# Polymorphic Transitions of Cocoa Butter Affected by High Hydrostatic Pressure and Sucrose Polyesters

**Jun-Hyun Oh[a] and Barry G. Swanson[b,*]**

[a]Department of Food and Nutritional Sciences, Tuskegee University, Tuskegee, Alabama 36088, and [b]Department of Food Science and Human Nutrition, Washington State University, Pullman, Washington 99164-6376

**ABSTRACT**: Form V to Form VI transitions of cocoa butter (CB) were investigated by varying the temperature between 28 and 21°C during storage. High hydrostatic pressure (HHP) treatments of CB melt at 60 or 21°C did not affect the rate of Form V to Form VI transitions in CB crystallized in Form V during temperature fluctuations. The HHP treatments with 100, 300, or 600 MPa of CB crystallized in Form V crystals did not alter the rate of Form V to Form VI transitions of CB. The addition of sucrose polyesters to CB melts altered the rate of Form V to Form VI transitions of CB and was dependent on the FA chain lengths and hydrophile-lipophile balance (HLB) values of the SPE. The addition of most SPE to CB melts promoted the polymorphic transitions; however, sucrose polyester S-170 containing FA of chain length similar to CB with small HLB values inhibited Form V to Form VI transitions of CB for 10 temperature fluctuation cycles. Therefore, HHP treatments can be applied to foods containing high fat with little effect on the polymorphic transitions, and selected SPE may be used to retard adverse polymorphic transitions.

Paper no. J11341 in *JAOCS 83*, 1007–1014 (December 2006).

**KEY WORDS:** Cocoa butter, high hydrostatic pressure, polymorphic transition, sucrose polyesters.

Polymorphism is defined as the ability of a substance to exist in more than one crystalline phase that exhibits characteristic arrangement of the molecules in a crystal lattice (1). Cocoa butter (CB) is polymorphic, and the polymorphic behavior of CB dictates the quality of chocolate products (2–4). Among the six polymorphic forms of CB—from Form I crystals to Form VI crystals—Form V crystals are the most desirable because they provide the desired gloss, snap, and textural quality of chocolate products (2,5–7). Form V crystals, however, are prone to transition to the most stable Form VI crystals, resulting in chocolate bloom, one of the major defects in chocolate products (2,8–11).

The application of high hydrostatic pressure (HHP) to various food systems is receiving considerable attention for altering the functionality of foods (12,13). Pressure affects solid-liquid transitions of lipids by changing the equilibrium of the solid and liquid state toward the solid state (1). The specific volume of the liquid state is less than that of the solid state, so an increase in pressure will shift the equilibrium toward more solid. This shift results in an increase in m.p. of the lipid as the treatment pressure increases (Clausius–Clapeyron equation) (1). The m.p. of alkanes and phospholipids increase by 0.25°C per MPa during pressure treatment (14). HHP treatments ranging from 100 to 500 MPa accelerate the crystallization of milkfat emulsions by increasing the m.p. about 2°C per MPa (15,16). Since HHP treatment favors volume reduction reactions, HHP treatment can be hypothesized to accelerate polymorphic transitions to denser polymorphic forms of fats. However, information on the effects of HHP on polymorphic transition of fats is not available.

The addition of food additives such as emulsifiers to chocolate products retards polymorphic transition and prevents chocolate bloom (7,17–19). Sucrose polyesters (SPE), defined as having more than six FA esterified to the hydroxyl groups of sucrose, are lipophilic, nonabsorbable, noncaloric fat substitutes approved for use in selected foods (20). SPE are also approved for use in selected foods as emulsifiers at less than 1% concentration (20,21). The functionality of SPE other than as fat substitutes or emulsifiers has not been extensively investigated. Our previous research demonstrated that the addition of selected SPE to tristearin significantly retarded polymorphic transitions of tristearin (22).

The objectives of this research were to investigate (i) the effects of HHP treatments of CB melts or Form V crystals on polymorphic transition of Form V to Form VI crystals during temperature fluctuations known to accelerate polymorphic transition and (ii) the effects of the addition of SPE to the CB melt on polymorphic transition of Form V to Form VI crystals during cycled temperature fluctuations during storage.

## EXPERIMENTAL PROCEDURES

*Materials*. An African deodorized cocoa butter (CB 302) was obtained from Barry Callebaut U.S.A. Inc. (Pennsauken, NJ). Ryoto sugar esters were obtained from Mitsubishi-Kasei Food Co. (Tokyo, Japan). The experimental SPE included sucrose oleate with a hydrophile-lipophile balance (HLB) value of 15 (O-1570); sucrose stearate with HLB values of 16 (S-1670), 5 (S-570) or 1 (S-170); sucrose palmitate with an HLB value of 16 (P-1670); sucrose myristate with an HLB value of 16 (M-1695); and sucrose laurate with an HLB value of 5 (L-595). The properties of selected commercial SPE are presented in Table 1.

*HHP treatments*. The HHP treatments were performed in an isostatic pressing system (Engineered Pressure Systems, Inc., Andover, MA) with a temperature controller. The volume of

*To whom correspondence should be addressed. E-mail: swansonb@wsu.edu

**TABLE 1**
**Properties of Selected Commercial Sucrose Polyesters[a]**

| Sucrose polyester | Ryoto name | Approximate HLB[b] | Approximate % FA | Approximate % polyester |
|---|---|---|---|---|
| Sucrose laurate | L-595 | 5 | 95 | 70 |
| | L-1695 | 16 | 95 | 20 |
| Sucrose myristate | M-1695 | 16 | 95 | 20 |
| Sucrose palmitate | P-1670 | 16 | 70 | 20 |
| Sucrose stearate | S-170 | 1 | 70 | 100 |
| | S-570 | 5 | 70 | 70 |
| | S-1670 | 16 | 70 | 25 |
| Sucrose oleate | O-1570 | 15 | 70 | 30 |

[a]From Ryoto (Mitsubishi-Kasei Food Co., Tokyo, Japan) sugar ester technical information (2000).
[b]HLB, hydrophile-lipophile balance values.

the cylindrical pressure chamber was 1.96 L (height of 25 cm and i.d. of 10 cm). A 5% Mobil Hydrosol 78 (anticorrosive) water solution was used as a pressure transfer medium. The times needed to reach the pressures of 100, 300, and 600 MPa were approximately 2, 4, and 8 min, respectively. The decompression time was less than 15 s. The temperature of the chamber decreased by approximately 2, 4, and 6°C after applying HHP of 100, 300, and 600 MPa, respectively.

*HHP treatments applied to the CB melt*. About 4 g of CB was placed into plastic bags (5 × 9 cm), melted at 60°C, and the plastic bags were heat-sealed prior to HHP treatment. HHP with 300 MPa was applied to the CB melt either at 60°C before crystallization or at 21°C during crystallization to obtain HHP-induced Form V crystals. Duplicate bags of CB melt were treated with 300 MPa HHP at 60°C for 0.5 h and allowed to crystallize at 21°C for 24 h. Duplicate bags of CB were placed in a water bath at 60°C for 0.5 h and treated with 300 MPa at 21°C for 1 h, followed by storage at 21°C for 24 h. The control Form V crystals were prepared by placing CB melt in the HHP chamber at 60°C for 0.5 h, and the melt was crystallized at 21°C for 24 h as described by Garti *et al*. (5).

*HHP treatments applied to the CB crystallized in Form V*. The HHP was also applied to CB crystallized in Form V crystals at 21°C for 24 h without HHP treatments to obtain HHP-treated Form V crystals. The CB crystallized in Form V crystals was treated with 100, 300, or 600 MPa of HHP at 21°C for 1 h.

*Crystallization of Form V crystals in the presence of SPE*. Five percent (w/w) of selected SPE were added to approximately 4 g of CB melt and blended at 60°C for 0.5 h to destroy crystal memory and obtain a homogeneous mixture. The CB melts containing SPE were crystallized at 21°C for 24 h to obtain Form V crystals in the presence of SPE.

*Temperature fluctuations of CB crystallized in Form V*. Temperature cycling experiments were performed to accelerate the polymorphic transition of CB from Form V to Form VI crystals (5,6). Duplicate CB samples crystallized in Form V with HHP treatments and CB crystallized in Form V in the presence of SPE were stored at 28 and 21°C for 12 h. One temperature fluctuation cycle involved storage of Form V crystals at 28°C for 12 h and at 21°C for 12 h. After each cycle, the identification of polymorphic forms of CB was conducted using DSC and X-ray diffractometry (XRD).

*DSC*. Thermal analyses of CB were conducted on a PerkinElmer DSC-7 (Norwalk, CT). The DSC was calibrated with indium, and an empty pan was used as reference. Three replicates of approximately 20 mg of CB were scanned in a temperature range from 20 to 40°C at a heating rate of 2°C/min (5).

*XRD*. A D500 X-ray powder diffractometer (Siemens, Gilroy, CA) using Cu KA (λ = 1.5418 Å) radiation with a Ni filter equipped with a diffracted beam graphite crystal monochromator was used to collect diffraction patterns of CB crystals. The instrument settings were 35 kV with filament currents of 30 mA. Approximately 200 mg of CB crystals were placed on a glass slide and spread with a spatula. Date collection was performed at an angle range between 15 and 30° (2θ) with a scan speed of 0.2°/s. The identification of polymorphic forms of CB was performed based on the XRD short-spacing values reported in the literature (Table 2).

## RESULTS AND DISCUSSION

*HHP-induced Form V crystals*. The XRD patterns of CB crystallized at 21°C for 1 h are presented in Figure 1A. The X-ray short-spacings of the CB without HHP treatment at 60°C exhibited two weak peaks at 4.32 and 4.13 Å indicating Form IV crystals, and a strong peak at 4.58 Å and two weak peaks at 3.98 and 3.65 Å indicating Form V crystals. The CB without HHP treatment crystallized into a mixture of Form IV and Form V crystals, as reported by Chaiseri and Dimick (3). CB crystallized at 21°C for 1 h after 300 MPa HHP treatment of the CB melt at 60°C exhibited two strong peaks at 4.32 and 4.13 Å indicating Form IV crystals, and weak peaks at 4.58, 3.98 and 3.65 Å indicating Form V crystals. This profile implies that the 300 MPa HHP-treated CB melt crystallized primarily into Form IV crystals, when compared with the mixture of Form IV and Form V crystals of the CB without HHP treatment. The CB treated with 300 MPa HHP during crystallization at 21°C for 1 h exhibited a mixture of Form III and Form V crystals, evident from a strong peak at 4.20 Å indicating Form III crystals, and a peak at 4.58 Å and a peak between 3.98 and 3.65 Å indicating Form V crystals. The results suggested that the HHP treatments of the CB melts resulted in the induction of less stable Form IV crystals or Form III crystals than

**TABLE 2**
**Short-Spacings (Å) of Polymorphic Forms of Cocoa Butter Reported in the Literature**

| Reference | Form I | Form II | Form III | Form IV | Form V | Form VI |
|---|---|---|---|---|---|---|
| 2 | 4.19(vs)[a] | 4.24(vs) | 4.25(vs) | 4.35(vs) | 4.58(vs) | 4.95(vs) |
| | 3.70(s) | | 3.86(s) | 4.15(vs) | 3.98(vs) | 3.70(s) |
| | | | | | 3.67(w) | |
| 23 | 3.87(m) | 4.20(vs) | 4.20(vs) | 4.32(s) | 4.58(vs) | 4.53(vs) |
| | | | 3.87(w) | 4.13(s) | 3.98(ms) | 3.84(m) |
| | | | | | 3.65(ms) | 3.67(s) |
| 14 | 3.87(ms) | 4.20(vs) | 3.87(vw) | 3.75(m) | 3.65(s) | 3.67(s) |
| | 4.17(s) | | 4.20(vs) | 3.88(w) | 3.73(s) | 3.84(m) |
| | | | | 4.13(s) | 3.87(w)) | 4.01(w) |
| | | | | 4.32(s) | 3.98(s) | 4.21(vw) |
| | | | | | 4.22(w) | 4.53(vs) |
| | | | | | 4.58(vs) | 5.09(vw) |
| | | | | | 5.13(w) | 5.37(m) |
| | | | | | 5.38(m) | |

[a]Letters in parentheses indicate the following: vs: very strong; s: strong; ms: medium strong; m: medium; mw: medium weak; w: weak; vw: very weak.

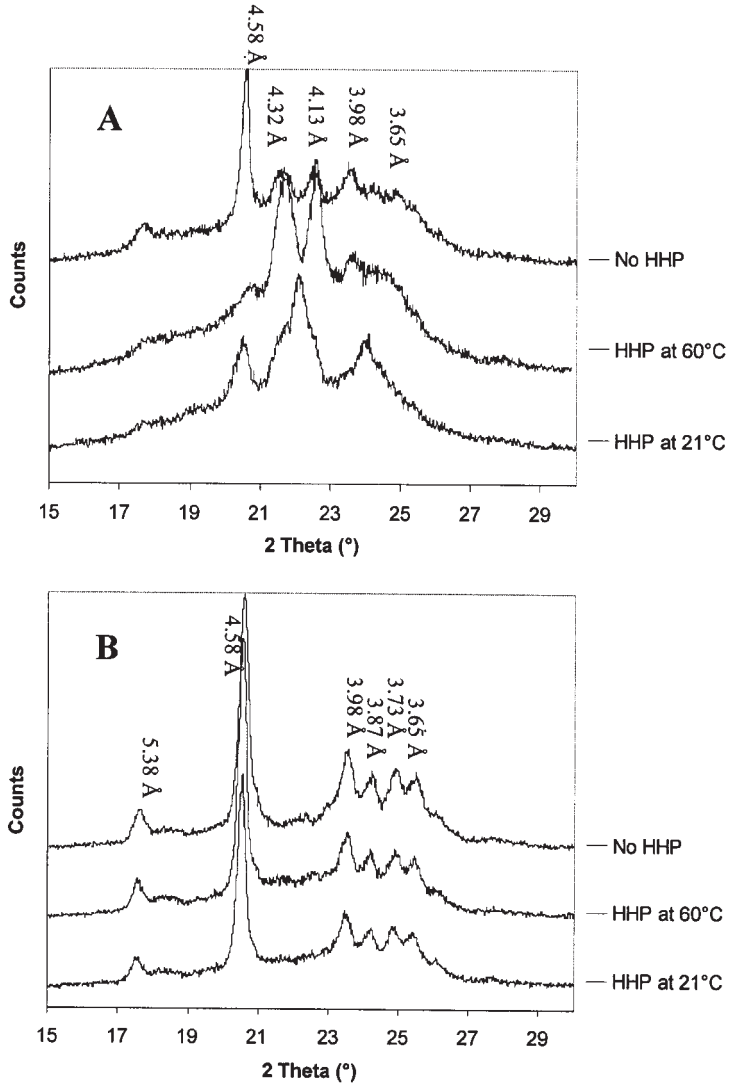


**FIG. 1.** X-ray diffraction (XRD) patterns of cocoa butters (CB) crystallized at 21°C for 1 h (A) and 24 h (B) after high hydrostatic pressure (HHP) treatments. No HHP indicates crystallization at 21°C from a melt at 60°C with no HHP treatment, HHP at 60°C indicates HHP treatment of 300 MPa at 60°C for 0.5 h and crystallization at 21°C, and HHP at 21°C indicates crystallization under HHP treatment of 300 MPa at 21°C for 1 h from a melt at 60°C.

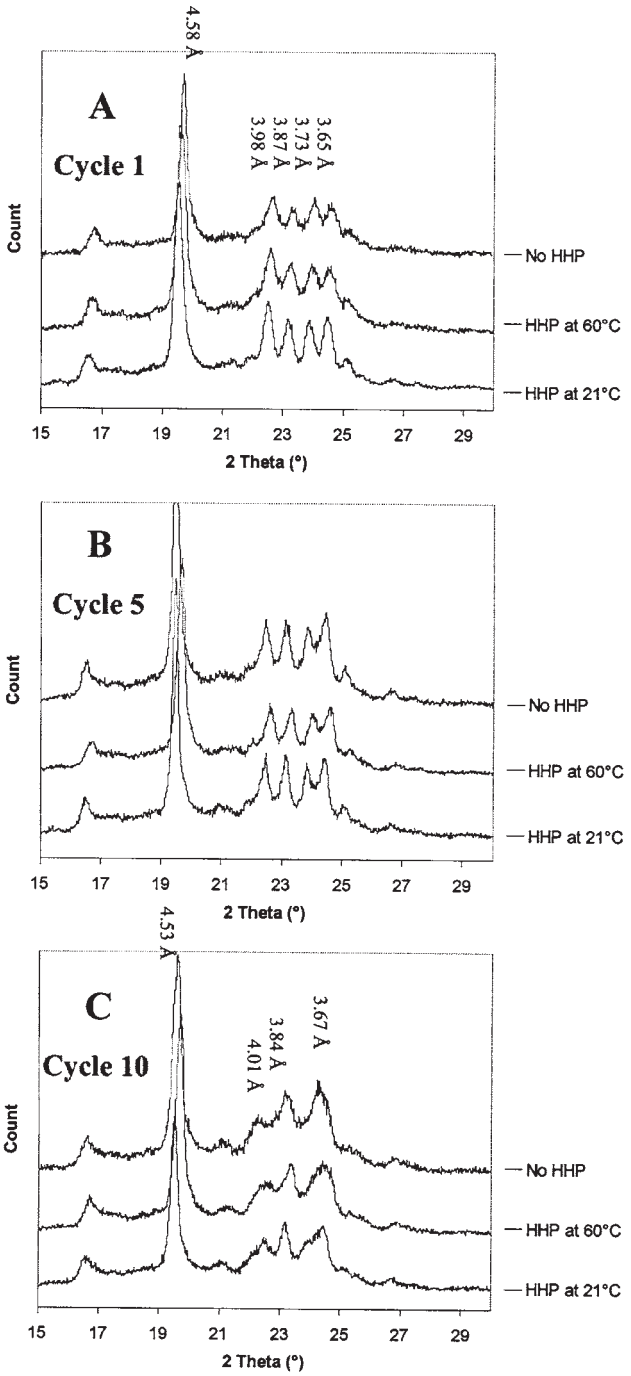


**FIG. 2.** XRD patterns of Form V crystals during 1 (A), 5 (B), and 10 (C) temperature fluctuation cycles at 28 and 21°C. One cycle involves warming at 28°C for 12 h and cooling at 21°C for 12 h. For abbreviations see Figure 1.

the Form IV and Form V crystals formed during crystallization of the CB without HHP treatment. The induction of the unstable polymorphic forms requires more supercooling to lower the crystallization temperature than the induction of stable polymorphic forms (14). The application of HHP may provide more supercooling effects on CB crystallization than no HHP treatment, resulting in the induction of unstable forms.

The XRD patterns of CB crystallized at 21°C for 24 h after HHP treatments on CB melts at either 60 or 21°C are presented in Figure 1B. The control and HHP-induced Form V crystals exhibited X-ray short-spacings at 5.38, 4.58, 3.98, 3.87, 3.73, and 3.65 Å indicating Form V crystals (14). There were no differences in X-ray short-spacings between the control and HHP-induced Form V crystals. Based on our experience, the transition of Form IV to Form V crystals in 300 MPa-treated CB at 21°C occurred within 3 h, and the transition of Form III to Form V crystals in CB treated with 300 MPa of HHP at 60°C occurred within 6 h. Therefore, storage of CB at 21°C for 24 h after HHP treatments provides sufficient time for transitions from Form III or Form IV crystals to Form V crystals.

*Polymorphic transitions from HHP-induced Form V to Form VI crystals during temperature fluctuations.* Since Form V crystals of CB are stable for several months at 21°C (5), the temperature fluctuation experiments at 28 and 21°C were conducted in an attempt to accelerate the polymorphic transition of Form V to Form VI crystals. The Form V to Form VI transition of CB crystals is hypothesized to occur through solid-solid transition because Form VI crystals cannot be obtained directly from a CB melt (5). The m.p. of the Form V crystals of CB determined by DSC ranged between 30.5 and 31.5°C. The CB crystallized in Form V crystals stored above 30.5°C may melt and recrystallize into Form V crystals during storage at 21°C for 12 h, instead of transition of Form V to Form VI crystals. The CB crystallized in Form V crystals stored at 28°C was not melted, and the transition of Form V to Form VI crystals was accelerated by temperature fluctuation cycles and required 10 cycles to complete the polymorphic transitions.

The XRD patterns of the control or HHP-induced Form V crystals as a function of storage at fluctuating temperatures are presented in Figure 2. As the number of temperature fluctuation cycles increased, the intensity of the peak at 3.98 Å decreased, the intensity of peak at 3.87 Å increased, and the two peaks at 3.73 and 3.65 Å became one peak at 3.67 Å. The Form V crystals transitioned to Form VI crystals after 10 temperature fluctuation cycles, exhibiting characteristic X-ray short-spacings of Form VI crystals (4.53, 4.01, 3.84, and 3.67 Å) (14). There were no differences in X-ray short-spacings between the control or HHP-induced Form V crystals after 10 cycles, implying that HHP-induced Form V crystals did not alter the polymorphic transition rate of CB from Form V to Form VI crystals.

The DSC curves of the control or HHP-induced Form V crystals during the temperature fluctuations are presented in Figure 3. The control or HHP-induced Form V crystals crystallized at 21°C for 24 h exhibited m.p. ranging from 30.5 to 31.5°C, indicating that the m.p. of HHP-induced Form V crystals were equivalent to the m.p. of the control Form V crystals. As the numbers of temperature fluctuation cycles increased, the peaks for Form V crystals approximately at 31°C decreased, and the peaks for Form VI crystals approximately at 34°C appeared and the size of the peak increased. The melting temperatures of Form VI crystals are in the range of 33.5–36.3°C (7). The appearance of the m.p. peak at 34°C implies that Form V crystals with a m.p. of 31°C transitioned to Form VI crystals with a m.p. of 34°C.

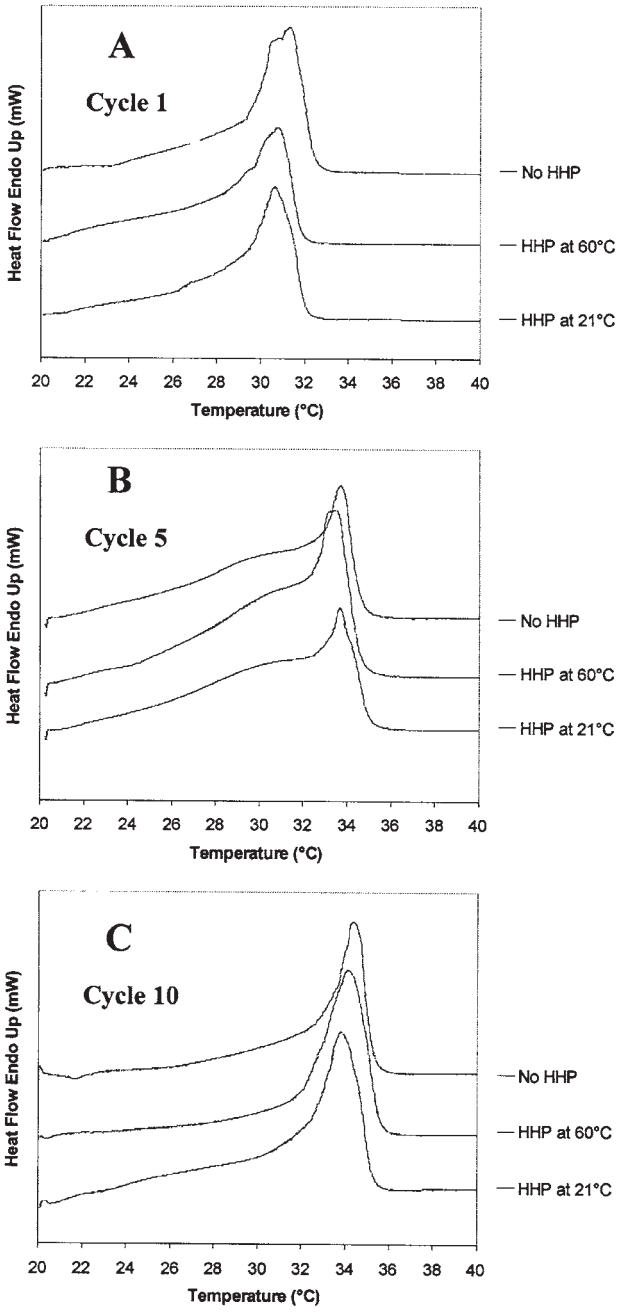


**FIG. 3.** DSC curves of Form V crystals during 1 (A), 5 (B), and 10 (C) temperature fluctuation cycles at 28 and 21°C. One cycle involves warming at 28°C for 12 h and cooling at 21°C for 12 h. For abbreviations see Figure 1.

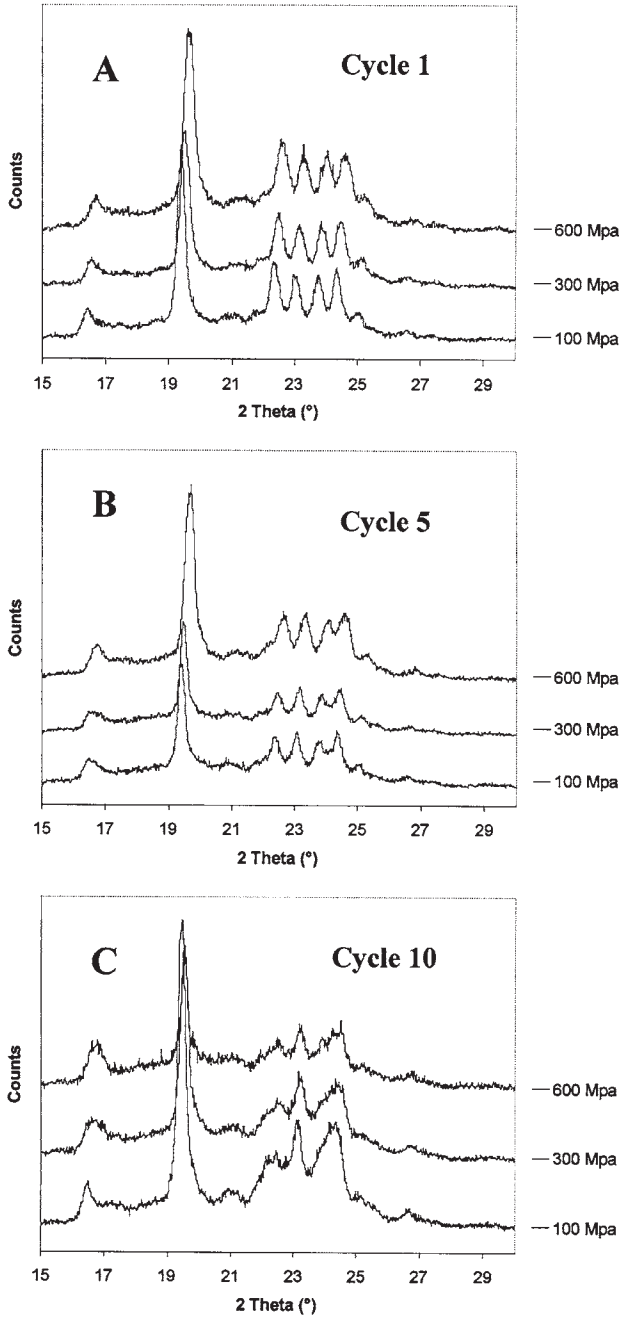


**FIG. 4.** XRD patterns of HHP-treated Form V crystals during 1 (A), 5 (B), and 10 (C) temperature fluctuation cycles at 28 and 21°C. The 100, 300, and 600 MPa indicate HHP treatments of 100, 300, and 600 MPa, respectively, to CB crystallized in Form V at 21°C for 24 h. One cycle involves warming at 28°C for 12 h and cooling at 21°C for 12 h. For abbreviations see Figure 1.

The DSC curves of CB also confirmed that the polymorphic transitions of Form V to Form VI crystals occurred after 10 cycles by exhibiting one melting peak of 34°C, characteristic of Form VI crystals. The HHP-induced Form V crystals exhibited DSC curves and XRD patterns similar to the untreated Form V crystals during the temperature fluctuation experiments, implying that the polymorphic transitions of Form V to Form VI crystals were not affected by the HHP treatment.

*Polymorphic transitions from HHP-treated Form V to Form VI crystals during temperature fluctuations*. The HHP was applied to Form V crystals induced at 21°C for 24 h to investigate the effects of HHP treatments of Form V crystals on the polymorphic transition of CB from Form V to Form VI crystals. The polymorphic transitions of Form V to Form VI crystals after HHP treatments of Form V crystals monitored by XRD are presented in Figure 4. There were no differences of

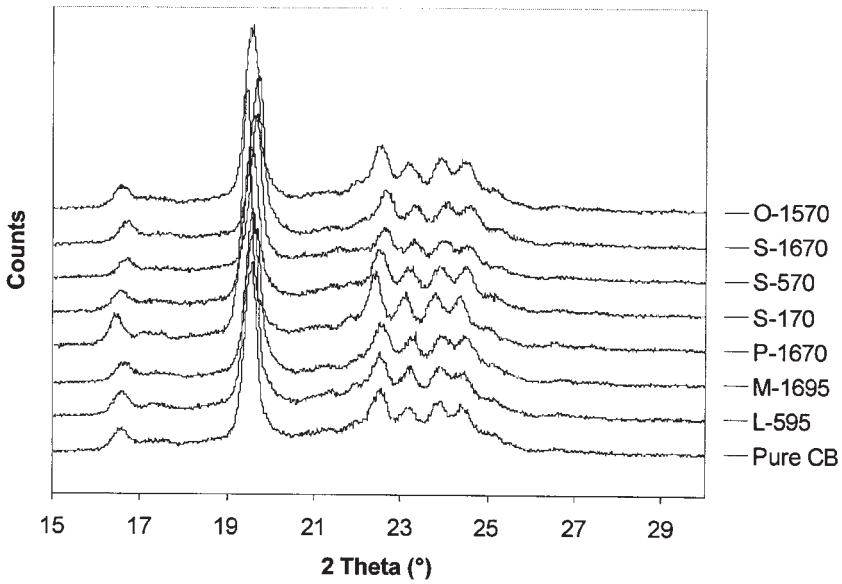


**FIG. 5.** XRD patterns of Form V crystallized in the presence of seven different sucrose polyesters at 21°C for 24 h. Pure CB indicates the CB crystallized in Form V without sucrose polyesters. For abbreviations see Table 1.

X-ray short-spacings among control Form V crystals (Fig. 1B) or Form V crystals treated with 100, 300, or 600 MPa at 21°C for 1 h (data not shown), indicating that the HHP treatments of Form V crystals did not alter the crystalline structures of Form V crystals. HHP-treated Form V crystals exhibited similar X-ray short-spacings as the control Form V crystals during the temperature fluctuation cycles, indicating that the HHP treatments of Form V crystals for 1 h did not alter the rate of polymorphic transition of CB from Form V to Form VI crystals.

HHP treatment favors volume reduction reactions (13). The polymorphic transitions from unstable to stable forms also involve volume reduction, thus altering the molecular arrangement to a more compact and denser structure (1). Therefore, it can be hypothesized that HHP treatment may accelerate polymorphic transitions. The major advantage of HHP treatment is that foods can be preserved without input of large amounts of heat, thus improving the quality of foods, since HHP can inactivate microorganisms and in some cases enzyme activity (12,13). However, the acceleration effects of HHP treatments on undesirable polymorphic transitions may result in an adverse effect of HHP on foods with high contents of fats and oils. However, our results suggest that the applications of HHP to fats such as CB in melt and solid states did not affect the rate of polymorphic transitions from unstable to stable forms.

*Polymorphic transitions from Form V to Form VI crystals in the presence of SPE*. The XRD patterns of CB crystallized in Form V crystals in the presence of SPE at 21°C for 24 h are presented in Figure 5. Form V crystals crystallized in the presence of SPE exhibited equivalent X-ray short-spacings to those of the pure Form V crystals crystallized from the CB melt. The addition of SPE to CB melts did not alter the crystalline structure of Form V crystals crystallized at 21°C for 24 h. Aronhime *et al*. (24) reported that the addition of emulsifiers such as Span 60 to CB melts inhibited crystallization at 22°C for 10 h; however, after 10 h, crystallization was promoted, exhibiting similar DSC curves as pure Form V crystals crystallized at 22°C for 13 h. A crystallization time of 24 h is sufficient to induce Form V crystals at 21°C.

The polymorphic transitions of CB from Form V to Form VI crystals in the presence of SPE were accelerated by temperature fluctuations. The XRD patterns of CB crystallized in Form V crystals as a function of temperature fluctuation cycles are presented in Figure 6. The pure Form V crystals of CB and most Form V crystals crystallized in the presence of SPE exhibited X-ray short-spacings at 5.38, 4.58, 3.98, 3.87, 3.73, and 3.65 Å after one temperature fluctuation cycle (Fig. 6A). CB crystallized in Form V in the presence of O-1570 exhibited a decreased peak height at 3.98 Å, an increased peak height at 3.87 Å, and the combining of two peaks at 3.73 and 3.65 Å, implying that transition of Form V to Form VI crystals was starting. The transition to Form VI crystals from Form V crystals, crystallized in the presence of O-1570, was completed after five cycles, and X-ray short-spacings characteristic of Form VI crystals were evident after five temperature fluctuation cycles.

Pure CB crystallized in Form V and CB crystallized in Form V with S-570 also started transition to Form VI crystals after five temperature fluctuation cycles, as indicated by XRD patterns similar to the XRD patterns of CB crystallized in Form V crystals in the presence of O-1570 after one temperature fluctuation cycle (Fig. 6B). CB crystallized in Form V crystals in the presence of L-595, M-1695, P-1670, and S-1670 exhibited X-ray short-spacings of Form VI crystals (4.53, 4.01, 3.84, and 3.67 Å) after five temperature fluctuation cycles, indicating that transitions of Form V to Form VI crystals occurred after five temperature fluctuation cycles. However, the CB crystallized in Form V crystals in the presence of S-170 exhibited X-ray

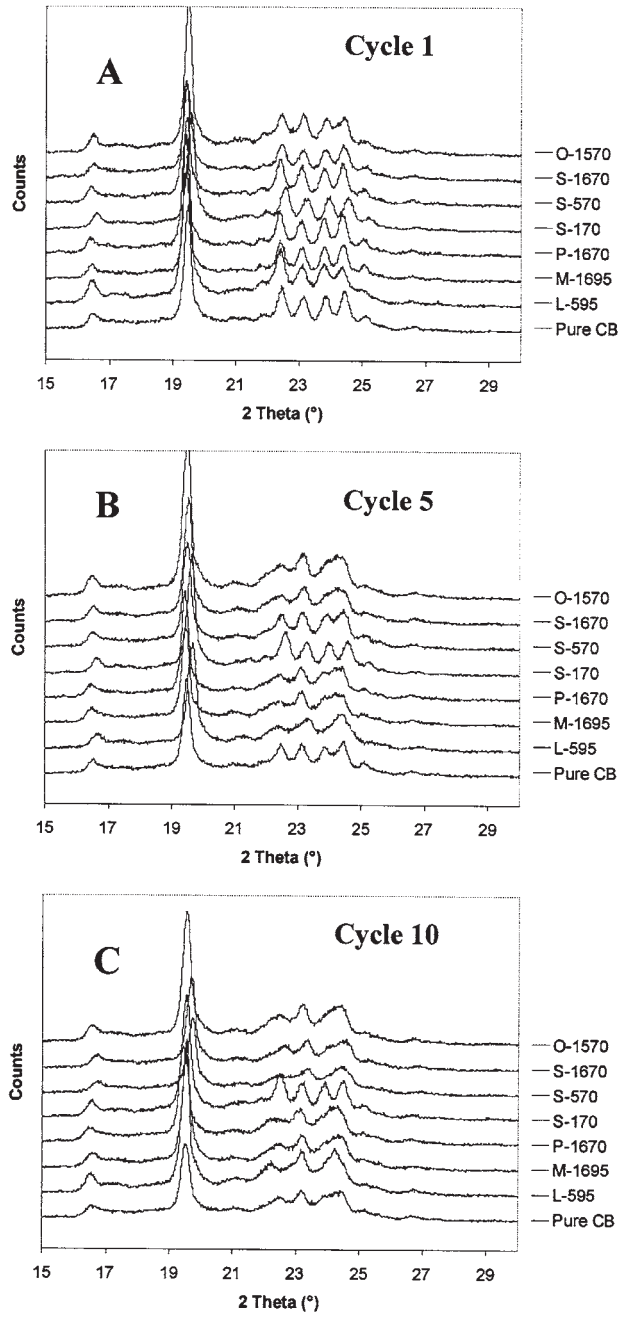


**FIG. 6.** XRD patterns of Form V crystallized in the presence of sucrose polyesters during 1 (A), 5 (B), and 10 (C) temperature fluctuation cycles at 28 and 21°C. Pure CB indicates CB crystallized in Form V without sucrose polyesters. One cycle involves warming at 28°C for 12 h and cooling at 21°C for 12 h. For abbreviations see Table 1.

short-spacings of Form V crystals after five temperature fluctuation cycles. Even though pure CB crystallized in Form V crystals and CB crystallized in Form V crystals in the presence of S-570 transitioned to Form VI crystals after 10 temperature fluctuation cycles, the CB crystallized in Form V crystals in the presence of S-170 were preserved with no transition to Form VI crystals (Fig. 6C).

The addition of S-170 to the CB melt inhibits polymorphic transition from Form V to Form VI crystals by stabilizing Form V crystals. The addition of S-570 or other selected SPE to CB melts exhibited little effect, or promoted polymorphic transitions from Form V to Form VI crystals. The retardation or promotion effects of SPE on the polymorphic transitions of CB from Form V to Form VI crystals were dependent on the FA chain length and HLB values of SPE. The addition to CB of SPE containing fatty acids other than stearic acid promoted polymorphic transitions from Form V to Form VI crystals. Among the SPE containing 70% stearic acid, S-1670, with an HLB value of 16, promoted the rate of polymorphic transition; S-570 with an HLB value of 5 did not alter the rate of polymorphic transition; and S-170 with an HLB value of 1 retarded polymorphic transition.

Previous studies on the addition of SPE to tristearin melts reported that the addition of SPE containing fatty acids other than stearic acid with low HLB values, such as S-170 or S-570, to tristearin melts retarded polymorphic transitions of $\alpha$ or $\beta'$ to $\beta$ forms of tristearin (22). SPE containing other than stearic acids did not affect the polymorphic transitions of tristearin. It is hypothesized that the FA chain length of SPE is one of the most important factors in retardation of the polymorphic transitions of tristearin.

The second important factor in retardation of polymorphic transitions of tristearin is the HLB value of SPE (22). HLB is described as an indication of the overall affinity of an emulsifier for the oil and/or aqueous phase, and the HLB values can be calculated from the number and type of hydrophilic and lipophilic groups in a compound (25). According to the manufacturer, the HLB values of SPE are related to the number of FA attached to sucrose molecules in that the SPE with small HLB values are composed of larger amounts of polyesters, whereas SPE with large HLB values are largely composed of monoesters (Table 1). Among the SPE containing FA chain lengths equivalent to tristearin, the addition of SPE with small HLB values retarded the transition of tristearin to the greatest extent.

Three predominant TAG of CB are 1-palmitoyl-2-oleoyl-3-stearoyl-*sn*-glycerol (POS), 1,3-distearoyl-2-oleoly-*sn*-glycerol (SOS) and 1,3-dipalmitoyl-2-oleoly-*sn*-glycerol (POP), making up about 40, 27.5, and 15% of total TAG, respectively (4,7). SPE containing palmitic acids, stearic acids, or oleic acids may retard the polymorphic transitions of CB Form V to Form VI crystals. Experimentally, the SPE containing 70% stearic acids retarded polymorphic transition. The fact that stearic acids are the most predominant FA in CB may result in retardation effects of SPE containing stearic acids on polymorphic transitions of CB. The effects of SPE on polymorphic transitions were also dependent on HLB values of SPE. The addition of S-170, with a small HLB value of 1, produced maximum retardation effects on the polymorphic transition of CB from Form V to Form VI crystals. S-170 may easily incorporate into the CB melt at 60°C because of a small HLB value of S-170 and potentially may co-crystallize with CB. The interaction of S-170 with the FA of CB in the solid state may stabilize Form V crystals, resulting in inhibition of polymorphic transi-

tion from Form V to Form VI crystals. Therefore, this study provides evidence that the addition of SPE may improve the quality and shelf life of chocolate products containing CB by stabilizing the desirable Form V crystals.

## REFERENCES


1. Brittain, H.G., *Polymorphism in Pharmaceutical Solids*, Marcel Dekker, New York, 1999, pp. 35–72.
2. Wille, R.L., and E.S. Lutton, Polymorphism of Cocoa Butter, *J. Am. Oil Chem. Soc. 43*:491–496 (1966).
3. Chaiseri, S., and P.S. Dimick, Dynamic Crystallization of Cocoa Butter. II. Morphological, Thermal and Chemical Characteristics During Crystal Growth, *Ibid. 72*:1497–1504 (1995).
4. Loisel, C., G. Keller, G. Lecq, C. Bourgaux, and M. Ollivon, Phase Transition and Polymorphism of Cocoa Butter, *Ibid. 75*:425–439 (1998).
5. Garti, N., J. Schlichter, and S. Sarig, Effect of Food Emulsifiers on Polymorphic Transitions of Cocoa Butter, *Ibid. 63*:230–236 (1986).
6. Hachiya, I., T. Koyano, and K. Sato, Seeding Effects on Crystallization Behavior of Cocoa Butter, *Agric. Biol. Chem. 53*:327–332 (1989).
7. Lawler, P.J., and P.S. Dimick, Crystallization and Polymorphism of Fats, in *Food Lipids*, edited by C.C. Akoh and D.B. Min, Marcel Dekker, New York, 1997, pp. 229–250.
8. Davis, T.R., and P.S. Dimick, Solidification of Cocoa Butter, *Proc. PMCA Ann. Prod. Conf. 40*:104–108 (1986).
9. Cebula, D.J., and G. Ziegler, X-Ray Diffraction Studies of Bloom Formation in Chocolate After Long-Term Storage, *Fett. Wissen. Technol. 95*:340–344 (1993).
10. Loisel, C., G. Lecq, G. Ponchel, G. Keller, and M. Ollivon, Fat Bloom and Chocolate Structure Studied by Mercury Porosimetry, *J. Food Sci. 62*:781–788 (1997).
11. Tietz, R.A., and R.W. Hartel, Effects of Minor Lipids on Crystallization of Milk Fat–Cocoa Butter Blends and Bloom Formation in Chocolate, *J. Am. Oil Chem. Soc. 77*:763–771 (2000).
12. Farr, D., High Pressure Technology in the Food Industry, *Trends Food Sci. Technol. 1*:14–16 (1990).
13. Pothakamury, U.R., G.V. Barbosa-Casovas, and B.G. Swanson, The Pressure Builds for Better Food Processing, *Chem. Eng. Prog. 3*:45–53 (1995).
14. Larsson, K., *Lipids—Molecular Organization, Physical and Technical Applications,* The Oily Press Ltd., Dundee, Scotland, 1994, pp. 7–45.
15. Buchheim, W., and A.M. Abou El-Nour, Induction of Milkfat Crystallization in the Emulsified State by High Hydrostatic Pressure, *Fat Sci. Technol. 94*:369–373 (1992).
16. Buchheim, W., M. Schutt, and E. Frede, High Pressure Effects on Emulsified Fats, *High Pressure Biosci. Biotechnol.*:331–336 (1996).
17. Garti, N., E. Wellner, and S. Sarig, Crystal Structure Modification of Tristearin by Food Emulsifiers, *J. Am. Oil Chem. Soc. 59*:181–185 (1982).
18. Aronhime, J.S., and N. Garti, Solidification and Polymorphism in Cocoa Butter and the Blooming Problems, in *Crystallization and Polymorphism of Fats and Fatty Acids,* edited by N. Garti, and K. Sato, Marcel Dekker, New York, 1988, pp. 363–393.
19. Elisabettini, P., A. Desmedt, and F. Durant, Polymorphism of Stabilized and Nonstabilized Tristearin, Pure and in the Presence of Food Emulsifiers, *J. Am. Oil Chem. Soc. 73*:187–192 (1996).
20. Akoh, C.C., and B.G. Swanson, *Carbohydrate Polyesters as Fat Substitutes,* Marcel Dekker, New York, 1994, pp. 9–35.
21. Akoh, C.C., Fat Replacers, *Food Technol. 52*:47–53 (1998).
22. Oh, J.-H., A.R. McCurdy, S. Clark, and B.G. Swanson, Stabilizing Polymorphic Transitions of Tristearin Using Diacylglycerols and Sucrose Polyesters, *J. Am. Oil Chem. Soc. 82*:13–19 (2005).
23. Chapman, G.G., Cocoa Butter and Confectionery Fats. Studies Using Programmed Temperature X-Ray Diffraction and Differential Scanning Calorimetry, *Ibid. 48*:824–830 (1971).
24. Aronhime, J.S., S. Sarig, and N. Garti, Reconsideration of Polymorphic Transformations in Cocoa Butter Using DSC, *Ibid. 65*:1140–1143 (1988).
25. McClements, D.J., Lipid-Based Emulsions and Emulsifiers, in *Food Lipids*, edited by C.C. Akoh and D.B. Min, Marcel Dekker, New York, 1997, pp. 55–88.


[Received February 16, 2006; accepted August 25, 2006]