Influence of Thermal Conditions and Presence of Additives on Fat Bloom in Chocolate

Peggy Walter and Paul Cornillon*

Purdue University, Department of Food Science, Whistler Center for Carbohydrate Research, West Lafayette, Indiana 47907-1160

ABSTRACT: This study focused on the analysis of the effects of thermal history and presence of additives on fat bloom in chocolate. Magnetic resonance data obtained on specific chocolate samples were useful in evaluating the effect of thermal history on the appearance of fat bloom and also in understanding the underlying mechanism. Fat bloom was induced by thermal history such as storage for 3 d at 32 or 28°C. Increasing storage time at 21°C after each thermal treatment also promoted fat bloom. Differential scanning calorimetry experiments confirmed the appearance of polymorphic form VI in the bloomed samples. Also, three different components were added separately to the initial composition of dark chocolate and the appearance of fat bloom was monitored. 1,3-Dibehenoyl, 2-oleoylglycerol (BOB) did prevent fat bloom. However, magnetic resonance and differential scanning calorimetry data collected on chocolate samples did not confirm that either added sucrose or milk powder prevented fat bloom. Indeed, fat bloom occurred for these samples, but its characteristics were different from those with pure chocolate.

Paper no. J9577 in *JAOCS 78,* 927–932 (September 2001).

KEY WORDS: Additives, chocolate, DSC, fat bloom, MRI, NMR, relaxation times, thermal conditions.

Fat bloom is the major issue affecting chocolate products, especially confectionery containing fatty filling (1). During storage, a dusty white layer appears on the chocolate surface, caused by the formation of fat crystals (1). This physical defect makes the chocolate undesirable for consumers who expect to buy a product with the required glossy surface and desired brown shade (2). Although the mechanism of its formation is not completely understood, the causes seem to be multiple, such as improper tempering, use of incompatible fats, and large temperature fluctuations during storage (2).

Because chocolate contains more than 30% fat, its successful use depends on the proper manipulation of cocoa butter (2) and cocoa butter properties such as thermal behavior (1). Cocoa butter is a natural fat composed of a mixture of three classes of triglycerides (unsaturated, monounsaturated, and polyunsaturated) where the monounsaturated fats represent more than 80% of the total fat content (3). Moreover, only three triacylglycerols (1,3-dipalmitoyl, 2-oleoylglycerol, or POP; 1,3-palmitoyl-stearoyl, 2-oleoylglycerol or POSt; and 1,3-distearoyl, 2-oleoylglycerol or StOSt) account for more than 95% of this fraction (3). However, the thermal behavior of cocoa butter is complicated because of the polymorphism of these triacylglycerols (3). Cocoa butter is generally described by six different polymorphic forms, I to VI in order of increasing melting point (4). However, I, III, and VI are now considered to be a mixture or a phase separation from the other forms (5,6).

It is now accepted that fat bloom is linked to the separation of the liquid fraction of cocoa butter from the chocolate matrix, followed by migration of this fat toward the surface where it recrystallizes, inducing the appearance of a white layer and loss of the glossy aspect (1,7). Moreover, the appearance of fat bloom is generally characterized by a polymorphic transition of the fat crystal from form V to the most stable form VI (also denoted β) (4,8–10). The relationship between blooming and polymorphic transition is still unclear, and this study presents data to clarify this relationship.

Nuclear magnetic resonance (NMR) spectroscopy and imaging (MRI) are noninvasive and nondestructive techniques based on the magnetic properties of particular nuclei, like protons (11). NMR can be used to study the chemical environments, physical domains, and molecular dynamics of food components present in a product. Published data are often based on the changes of the spin-spin (T_2) and spin-lattice (T_1) relaxation times, which give information about the mobility of the nuclei inside a sample and about the physical structure of the environment of the spins, respectively. MRI allows the same NMR information to be spatially resolved (11). This technique takes a slice through the sample and draws a spatial map derived from the NMR responses of the mobile spins, mostly protons of lipids in the case of chocolate (12). MRI has already been used to study the crystallization of cocoa butter, its polymorphic state (12,13), and the migration of liquid triacylglycerol in chocolate (14). However, MRI and NMR have never been used in the evaluation of fat bloom as related to its mechanism of formation and the effect of additives.

The main objectives of the study were (i) to analyze the appearance of fat bloom on dark chocolate as a function of thermal history and (ii) to characterize the appearance of fat bloom in the presence of a particular triacylglycerol (e.g., 1,3-dibehenoyl, 2-oleoylglycerol, BOB), sucrose, or milk powder.

EXPERIMENTAL PROCEDURES

Effect of thermal history on fat bloom. (i) Samples. Dark unsweetened chocolate was purchased at a local store. To prepare

*To whom correspondence should be addressed at Purdue University, Department of Food Science, Whistler Center for Carbohydrate Research, 1160 Food Science Building, West Lafayette, IN 47907-1160.
E-mail: cornillo@foodsci.purdue.edu

for NMR experiments, several 18-mm o.d. NMR tubes (samples 1 to 10), each containing about 5 g of chocolate, were heated at 50°C for 1 h to melt all fat crystals. These samples were then placed at 21°C to allow slow cooling of the chocolate and crystallization of the fat in the stable V form (12). This process erased the former thermal history of all the samples. After a few days at 21°C, each sample tube was put through a specific thermal history (Table 1) in a water bath and then transferred back to 21°C for times indicated in Table 1. Each sample was then analyzed by NMR and differential scanning calorimetry (DSC).

Pure (approx. 99%) triglycerides (i.e., POP, POSt, StOSt) were purchased from Sigma Chemical Co. (St. Louis, MO). Stored at −18°C, about 10 mg of each triglyceride was used to determine the melting point of the cocoa butter's main components, which were in accordance with the literature (4,15). The melting points were 40.8, 34.7, and 36.2°C for StOSt, POSt, and POP, respectively.

(ii) NMR relaxometry experiments. The ^{1}H NMR experiments were carried out at 20°C on a 15 MHz Maran benchtop spectrometer (Resonance Instruments Ltd., Whitney, United Kingdom) while the magnet temperature was held at 35°C. The pulse lengths were 23.4 and 46.8 µs, respectively, for the 90 and 180° pulses. The dwell time was 0.5 µs, and the receiver gain was set to obtain a maximum signal. The other NMR parameters were set up to collect data related to the lipid protons. The inversion-recovery pulse sequence was used to determine the T_1 relaxation times. The relaxation delay was fixed to 1 s. Four scans were used for signal averaging. Ten pulse spacing values, between 1 ms and 1 s, were used to sample the whole recovery curve. For each sample, T_1 times were collected twice. T_2 relaxation times were determined with a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence using 2,048 points and an echo time of 0.3 ms. Four scans were accumulated with a relaxation delay of 1 s between each scan. The NMR relaxation data were fitted to a single exponential decay (for T_1) and a multiexponential decay (for T_2) using software provided by the vendor.

TABLE 1
Effect of Thermal History: Experimental Conditions and Melting Point of Samples 1 to 10

Sample		Thermal history	Storage	Melting point (°C)
Control	1	—	21°C, 2 d	33.6 ± 0.4
	2	32°C, 3 d	21°C, 2 d	38.6 ± 0.9
	3	32°C, 3 d	21°C, 4 d	38.6 ± 0.9
	4	32°C, 3 d	21°C, 7 d	38.6 ± 0.9
	5	28°C, 3 d	21°C, 2 d	40.3 ± 0.7
	6	28°C, 3 d	21°C, 4 d	40.3 ± 0.7
	7	28°C, 3 d	21°C, 7 d	40.3 ± 0.7
	8	32°C, 1 d; 20°C, 1 d; 28°C, 1 d	21°C, 2 d	39.4 ± 0.7
	9	32°C, 1 d; 20°C, 1 d; 28°C, 1 d	21°C, 4 d	39.4 ± 0.7
	10	32°C, 1 d; 20°C, 1 d; 28°C, 1 d	21°C, 7 d	39.4 ± 0.7

(iii) MRI experiments. All images were acquired at 20°C using the same Maran benchtop spectrometer as for the relaxometry measurements. The linear magnetic field gradient was generated using gradient coils made by the vendor. A standard spin-echo imaging pulse sequence was used with an echo time (TE) of 8 ms and a relaxation delay (RD) of 200 ms. The number of scans was 32, and the 64 × 64 data matrix images were acquired in about 7 min. Images were analyzed with an image display macro written in the IDL programming language (Research Systems Inc., Boulder, CO). The field of view was 3.9 cm. Further image processing was also carried out with the freely distributed software Scion PC (http://www.scioncorp.com).

(iv) DSC analysis. Melting points of chocolate were determined by using a MDSC™ 2920 calorimeter (TA Instruments, New Castle, NJ). About 10 mg of chocolate was placed in a hermetic aluminum pan while an empty pan served as reference. Two samples were collected from each chocolate sample used for the NMR experiments. Two measurements were made for each so that the reported melting point is an average of four values. After stabilization for 2 min, between −5 and 5°C, the samples were heated to 60°C at 10°C·min^{-1}. For each thermogram, the melting point of the samples was determined using software provided by the vendor.

Effect of additives on fat bloom. (i) Samples. Fourteen NMR tubes were filled to a height of 2 cm with chocolate samples with different additives (Table 2). The commercial triglyceride BOB contained 50% sucrose and 50% pure triglyceride. The concentration indicated in Table 2 relates to the percentage of pure triglyceride. NMR tubes, each containing about 10 g of chocolate, were heated at 50°C for 1 d then stored at 21°C for a few days, heated at 28°C for 1 d, and finally stored at 21°C for 3 d. All 15-, 16-, and 17-sample series did not melt completely at 50°C because of the high amount of sucrose and milk powder present in them.

(ii) NMR relaxometry experiments. In these experiments, the pulse lengths were 20.1 and 40.1 µs for the 90 and 180° pulses, respectively. The dwell time was 0.5 µs, and the receiver gain was set to obtain the highest possible signal from the sample. The values of T_1 and T_2 were determined by using the same sequences and parameters as described previously.

(iii) MRI experiments. With the same benchtop spectrometer, 64 × 64 data matrix images were acquired. The echo time was 7 ms, and the relaxation delay was 200 ms. The number of scans was set to 32, and the images were acquired in about 7 min. The field of view was 3.9 cm.

(iv) DSC analysis. The melting point of one chocolate species was determined on two samples using the same instrument and method described previously. Three measurements were made for each sample, so that the average melting point reported for a specific sample was the average of six values.

RESULTS AND DISCUSSION

Effect of thermal history on fat bloom. Every sample presented fat bloom but not in the same proportion. Sample 1 (e.g.,

TABLE 2
Effect of Additives: Composition[a], Qualitative Evaluation of Defects, and Magnetic Resonance Imagery (MRI) and Differential Scanning Calorimetry Data of Samples 11 to 17

Samples	Additives	Fat bloom	Hardness	Brittleness	Other crystals	T_1 (ms)	T_2 (ms)		Maximum intensity in MRI image	Melting point (°C)
							Long	Short		
Control	—	+ + +	—	+ + +	—	76.1 ± 1.1	52.4 ± 3.7	12.7 ± 1.0	21	36.9 ± 1.7
11	0.5 % (wt) of BOB	+ + +	—	+ + +	—	85.8 ± 1.6	54.5 ± 4.5	13.7 ± 0.8	20	37.2 ± 0.7
12	1.25% (wt) of BOB	+ +	—	+ + +	—	82.2 ± 1.5	46.4 ± 6.3	12.7 ± 1.7	23	37.1 ± 0.5
13	2.5% (wt) of BOB	+	+	+ +	—	79.3 ± 0.3	45.2 ± 1.2	11.5 ± 1.3	32	37.1 ± 0.5
14	40% (wt) of sucrose	+ + +	+ + +	+	Sucrose	107.1 ± 3.7	59.5 ± 1.8	14.5 ± 0.5	19	36.4 ± 1.0
15	60% (wt) of sucrose	+ + +	+ + +	+	Sucrose	114.6 ± 1.6	62.6 ± 7.2	15.5 ± 1.7	26	36.1 ± 0.8
16	10% (wt) of milk powder	+ + +	+ + +	+	+ +	63.4 ± 1.1	53.2 ± 4.3	12.6 ± 1.2	25	38.2 ± 0.7
17	30% (wt) of milk powder	+ + +	+ + +	+	+ +	75.3 ± 0.2	70.5 ± 6.9	16.4 ± 1.8	22	36.8 ± 0.7

[a]Basic composition of control sample is 40% cocoa butter and 60% ground mass of cocoa. BOB, 1,3-dibehenoyl, 2-oleoyl; +++, very high; ++, high; +, average; —, not noticeable; T_1, spin-lattice relaxation time; T_2, spin-spin relaxation time.

control) showed bloom on about 45% of the surface, whereas the other samples had bloom on more than 80% of their surface. Samples stored for 3 d at 32°C had the most dramatic bloom. T_1 and T_2 relaxation times are presented in Figure 1. Since the standard deviations were between 0 and 20 ms, T_1 values were not significantly different between samples. Hence, the effect of thermal history could not be analyzed with this parameter. Solid protons in the cocoa mass have very short T_2 that do not contribute to the signal (12). A bi-exponential curve was used to obtain T_2 values of the relaxation decay curves and to indicate a two-component population of spins. Previous studies showed that T_2 could be useful to differentiate liquid from crystalline fat (11,12). Indeed, the lowest T_2 component (around 10–20 ms) is from lipids in solid-crystalline environments, whereas the highest T_2 (around 40–80 ms) is due to the relaxation of fat protons in liquid environments. The standard deviations (between 1 and 12%) fluctuate more for high values of T_2 than for low values because high T_2 values reflect only 30% of the total signal. So, approximately 30% of the lipids are in a liquid-like state. An increase of T_2 was observed for all samples after temperature variations (Fig. 1), suggesting an increase in the mobility of the liquid-like protons. Hence, when chocolate experiences a rise in temperature, lipids tend to become more liquid and

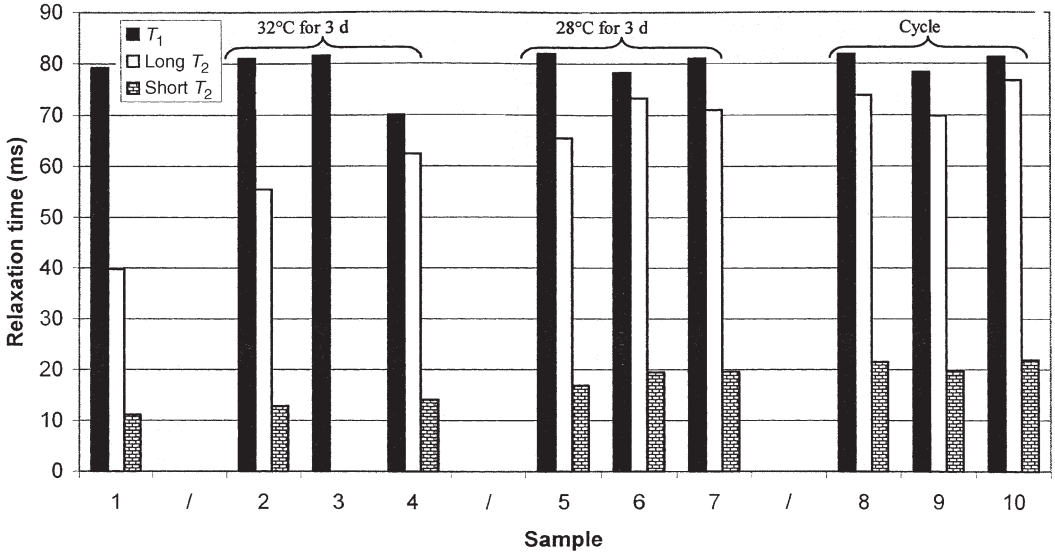

FIG. 1. Spin-lattice (T_1) and spin-spin (T_2) relaxation times of chocolate samples as a function of thermal history.

melt. The 32–20–28°C temperature cycle had the most dramatic effect on the increase of T_2. At 32°C, lipids are almost melted. Then, during storage at 21°C, they tend to recrystallize but there is not enough time for them to reach the most stable form. Thus, if a sample containing less stable fat crystals were stored at 32°C, the amount of liquid lipids would be higher than for another sample stored for 3 d at 32°C. Storage at room temperature after the specific thermal history also affected the proton mobility. In general, with the increase of storage time, lipids tend to be in a more liquid-like state.

The intensity of a pixel in an NMR image is defined by the following equation:

$$M = M_0 \cdot \exp(-\mathrm{TE}/T_2) \cdot [1 - \exp(-\mathrm{RD}/T_1)] \quad [1]$$

where M is the observed pixel intensity, M_0 the total liquid proton density of the pixel, TE the echo time, and RD the relaxation delay between each acquisition scan. Since RD was greater than $5T_1$ in this study, the term $\exp(-\mathrm{RD}/T_1)$ becomes negligible and the distribution of T_1 in the sample has little influence on the image intensity. This confirms the results of previous research where images were influenced only by M_0 and T_2 rather than by T_1 (11).

In Figure 2, two-dimensional images of samples 1, 3, 5, and 8 are presented. High- and low-intensity values for sample 3 are indicated since the distribution of lipids in the sample is not homogeneous. This feature has been previously observed (14). For the control sample having less bloom as compared to the other samples, the mean intensity was 181 with a 256 maximum intensity possible. The image of sample 3, like that of the other samples stored at 32°C, showed a nonhomogeneous intensity suggesting an important modification of the lipid composition and structure into the chocolate. However, samples 5 and 8 had less variation in the intensity distribution of pixels.

Figure 3 presents the intensity (i.e., mean for samples 1, 5–10; or maximum and minimum for samples 2–4) in all images. The standard deviation was between 0 and 10% for samples 1 and 5–10. However, in heterogeneous images obtained for samples 2–4, the standard deviation was 25% maximum. Three days at 32°C induced a decrease of about 29% of the mean intensity, whereas the thermal history of 3 d at 28°C or of 32–20–28°C temperature cycle induced a decrease of the image intensity of 1% and an increase of 7%, respectively.

As previously indicated, the intensity of an image increases if the density of mobile protons (e.g., M_0) and/or T_2 increases. T_2 increases with the increase in proton mobility, and M_0 is higher when the density of mobile protons increases. Since every sample was bloomed, fat crystals were preferentially in form VI rather than in form V (1,7). Even though crystals of forms VI are more stable, they have a more compact structure and they reject triglycerides during their formation, which explains the increase in lipid mobility.

After 3 d at 32°C, a phase separation in the samples was observed and the intensity of the images dramatically decreased in some areas. Since on average T_2 increased (Fig. 1), this suggested that the density of mobile protons M_0 decreased in these specific regions, indicating that more lipids were in a solid-like form. After 3 d at 28°C, the intensity was almost equal to the intensity of the control sample even if T_2 was greater. Hence, the proton density decreased, possibly due to crystallization of lipids. However, after the 32–20–28°C temperature cycle, the image intensity slightly increased as compared to the control sample. Since T_2 increased as well, the evolution of the proton density could not be easily characterized because it varied from sample to sample.

Stored at 21°C, lipids seemed to recrystallize in the most stable form (e.g., form VI). It is known that crystallization from form V to form VI is a solid-state transformation (6) and that if some liquid lipid fraction was removed from chocolate samples, then crystal formation of form VI from form V would be induced. This suggests that heating chocolate with the

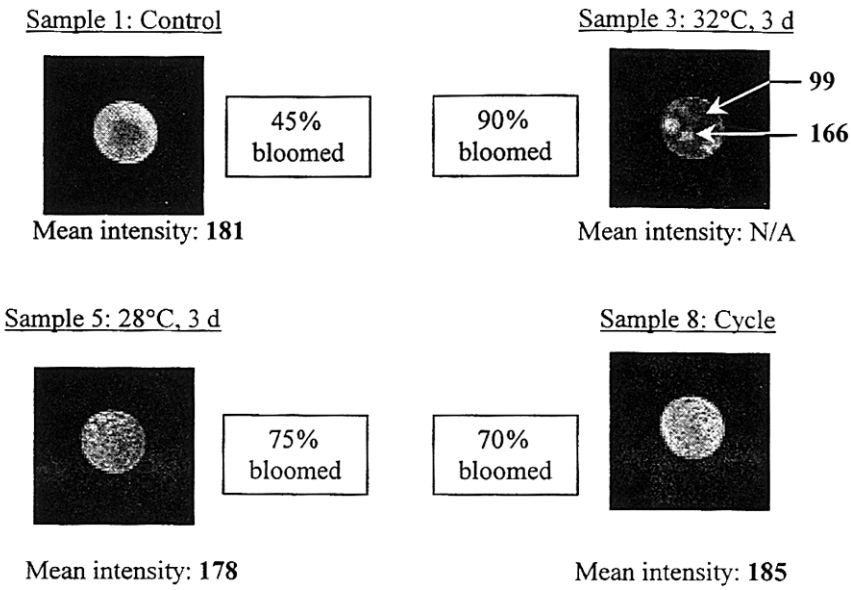

FIG. 2. Two-dimensional nuclear magnetic resonance images of samples 1, 3, 5, and 8. N/A: not calculated because of nonhomogeneity in images.

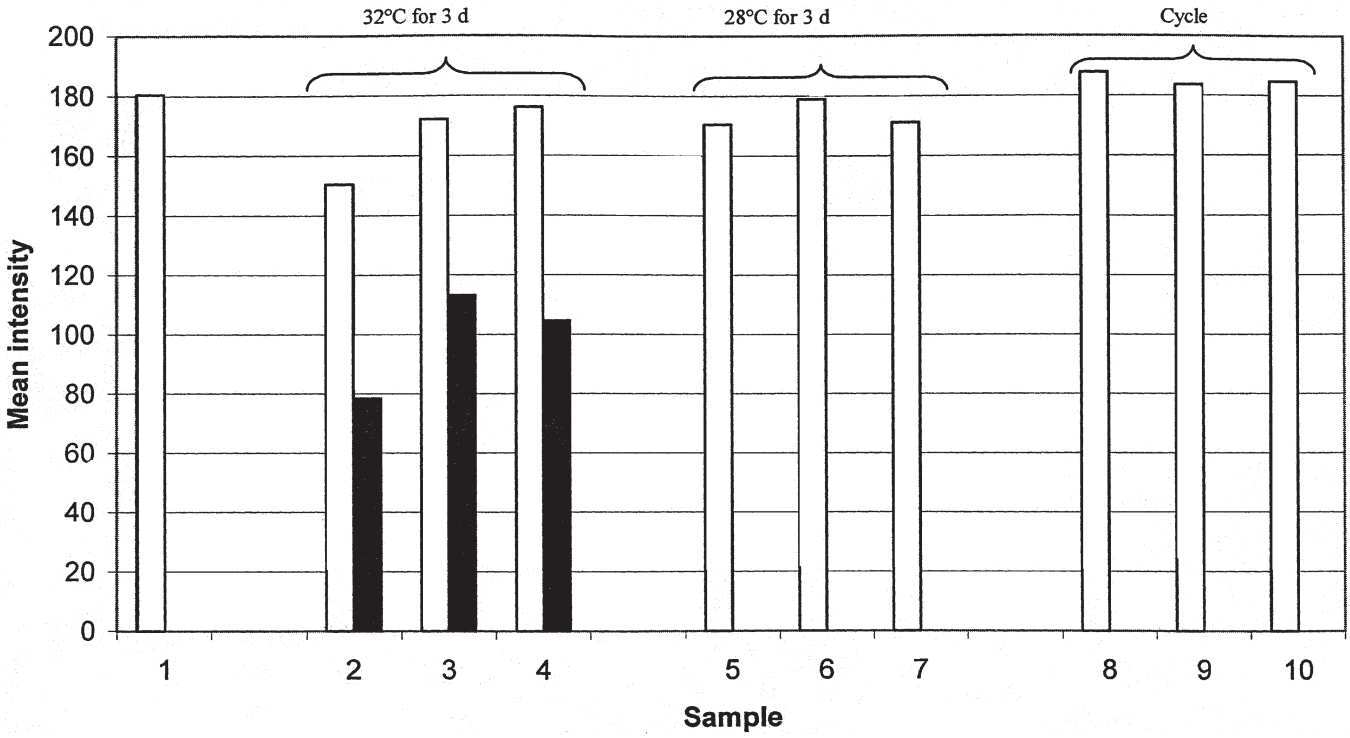

FIG. 3. Mean intensity in images for samples 1, 5–10. Maximal (open bars) and minimal (solid bars) intensities for nonhomogenous samples 2–4.

tested thermal histories increased the liquid lipid fraction moving toward the surface of the sample. The solid–crystalline state would then be more concentrated in the center of the sample and the polymorphic transformation would occur.

DSC measurements were used to determine the relationship between melting point, triglycerides composition, and crystal composition of the bloomed regions in the samples. Melting points of different allomorphs of cocoa butter were reported elsewhere (4). Form V had a melting point of 33.8°C, whereas form VI had a melting point of 36.3°C. The endothermic curves obtained for all samples were similar to that presented in Figure 4 for samples 1 and 4. The average melting point and standard deviation are presented in Table 1. As it is well known, thermal history has a strong influence on the increase in the melting point of chocolate. For the bloomed regions, a larger amount of very stable crystals (e.g., form VI) was found, as expected. The value of the melting point also suggested that these areas were composed of an important fraction of a specific triglyceride (e.g., StOSt). It is even more enhanced for samples 5, 6, and 7, which were stored for 3 d at 28°C. Moreover, DSC measurements suggest that specific thermal history conditions increased the transformation of lipid crystals from crystal V to VI. Indeed, there also was a composition change of these crystals by an increase in the proportion of StOSt in the bloomed regions. This last observation is not in accordance with previous studies where no changes in chemical composition between bloomed and nonbloomed areas were found (10).

Effect of additives on fat bloom. Before heating to 50°C, samples gave rise to fat bloom due to previously noncontrolled thermal conditions (Table 2). Blooming only occurred inside the samples and not on their surface because the samples were wrapped in aluminum foil, which is known to prevent fat bloom in chocolate (1). This suggests that BOB mixed at 2.5% was an excellent additive to prevent fat bloom appearance. After heating to 50°C and storage at 21°C, all samples were placed at 28°C for 1 d and then stored at 21°C for a few days.

Table 2 also indicates NMR and MRI data for all samples 11–17. Results for samples 11–13 with BOB were in accordance with the fact that BOB was a good additive to prevent fat bloom (17). It is suggested that BOB increased the interactions between lipid molecules by controlling their mobility, thus stabilizing the lipid crystals of cocoa butter. However, it is unclear why the melting point of these samples was similar to that of the control sample. For samples 14 and 15 with sucrose, the higher values of T_1 and T_2 indicate more interactions between the populations of protons. Because of this enhanced molecular mobility, the melting point decreased. Since sucrose did not influence the stability of lipid crystals, migration of lipids toward the surface was still occurring, producing fat bloom. For samples 16 and 17 with milk powder, interactions between protons were lower than in dark chocolate (control), and their molecular mobility was enhanced. In addition, the melting point of these samples was higher than for dark chocolate, suggesting that the transformation of the lipid crystals into a more stable form was not preventing fat bloom. These results confirm that fat bloom can occur even if the lipid molecules are in the most stable form (10).

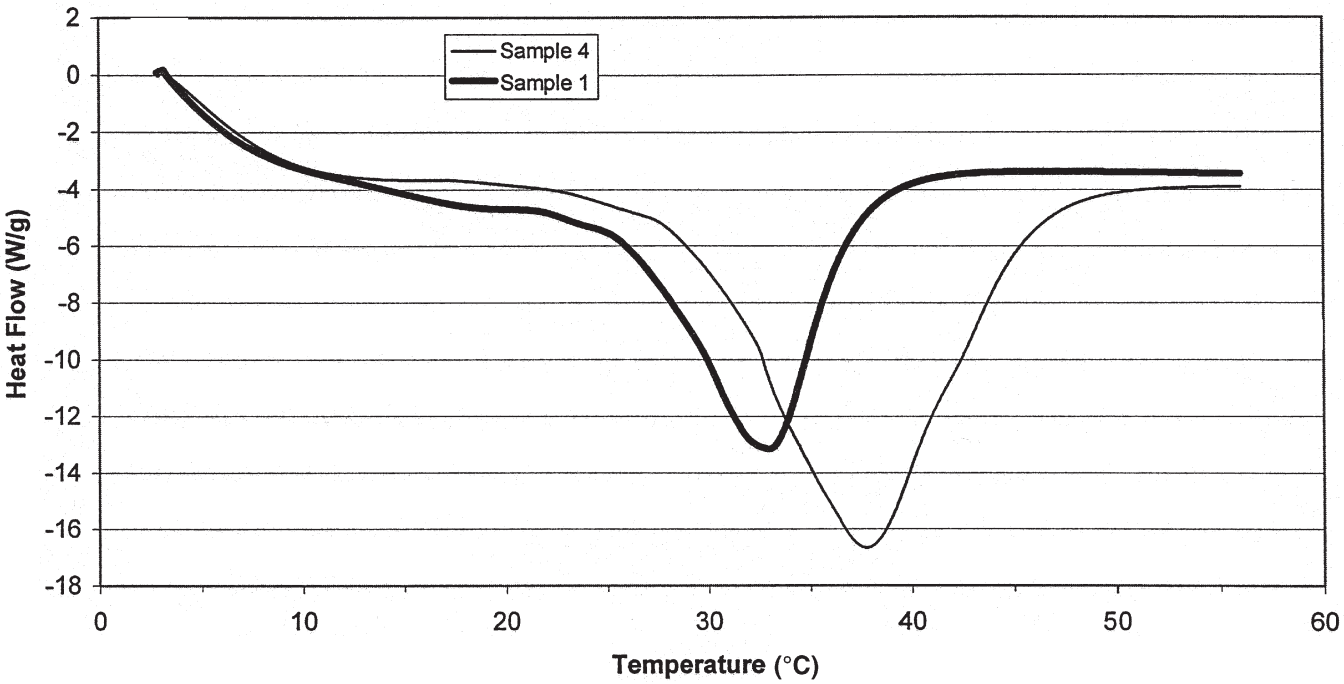

FIG. 4. Differential scanning calorimetry thermograms for samples 1 and 4. Heating rate: 10°C/min.

All samples, even those with BOB, bloomed after completion of the experiment, indicating that heating chocolate samples to 50°C and allowing them to slowly cool down afterward was not the best method to achieve a good tempering. As long as the lipid crystals were not in their stable forms, fat bloom could occur. The physical characteristics of fat bloom differ, depending on the nature of the additive being used when mixed in chocolate. Fat bloom in pure chocolate appears like rounded circles and rings. With BOB, it is composed of little stars, and with milk powder and sucrose, it has more medium-size dots, which are larger than those observed for pure chocolate.

ACKNOWLEDGMENT

Journal paper no. 16245 of the Purdue University Agricultural Experiment Station.

REFERENCES

1. Adenier, H., H. Chaveron, and M. Ollivon, Mechanism of Fat Bloom Development on Chocolate, in *Shelf-Life Studies of Foods and Beverages: Proceedings of the International Flavor Conference*, edited by G. Charalambous, Elsevier Science Publishers, London, 1993, pp. 353–389.
2. Stauffer, C.E., Chocolate and Confectionery Coatings, in *Fats and Oils*, Eagan Press Handbook Series, St. Paul, 1996, p. 91.
3. Loisel, C., G. Keller, G. Lecq, C. Bourgaux, and M. Ollivon, Phase Transition and Polymorphism of Cocoa Butter, *J. Am. Oil Chem. Soc. 75*:425–439 (1998).
4. Wille, R.L., and E.S. Lutton, Polymorphism of Cocoa Butter, *Ibid. 43*:491–496 (1966).
5. Merken, G.V., and S.V. Vaeck, Etude du Polymorphisme du Beurre de Cacao par Calorimetrie DSC, *Lebensm. Wiss. Technol. 13*:314–317 (1980).
6. Schlichter-Aronhime, J., and N. Garti, Solidification and Polymorphism in Cocoa Butter and the Blooming Problems, in *Crystallization and Polymorphism of Fats and Fatty Acids*, Surfactant Science series, edited by N. Garti and K. Sato, Marcel Dekker Inc., New York, 1988, Vol. 31, pp. 363–393.
7. 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).
8. Chapman, G.M., E.E. Akehurst, and W.B. Wright, Cocoa Butter and Confectionery Fats—Studies Using Programmed Temperature X-Ray Diffraction and Differential Scanning Calorimetry, *J. Am. Oil Chem. Soc. 48*:824–832 (1971).
9. Huyghebaert, A., and H. Hendrickx, Polymorphism of Cocoa Butter Shown by DSC, *Lebensm. Wiss. Technol. 4*:59–64 (1975).
10. Adenier, H., M. Ollivon, and H. Chaveron, Le Blanchiment Gras. I. Observation et Commentaires, *Chocolat. Conf. France 315*:7–19 (1975).
11. Miquel, M.E., and L.D. Hall, A General Survey of Chocolate Confectionery by MRI, *Lebensm. Wiss. Technol. 31*:93–99 (1998).
12. Duce, S.L., A. Carpenter, and L.D. Hall, Nuclear Magnetic Resonance Imaging of Chocolate Confectionery and the Spatial Detection of Polymorphic States of Cocoa Butter in Chocolate, *Ibid. 23*:545–549 (1990).
13. Simoneau, C., M.J. McCarthy, D.S. Reid, and J.B. German, Measurement of Fat Crystallization Using NMR Imaging and Spectroscopy, *Trends Food Sci. Technol. 3*:208–211 (1992).
14. Guiheneuf, T.M., P.J. Couzens, H.J. Wille, and L.D. Hall, Visualization of Liquid Triacylglycerol Migration in Chocolate by Magnetic Resonance Imaging. *J. Sci. Food Agric. 75*:265–279 (1997).
15. Cebula, D.J., K.W. Smith, and G. Talbot, DSC of Confectionery Fats, Pure Triglycerides. Effects of Cooling and Heating Rate Variation, *Manufact. Confect. 9*:135–139 (1992).
16. Eads, T.M., Magnetic Resonance, in *Food Analysis*, edited by S.S. Nielsen, 2nd edn., Aspen Publishers, Gaithersburg, 1998, pp. 455–481.
17. Hachiya I., T. Koyano, and K. Sato, Seeding Effects on Solidification Behavior of Cocoa Butter and Dark Chocolate. II. Physical Properties of Dark Chocolate, *J. Am. Oil Chem. Soc. 66*: 66–75 (1989).

[Received March 30, 2000; accepted May 23, 2001]