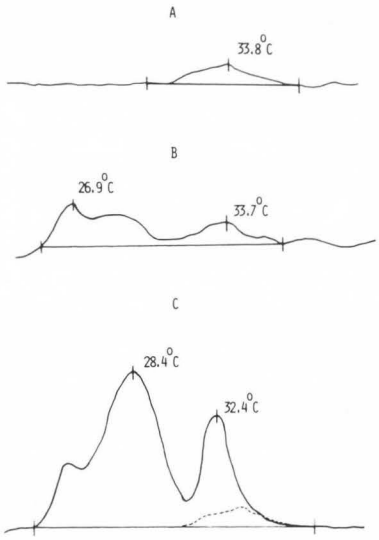



Fig. 14. DSC endotherm of the initial high melting point seed semi-sweet chocolate formed at 28.0°C (A); melting curve of the unstable crystals forming during cooling on the DSC sample head and the 33.7°C melting point seed (B); illustration of the less stable 32.4°C crystal that crystallized from the high melting point seed which is present -- but hidden under the large endotherm (C).

Throughout these dynamic studies, crystals of differing stability formed in varying amounts depending on the tempering cycle used. To determine the influence the different triglyceride types exert throughout the dynamic crystallization process, triglyceride analyses were performed during two different temperature cycles. Figures 15 and 16 represent typical cocoa butter-Celite viscosity curves for 32.5° - 28.0° - 32.5°C and 32.5° - 30.0° - 32.5°C tempering cycles. Samples were removed from the cup at three different times during agitation. Sample 1 was removed after a 40 BU viscosity increase to determine the triglyceride composition of the initial seed formed during both the 28° and 30°C tempering cycles. In the 32.5° - 28.0° - 32.5°C cycle, samples 2 and 3 were collected in duplicate from the Brabender cup.

Each sample drawn during the two temperature cycle experiments demonstrated a decrease in the concentration of SOS triglycerides in liquid cocoa butter filtrate. For example, the weight percent of SOS in the liquid cocoa butter filtrate of a 32.5° - 28.0° - 32.5°C tempering cycle decreased from 28.8% to 21.5% (Fig. 15). This decrease in SOS in the liquid butter signaled that these triglycerides were crystallizing and not passing through the filtering centrifuge in the liquid filtrate. The decrease in SOS glycerides in the liquid resulted in the concurrent increase in the solid crystals at all sampling times. Thus, since the viscosity increased after each cycle it appeared that the SOS-rich fraction was instrumental in the crystallization process. The triglyceride POS did not exhibit a consistent trend with regard to concentration during any of the temperature cycles. It is believed that since POS remained at approximately 46% of the total glycerides and did not consistently increase in percent composition in the liquid filtrate, it must have contributed to the solid fraction to some extent. For both tempering cycles large decreases in SOS in the liquid butter resulted in proportional increases in POO, PLiS, SOO, and POP indicated they were not crystallizing. For example, SOO increased from 3.4% to 4.7% in the liquid filtrate after two 32.5° - 28.9° - 32.5°C tempering cycles. The triglycerides SLiS and PLiP (not included in figures) were excluded from the crystalline structure because their percentage in the liquid increased after each sample was removed from the cup. Similar triglyceride trends were observed in the 32.5° - 30.0° - 32.5°C tempering cycle (Fig. 16).

COCOA BUTTER-CELITE, TEMPERATURE CYCLE 32.5° - 28.0° - 32.5°C, 2.3°C/MIN

| FRACTION COLLECTED | TRIGLYCERIDE TYPES | | | | | |
|---|---|---|---|---|---|---|
| | POO | PLiS | SOO | POP | POS | SOS |
| PURE BUTTER | 1.7A | 2.5A | 3.4A | 14.8A | 45.5A | 28.8A |
| SAMPLE 1 | 2.3B | 2.9B | 3.7A | 15.2A | 45.4A | 26.6B |
| SAMPLE 2 | 2.3B | 3.0B | 4.4B | 16.7B | 45.8A | 23.3C |
| SAMPLE 3 | 2.8C | 3.6C | 4.7B | 17.2B | 45.5A | 21.5D |

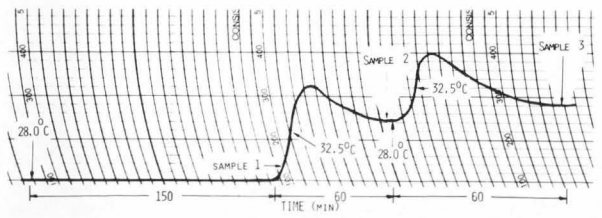



Fig. 15. Illustration of a 32.5° - 28.0° - 32.5°C tempering cycle for cocoa butter with the triglyceride analysis of samples 1, 2, and 3. (Means in a column with the same capital letter are not significantly different at the 0.05 alpha level).

COCOA BUTTER-CELITE, TEMPERATURE CYCLE 32.5° - 30.0° - 32.5°C, 2.3°C/MIN

| FRACTION COLLECTED | TRIGLYCERIDE TYPES | | | | | |
|---|---|---|---|---|---|---|
| | POO | PLiS | SOO | POP | POS | SOS |
| PURE BUTTER | 1.7A | 2.5A | 3.4A | 14.8A | 45.5A | 28.8A |
| SAMPLE 1 | 2.2B | 3.3B | 4.1B | 15.7B | 44.0A | 26.1B |
| SAMPLE 2 | 2.8C | 3.8C | 4.3B | 17.2C | 45.6A | 21.9C |
| SAMPLE 3 | 2.9C | 3.7BC | 4.9C | 17.7C | 45.9A | 20.7D |

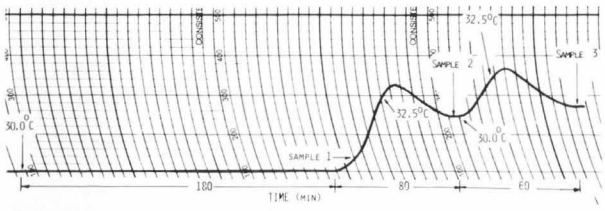



Fig. 16. Illustration of a 32.5° - 30.0° - 32.5°C tempering cycle for cocoa butter with the triglyceride analysis of samples 1, 2, and 3. (Means in a column with the same capital letter are not significantly different at the 0.05 alpha level).

## Summary

Techniques were developed using SEM, PLM, DSC, and HPLC to study the crystalline, thermal and compositional properties of cocoa butter crystals. The initial crystal formed during tempering exhibited the properties of a high-melting-point seed. The stability of the seed increased as the formation temperature in the cycle increased from 26.0° to 30.0°C. The composition of the seed was not positively identified, however it is believed to be an SOS-rich fraction. The stable seed acted as a surface for further crystallization to continue. After a rapid viscosity increase, the temperature was increased and the viscosity decreased as the crystals partially melt and anneal. Throughout the temperature increase and afterwards, the crystals annealed and exhibited higher melting points. During the tempering cycle, the triglyceride POS is partially excluded from the crystalline structure, whereas POP and other liquid triglycerides are excluded to a greater degree. The resulting crystal formed after the temperature cycle is composed of a high percentage of SOS and lesser amounts of POS.

This dynamic study is applicable in understanding the thermal and compositional trends occurring during tempering. These studies could be continued using different formation and final temperatures. Furthermore, a study defining the properties of crystals formed upon cooling after tempering would be beneficial in understanding the total solidification process.

## Acknowledgements

The authors wish to thank Dr. Ian R. Harrison for the use of the DSC facilities of the Polymer Science Program. This work was supported in part by the Pennsylvania Manufacturing Confectioners' Association. Authorized for publication as Paper No. 7090 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

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## Discussion with Reviewers

G.G. Jewell: Do you consider that the morphologies observed in a static system occur during dynamic crystallization?
Authors: No, we would not venture to say that. However, one could speculate that the 'feather' crystal seed ('bow-tie') or the 'feather' crystal itself is closely related to the seed formed during tempering. The morphological characteristics would not carry over, however, the compositional and thermal characteristics may be similar. The crystals formed during dynamic crystallization are extremely small while those formed during static crystallization are very large. The 'feather' crystals and those crystals formed during dynamic crystallization have compositions containing largely SOS and POS triglycerides.

G.G. Jewell: Did the centrifugation process produce a consistent separation of seed from the liquid? What percentage of liquid, if any, remained with the solid?
Authors: Centrifugation was carried out very rapidly. Approximately 3 seconds elapsed from the point of sampling to centrifuge start up. The temperature controlled centrifuge system was energized for a minimal preset time for each run. The cocoa butter - celite system was centrifuged 55 seconds while the dark chocolate filtrate samples were collected after 75 seconds. The amount of liquid butter collected was low to minimize the effect of crystallization after sampling. Thus, liquid still remained with the solid. It was not quantified. The data presented in the thesis "Thermal and Compositional Properties of Cocoa Butter during Static and Dynamic Crystallization" (1984) D.M. Manning, The Pennsylvania State University, exhibit compositional and viscosity differences based on formation temperature.

G.G. Jewell: Mention is made of changes in the liquid phase on sampling for DSC. Is it not possible that changes in the solid phase also occur, not only in the DSC, but during centrifugation?

Authors: The only changes to occur in the solid fat during DSC analysis would be annealing at slow scan rates. Solid material should not change if the temperature is lowered.

J.S. Patton: What is the lipid class composition of cocoa butter? I realize it is mostly TG, but what about minor components?
Authors: Approximately 97% of the fat is triglyceride, and about 1% may be diglyceride with less than 1% being free fatty acids. Minor components commonly found in natural cocoa butter would include tocopherols, phospholipids, organic acids and numerous lipid soluble compounds formed during cocoa fermentation and processing. The extraction method (solvent versus pressing) as well as the parameters of extraction will influence the composition. All samples used in these studies were extracted by pressing.

J.S. Patton: Is it possible that the 'individual' crystals and the 'blade' crystals (at 26°C) both originated from the same nucleation centers?
Authors: It is possible that the 'blade' crystals were formed through a transition of the 'individual' crystals. The 'blade' crystals were an exception to the commonly observed crystals formed at 26.0°C. As time progressed at 26.0°C, the 'individual' crystals slowly underwent a change and the 'blade' crystal gradually appeared. This transition was repeatedly seen.

K. Larsson: It is indicated in the paper that a main factor in the crystallization involves molecular segregation, so that high-melting crystallization nuclei separate, and even in crystal growth there should be an enrichment of high-melting triglycerides. Were experiments done at different cooling rates in order to evaluate the expected time dependence of such segregation?
Authors: Unfortunately, we did not pursue the effect of cooling on the seeded cocoa butter and chocolate. We are interested in determining what was occurring during moulding and cooling. The subject of cooling, seed formation, and crystal propagation is very important and worthy of future experimentation. We are currently initiating studies on characterization of the nucleation process.

K. Larsson: Although it was stated that there are only four crystal forms ("forms V and VI maybe forms differing in composition") I think that this is still an open question. With regard to your results and your interpretations in this respect, do you consider blooming as mainly a segregation phenomenon, not a phase transition towards a more stable form?
Authors: We feel that fat bloom is a combination of migrating triglycerides to form larger, more stable crystals, thus leaving a less homogeneous fat dispersion throughout the confection product. When chocolate is subject to higher temperatures the more stable crystals composed of higher proportions of SOS will anneal and become more stable. There are numerous other crystals formed after tempering and cooling which are not as stable as the initial seed. When the ambient temperature is increased these triglycerides partially melt and anneal. The newly formed liquid triglycerides may migrate and form larger crystals upon cooling or the liquid material may crystallize from the initial stable seed resulting in larger crystals.

Process variables like degree of temper, cooling temperature, and cooling time along with cocoa butter triglyceride composition probably exert a significant effect on chocolate fat stability and bloom formation. Simply stated, bloom is a combination of triglyceride segregation to larger crystals and also an increase in crystal stability.

J.M. deMan: What in your opinion would be required to resolve the uncertainties and lack of uniformity in the classification of the polymorphic forms as listed in Table 2?
Authors: To undertake a long term static study with numerous sources of cocoa butter. Techniques used in this paper would be useful along with traditionally used tempering cycles and procedures commonly used with DSC. Temperatures of formation should vary from approximately 5°C to 33°C. Thermal, morphological, and compositional data would be useful. Further development of new procedures using transmission electron microscopy or X-ray diffraction analysis would be very advantageous. It is a challenge.

J.M. deMan: With increasing use of SEM more of the spherical crystal structures are observed. In this paper they are described as 'feather' crystals. Are these the same type of crystals usually given the name spherulites?
Authors: Yes, 'feather' crystal is a term used to describe the internal structure of the spherulite as viewed by polarized light microscopy.