Surface Roughness During Storage of Chocolate: Fractal Analysis and Possible Mechanisms

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ABSTRACT: Laser scanning microscopy and fractal analysis were used to determine roughness in the surface of chocolate samples stored under cycling temperature conditions (16 to 26°C) for 24 d. The four samples varied in the source of fat: 100% cocoa butter (CB), lauric and nonlauric fat replacers, and CB with 2% of nonlauric fat replacer. The response variable was the area-scale fractal complexity (Asfc), equivalent to a fractal dimension. Asfc increased with time to an asymptotic value (AV) in much the same way as whiteness index, both being accepted proxies of surface bloom. Images produced from topographical data revealed clearly the increase in roughness. Chocolate samples prepared with CB replacers exhibited an induction period and a slower rate of change in surface roughness than chocolate containing only CB. A linear relationship between a normalized roughness and the square root of time was followed by CB chocolate samples for the period before reaching AV. This result suggests that either diffusion or capillary flow may be the mechanism involved in fat migration to the surface.

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KEY WORDS: Bloom, capillary flow, chocolate, cocoa butter, fat bloom, microscopy, roughness, surface topography.

Fat bloom is the whitish haze formed on the surface of chocolates. This physical phenomenon is caused by the dispersion of light on the small fat crystals (≥5 μm) that are formed on the surface (1) and deprives chocolates of a smooth appearance, a bright color, and gloss (2,3). This quality problem is of major concern to the confectionery industry, which has annual sales of about US$70 billion (4). How this phenomenon takes place is not clearly understood, but most theories point out that fat migration to the surface plays a determinant role. Beckett (5) explains that there are four main ways in which chocolate fat bloom occurs. One cause is related to an incorrect precrystallization step (tempering) of cocoa butter leading to form IV, a relatively soft structure, which transforms over a period of days to form V. During this transformation, contraction occurs and latent heat is released, a combination of effects that propels to the surface some of the liquid fat remaining between the solid particles; the mechanism possibly is mediated by temperature fluctuations (3). Another cause is related to the transition from form V to form VI over a long period of storage; transformations associated with this change are of the same nature, but at a much lower rate. An additional source of fat bloom is associated with storage temperature, where low-m.p. crystals melt, migrate to the surface, and recrystallize without occasion for re-tempering (5). The fourth mechanism is associated with oil migration in composite structures, such as a chocolate with a nut base filling.

The mechanism by which cocoa butter migrates to the surface of chocolate is not clearly understood. Some authors explain that the increase in volume when cocoa butter melts should force the liquid toward the surface through pores and microfractures (6). However, the most cited mechanism is fat diffusion (7–9). Recently and contrary to what has been stated so far, Aguilera *et al.* (4) have argued that diffusion does not seem to be a dominant mechanism for bulk flow of cocoa butter within the chocolate matrix, since fat is most likely to move under capillary forces. They explain that the traditional criterion used to verify the diffusion theory—a square-root-to-time dependence for mass transport at short times—is a necessary but not sufficient proof since the analytical solution to the Lucas–Washburn equation for capillary rise at short times has exactly the same time dependence.

As summarized by Aguilera *et al.* (4), researchers in the field have developed many different ways to generate and assess kinetic data of fat migration. Some researchers have conducted experiments under isothermal conditions (7,9) whereas others have induced fat bloom by cycling the temperature (2,10). Techniques used to assess or measure fat migration (and blooming) to the surface of chocolate vary from a simple visual inspection or color measurement to sophisticated analytical techniques such as HPLC, NMR imaging, and atomic force microscopy (4,7,9,10).

During storage of chocolate, small, spiky cocoa butter crystals begin to appear on the surface (11). Over time, these crystals continue to increase in number and size as bloom progresses (3). Hence, it can be hypothesized that surface roughness is directly related to the extent of fat crystallization at the surface and that this phenomenon, in turn, is the main cause of bloom in chocolate. To examine the previous hypothesis, one must rely on a precise method that allows measuring surface roughness at the relevant scale (microns). Changes in topography of food surfaces can be studied by means of a fractal parameter (12), and the scale-sensitive fractal analysis developed

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by Brown (13) seems to be an appropriate tool to characterize the surface of chocolate by means of the area-scale fractal complexity (Asfc) parameter (14).

The objective of this paper was to implement a technique based on laser scanning microscopy followed by fractal analysis to adequately measure the surface topography of chocolate and chocolate containing cocoa butter replacers (CBR) as they undergo simulated storage conditions and to study the kinetics of surface roughness development.

MATERIALS AND METHODS

Materials, sample composition, and chocolate preparation. Milk chocolates with different fat sources were prepared at the pilot plant of the chocolate manufacturer Arcor S.A. (Santiago, Chile). The different samples were: (i) chocolate containing only cocoa butter from Indonesia as fat source (sample CB); (ii) a compound coating having hydrogenated palm kernel oil as source of lauric fat (sample LF), (iii) a compound coating having hydrogenated cottonseed oil as source of nonlauric fat (sample NLF), and (iv) a chocolate that was made of cocoa butter and 2% of NLF on a total weight basis (sample CB/NLF). The approximate final formulation of chocolate samples (as they are generically referred to in the text) was the following: sugar, 50 ± 2%; total fat, 25 ± 3%; cocoa liquor, 12 ± 2%; nonfat milk powder, 10 ± 2%; cocoa powder, 2.4 ± 1%; and lecithin 0.5%. The fat source was melted at 60°C and mixed with the other ingredients. The resulting chocolate mass was tempered using a cyclothermic method similar to the one employed by Lohman and Hartel (1). The chocolate mass at 60°C was cooled initially to 26°C and held at that temperature until the viscosity reached a constant value (2 h). Then the temperature was raised and kept at 33°C for 30 min to melt unstable crystals and promote formation of stable polymorphs. The action was repeated (cool to 29°C and warm to 33°C), and the tempered chocolate was poured into plastic molds and cooled to 15°C and held for 24 h.

Bloom induction experiments. The samples were placed inside three chambers that cycled the temperature between 16 (±1) and 26°C (±1°C) every 3, 6, or 12 h. The chambers consisted of an expanded polystyrene box ($30 \times 30 \times 30$ cm^3) with two 7.5 W light bulbs placed at the bottom of the box, which were connected to a power source. The fluctuating temperature in each box was controlled and registered using a computer program written in Visual Basic V. 6.0 (Microsoft Corporation, Santa Monica, CA) that activated a cold air current into the chamber so that the transient time of the cycle was less than 20 min. Four rectangular pieces (20×10 mm and 6 mm thickness) of each sample (CB, LF, NLF, and CB/NLF) were introduced in each box, thereby cycling their temperature between 16 and 26°C every 3, 6, and 12 h. The relative humidity was maintained between 45 and 50% to avoid sugar bloom (15).

Measurement of surface topography. A scanning laser microscope (SLM) assembled at the Surface Metrology Laboratory of Worcester Polytechnic Institute was used to measure the surface topography (height z, as a function of position x,y) of chocolate samples. The SLM consisted of a triangulation laser sensor for height measurements (LC-2210; Keyence, Fair Lawn, NJ), positioning stages (Compumotor 10000 Series; Parker, Rohnert Park, CA), and controllers coupled with UBM software (with Microfocus v. 1.9; Messtechnik GmbH, Ettlingen, Germany). Measurements were made in rectangular pieces from the same chocolate sample using the microscope's finest resolution (1 μm). The same area (127×127 μm) in the chocolate bar was scanned in triplicate around a fixed point in the sample at every time during storage. Data were stored digitally for subsequent analysis.

Analysis of data. A scale-sensitive fractal analysis using SURFRAX® software Beta version 2.0 (Burlington Computer Systems, Waterbury Center, VT) developed by Brown *et al.* (16) was performed on data to determine some roughness parameters, such as the statistical average surface roughness (ARa), and the fractal parameter, Asfc. Asfc is determined by the patchwork method, an exercise of repeated virtual tiling with triangular patches applied to the measured data. In successive iterations a smaller triangular size is used, which represents the scale of measurement, and a relative area is obtained (i.e., a ratio between the area occupied by the triangular patches and the projected area of the surface). A log-log plot of relative area vs. the area of the triangle generates a graph similar to Richardson's plot for rough lines (14,16). Asfc is equal to (–1000) times the slope of the linear portion of the logarithmic area-scale plots; hence, it is related to a fractal dimension (FD), which is calculated as two minus twice the slope of the regression line fitting the linear region. Since linearity does not necessarily imply the self-similarity of fractals, Asfc rather than FD was used to describe the surface roughness. Large Asfc values are an indication of higher complexity, intricacy, or roughness of the surface (14,16). Images of topographical data were obtained directly from the SURFRAX software. For modeling purposes, data were normalized using the following relationship:

$$NR = \frac{Rough_t - Rough_o}{Rough_f - Rough_o} \quad [1]$$

where *Rough* stands for the value of the roughness parameter (either ARa or Asfc) and subscripts t, o, and f refer to a specific time, initial and final times of the experiment, respectively. NR relates the extent of roughness at any time to the total increase in roughness at the end of storage.

Analysis of the square-root-of-time dependence for mass transport. As discussed earlier, fat bloom is intimately related to liquid fat migration from the center to the surface of the chocolate piece. Researchers have analyzed fat migration by means of the transient diffusion equation (Fick's second law). This equation for a plane sheet, when expressed as the ratio m_t/m_∞, gives a linear relationship when plotted against $\sqrt{t}$:

$$\frac{m_t}{m_\infty} = \sqrt{\frac{4D_{app}}{\pi l^2}}\sqrt{t} = K\sqrt{t} \quad [2]$$

where m_t is the mass transported at time t, m_∞ the mass transferred when equilibrium is reached, and l the characteristic

length. From this equation a constant apparent diffusion coefficient D_{app} may be derived that represents the initial diffusion rate of the fat. Similar expressions have been used by Miquel *et al.* (7) and Ziegleder *et al.* (9) to describe fat migration within filled chocolate products.

The practical interpretation of the equation is that bloom varies with the square root of time, and data plotted accordingly yield a straight line. It can be assumed that the left-hand side of Equation 2 is proportional to the normalized roughness (NR) value if roughness is the result of the amount of fat crystallized over the surface. Thus, Equation 2 is transformed into:

$$\mathrm{NR} = K\sqrt{t} \qquad [3]$$

where K is the slope of the straight line.

In addition, fat bloom could be thought of as the movement of liquid cocoa fat through interparticle passages and connected pores, under capillary forces. As discussed by Aguilera *et al.* (4), the most common expression to analyze capillary rise is the Lucas–Washburn equation (17):

$$\frac{2}{r}\gamma\cos\theta = \frac{8}{r^2}\mu h\frac{dh}{dt} + \rho g h \qquad [4]$$

where h is the height of the fluid, γ its surface tension, θ the contact angle between the fluid and the capillary wall, r the radius of the capillary, ρ the density of the fluid, μ the viscosity of the fluid, and g the universal gravitational constant.

The short time limit ($t \to 0$) for Equation 4 predicts that the displacement h for a horizontal capillary should be proportional to the square root of time according to:

$$h = \sqrt{\frac{r\gamma\cos\theta}{2\mu}}t \qquad [5]$$

Capillary flow relies on parameters that are difficult to determine (i.e., pore radius, surface tension, viscosity, and contact angle) because they depend on conditions existing within the microstructure of chocolate. An "average" pore radius requires knowledge of the distribution of pore sizes within the matrix. Contact angle or equilibrium wetting angle is especially difficult to evaluate when the surface under study is rough or heterogeneous, as may be inside interparticle pores of chocolate. "Viscosity" refers to the viscosity of the mass flowing in the pores, which at any single temperature may include liquid fat and fat crystals.

As can be seen, analytical solutions at short times for both cases (Eqs. 2 and 5) yield to the same time dependence for mass transfer (Eq. 3); however, the mechanism involved is completely different.

The analysis presented in this paper is based on the root-square-of-time dependence shown in Equation 3. NR values were fit to Equation 3 when working with CB chocolate samples by using a linear least square fitting analysis. To evaluate the goodness of fit, the determination coefficient, the minimum sum of squares (mss), and the relative percent difference (P) between experimental and predicted values were calculated. The mss and P values were calculated as:

$$\mathrm{mss} = \sum^{v}(y_{\mathrm{exp}} - y_{\mathrm{calc}})^2 \qquad [6]$$

$$P = \left(\frac{100}{\nu}\right)\cdot\sum^{v}\frac{\left|(y_{\mathrm{exp}} - y_{\mathrm{calc}})\right|}{y_{\mathrm{exp}}} \qquad [7]$$

where y_{exp} and y_{calc} are the experimental and calculated values for NR and ν is the number of experimental points. For curves having a sigmoid shape, a P value ≤ 10 is considered to be a good fit and a value ≤ 5 an extremely good fit.

RESULTS AND DISCUSSION

Analysis of raw data. Changes of surface roughness parameters (Asfc or ARa) of samples subjected to a 3-h temperature cycle are shown in Figures 1A and 1B. Similar trends are observed when plotting either Asfc or ARa as the roughness descriptor. The surface of unbloomed chocolates was smooth, as reflected by the low initial ARa values (between 600 and 900 nm). These values increased as blooming progressed, reaching an ARa value of 2.4 μm in CB chocolate and values of 1.4–1.6 μm in the other samples, after 24 d of experiment. These results compare reasonably well with those reported by Hodge and Rousseau (10), who, using an atomic force microscope to characterize surface microstructural changes of milk chocolates, found a threefold increase in surface roughness after cycling the temperature between 20 and 34°C during three 24-h cycles. Data also exhibit the same tendency with time as those reported by Bricknell and Hartel (2), obtained by using the whiteness index, a color parameter derived from color measurements over the surface, but with a smoother trend and less data variation (e.g., SD).

Figures 1C and 1D show the changes in surface roughness expressed as the fractal-parameter Asfc, when cycling the temperature every 6 and 12 h. Surface roughness represented by either Asfc or by the statistical parameter ARa (data not shown) increased in all cases always at a faster rate and to a larger extent when cocoa butter was used as the unique fat source (CB chocolate). This is in agreement with results reported by Lohman and Hartel (1), who found that fat replacers may actually act as antibloom agents by slowing down the rate of polymorphic transformation (therefore bloom formation), as they might provide a more complex crystalline structure along with increased thermal stability.

The parameter ARa was not used in further analyses because statistical roughness parameters often fail to establish functional correlations with physical observations (18). Moreover, ARa is not a scale-sensitive parameter as is Asfc.

Although Asfc values of CB chocolate increased steadily from time zero to an asymptotic value, LF, NLF, and CB/NLF samples appeared to present a lag or induction period that was absent in CB chocolates. Hartel (19) also reported longer lag times for fat bloom when anhydrous milk fat was added to the chocolate formulation. It can be observed that in this set of

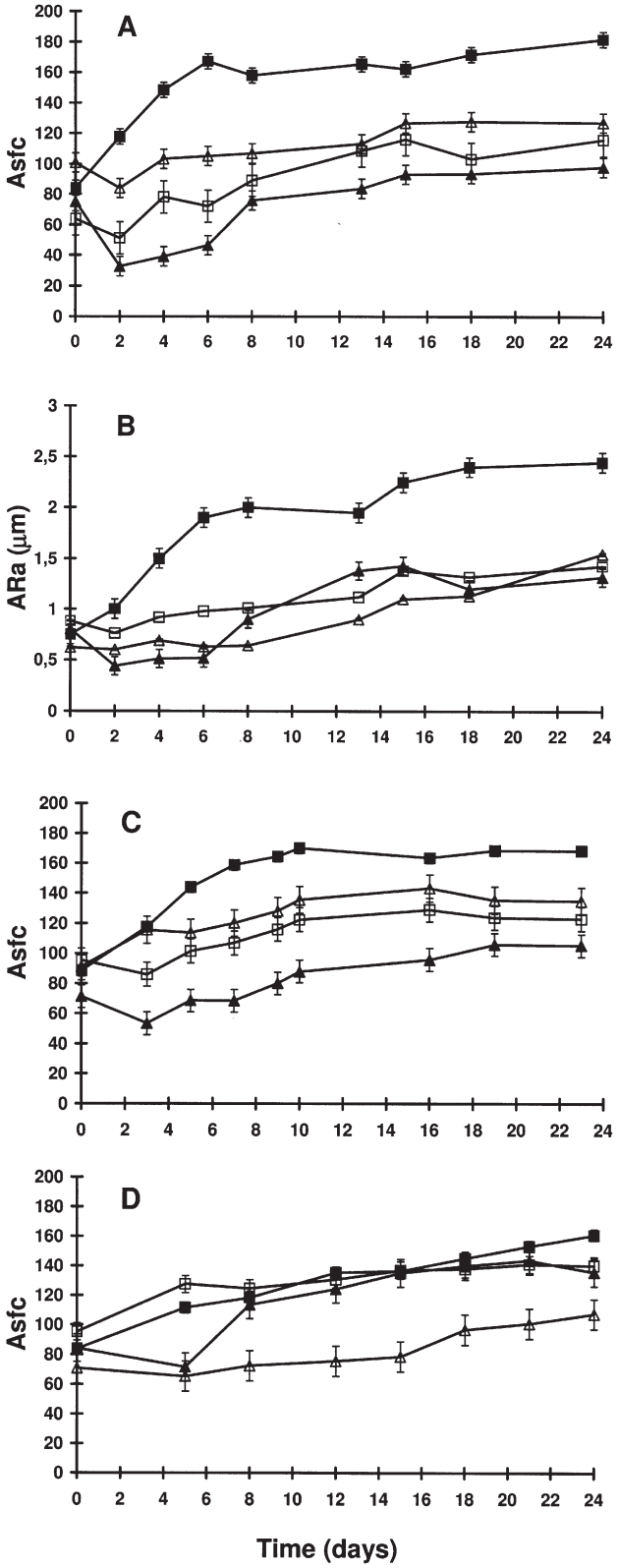

FIG. 1. Changes in surface roughness as a function of storage time for chocolate samples made of cocoa butter (■), lauric fat (△), nonlauric fat (□), and cocoa butter with 2% nonlauric fat (▲), subjected to temperature fluctuation between 16 and 26°C every (A) 3 h (Asfc parameter), (B) 3 h (ARa parameter), (C) 6 h (Asfc parameter), and (D) 12 h (Asfc parameter). Bars represent the SD. Asfc, area-scale fractal complexity; ARa, average surface roughness.

experiments the final constant Asfc value was higher for CB chocolate than for the other samples for all temperature conditions. The slower rate of surface roughness development shown by samples containing CBR may be due to the higher melting behavior (e.g., higher solid fat content at any temperature) of these fats when compared with that of cocoa butter (19). Bricknell and Hartel (2) followed the changes in the whiteness index of chocolates having amorphous sugar in their formulation (instead of the usual crystalline form), which were stored under temperature cycles between 19 and 29°C for 22 d. Their data followed the same general trend as the one reported here for surface roughness, a possible indicator that bloom (measured as color change) is related to surface roughness.

Since initial values of Asfc for samples varied between 65 and 100, data were normalized so that relative changes in surface roughness could be modeled. An asymptotic value of Asfc between 165 and 180 seemed to be achieved in all cases for the CB chocolate sample (although for the 12-h temperature cycle the value had not yet stabilized) independent of the time interval between fluctuations. However, it can be noticed that this value was achieved earlier as the time interval between fluctuations decreased.

Figure 2 exhibits a gallery of images representing in graphical form changes in surface topography of a CB chocolate sample (3-h fluctuation time interval) at different storage times. These images allow one to follow visually changes in roughness through time and their relation to the fractal parameter Asfc.

Analysis of the square-root-of-time dependence for mass transport in CB chocolate samples. Figure 3 shows plots of NR (using Asfc) as a function of the square-root-of-time for CB chocolate (3-, 6-, and 12-h fluctuation time intervals). As reported by Ziegleder *et al.* (20) the square-root-of-time dependence is only observed in early stages of fat migration whereas in a later stage the process slows down and approaches saturation. The slope of the linear portion of graphs (K) decreased as the time temperature cycles lengthened. The values obtained for K were significantly different: 0.35 ± 0.01, 0.30 ± 0.01, and 0.18 ± 0.01, when cycling every 3, 6, and 12 h, respectively. These results are a further confirmation of what has been exposed by Miquel *et al.* (7) and Aguilera *et al.* (4). Accordingly, in a study of triolein migration in chocolate under storage at constant temperature, Ziegleder *et al.* (9) found that saturation values were reached only at high temperatures (e.g., >26°C) whereas at lower temperatures the rate of migration was slower and could be completely described by a linear relationship for the whole storage period.

The linearity when plotting NR against $\sqrt{t}$ is in accordance with the behavior that has been observed by means of other descriptors such as direct quantification of fat migration and the whiteness index, confirming that surface roughness is intimately related to fat bloom. As mentioned previously, the square-root-of-time dependence is equally valid for Fickean diffusion as for flow in capillaries; therefore, the observed behavior cannot be conclusive in terms of the mechanism involved in the development of surface roughness. However, given that chocolate is a particulate medium at micron dimensions, capillary forces may be a major driving force for bulk flow of fat. On the other hand,

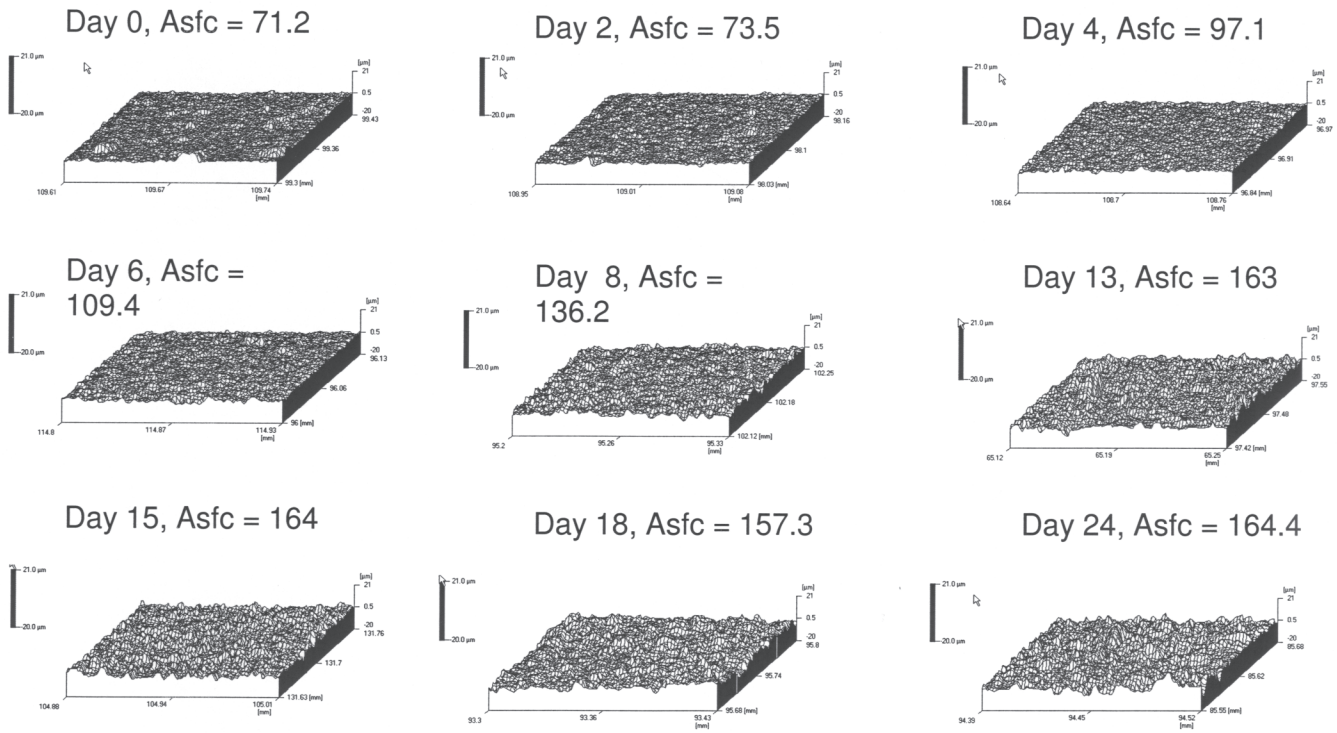

FIG. 2. Gallery of images (derived by SURFRAX®; Burlington Computer Systems, Waterbury Center, VT) representing changes in surface topography of a chocolate made of cocoa butter (3-h fluctuation time interval) at different storage times. For abbreviation see Figure 1.

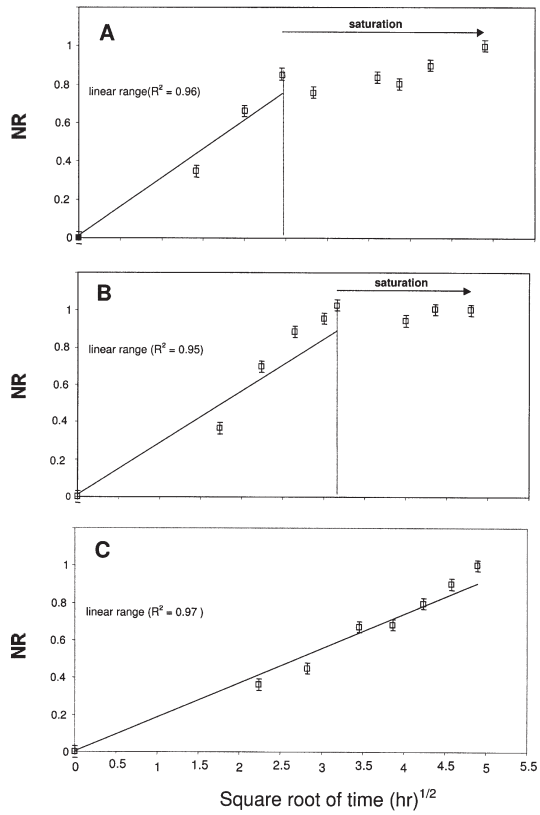

FIG. 3. Normalized surface roughness (NR) against square root of time of chocolate samples made of cocoa butter subjected to temperature fluctuation between 16 and 26°C every (A) 3 h, (B) 6 h, and (C) 12 h.

driving forces that promote molecular diffusion in plain chocolate have not been clearly demonstrated although a gradient in TAG concentration has been suggested in the case of chocolate fillings (8). Consequently, further mass transfer experiments and microstructural evidence are needed to elucidate the actual mechanism(s) by which fat migrates within the microstructure of chocolate.

Another question that may be asked after observing the different curves is: Why, as the time interval of temperature fluctuation increases, does the time to achieve the saturation value for roughness also increase, and hence the rate of change decrease? In fact, all samples were held at the high temperature of 26°C for the same time (12 d during the 24-d storage period). It can be postulated that if the square-root-of-time dependence of the rate holds even for very short times (e.g., hours) and is independent of the extent of the accumulated change at any moment (i.e., there is no memory), then the length of the time interval does affect the result. In effect, in a 24-h period the accumulated effect would vary for the 3-, 6-, and 12-h time intervals in the ratio $4 \times (3)^{1/2}$, $2 \times (6)^{1/2}$, and $1 \times (12)^{1/2}$, or 6.9:4.9:3.5 (or 1:0.80:0.51), respectively. This ratio is almost the same as that obtained for the ratios of K for the three time intervals, namely, 1.0:0.86:0.51. Hence, the lapse of the time interval during which the temperature fluctuates seems to have an impact on the rate, and thus on the time required to reach the saturation value.

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