

Recrystallization in Ice Cream After Constant and Cycling Temperature Storage Conditions as Affected by Stabilizers

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ABSTRACT

Storage under low constant temperature (-30°C) had no effect on the overall ice crystal size of stabilized or unstabilized ice cream samples; storage at a higher temperature (-16°C) showed clear evidence, based on sample microstructure, of recrystallization, probably through Ostwald ripening and accretion. Temperature cycles ($-15 \pm 5^{\circ}\text{C}$) of samples after hardening (-30°C) had an even greater effect than did storage at a high constant temperature (-16°C). Also, increase of the number or time length of cycles had greater impact than did an increase in amplitude. After extended thermal fluctuation, smaller crystals disappeared. The predominant recrystallization mechanism at this stage would have most likely involved partial melting and refreezing of ice crystals. With this mechanism, stabilizers exerted a measurable effect of retarding or preventing crystal growth. (**Key words:** ice crystals, size distribution, ice cream, stabilizers)

Abbreviation key: CMC = Carboxymethyl cellulose, LBG = locust bean gum, X_{50} = ice crystal diameter at 50% of the cumulative distribution function of the sample.

INTRODUCTION

Ice crystals formed after scraped-surface freezing and hardening of ice cream are unstable and will undergo recrystallization if they have not been effectively stabilized. Recrystallization is the process of changes in number, size, and shape of ice crystals during frozen storage. Although the amount of ice stays constant with constant temperature throughout this process (dictated by the equilibrium freezing curve), recrystallization can alter and damage the structure and texture of ice cream (11, 31). Recrystallization basically involves small crystals disappearing, large crystals growing, and crystals fusing

together (20). Isomass recrystallization (rounding off) refers to changes in surface or internal structure so that crystals with irregular shapes and large surface-to-volume ratios assume a more compact structure (9). Thus, sharper surfaces are less stable than flatter ones and will show a tendency to become smoother over time (20). Migratory recrystallization refers in general to the tendency of larger crystals to grow at the expense of smaller crystals (9). Ostwald ripening is a type of migratory recrystallization that occurs at constant temperature and pressure due to differences in surface energy between crystals. However, migratory recrystallization is greatly enhanced by temperature fluctuations (heat shock) inducing a melt-refreeze behavior due to ice content fluctuations. Melt-refreeze behavior can lead to complete disappearance of smaller crystals during warming and growth of larger crystals during cooling or to a decrease in size of crystals during partial melting and regrowth of existing crystals during cooling. Melt-refreeze should occur to a greater extent at higher temperatures and more rapidly for smaller crystals (20). Accretion refers to a natural tendency of crystals in close proximity to fuse together. The concentration gradients in the areas between the crystals are high, thus, material is transported to the point of contact between crystals, and a neck is formed. Further rounding off will occur because a high curvature surface like this has a natural tendency to become planar (20). Typically, ice crystals in ice cream exit the freezer with a mean size of ~ 30 to $35 \mu\text{m}$ and increase to ~ 45 to $50 \mu\text{m}$ after hardening (19). However, according to the recrystallization mechanisms previously described, recrystallization may take place immediately after draw (20) due to the low amounts of frozen water or during storage, especially during fluctuations of temperature.

Stabilizers used in ice cream formulations are added in relatively small amounts (0 to 0.5%). They increase the viscosity but have no significant effect on freezing point or freezing properties of the mix (1, 4, 5, 27, 29, 33). They do not affect the nucleation process (28) or thermomechanical properties of the mix or unfrozen phase (3, 13, 15, 17). Stabilizers have a high water holding capacity that is effective in

Received August 31, 1998.

Accepted March 15, 1999.

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smoothing the texture and giving body to the product, but their major role is to prevent crystal growth as temperature fluctuates during storage. In summary, stabilizers improve smoothness of body, retard or reduce recrystallization of ice and crystallization of lactose during storage, slow moisture migration from the product to the package or the air, give uniformity of product and hold flavoring compounds in dispersion (e.g., ripple sauces), and give desired resistance to melting (12, 22).

Harper and Shoemaker (18) showed that the viscosity of model solutions of frozen desserts was not related to the recrystallization behavior (rate) and that locust bean gum (**LBG**) was not an effective inhibitor of recrystallization under their test conditions. They also reported that migratory recrystallization was the predominant mechanism and that the effect of temperature fluctuations was quantitatively greater than recrystallization at constant storage temperature. Min et al. (25) concluded that stabilizers [sodium alginate, carboxymethyl cellulose (**CMC**), gelatin, carrageenan, and LBG] do not inhibit but rather delay recrystallization, and that differences between stabilizers are a result of the structure likely influencing water molecule migration. Sutton et al. (35) showed that recrystallization rates of a model solution of the unfrozen phase (40% fructose) was dependent on ice phase volume and temperature, (i.e., a decrease in ice phase volume or temperature decreased the rates). Accretion was initially the predominant mechanism, but migratory recrystallization became predominant as crystals grew and suggested that recrystallization in later stages was driven by a nonrandom diffusion process. The addition of LBG to the system decreased recrystallization rates (36) and was tentatively explained by weak absorption of a stabilizer onto the crystal surface impeding growth. Another study (34) showed that LBG concentration had a plateau effect on recrystallization rates (i.e., low concentration had no effect); an increase in concentration decreased the rate to a minimum value, which stayed constant for higher concentrations. However, guar gum reduced recrystallization and reached a minimum value similar to that of LBG yet increased at higher concentration, thus promoting recrystallization. The varied degrees of branching between the two gums were proposed as a possible cause of these differences. A later study (37) with enzyme-modified guar gum and pectins confirmed the plateau effect of stabilizers in the recrystallization rate-concentration curve. In a recent study, Sutton and Wilcox (38) reported no dependence of the recrystallization rate on the ice phase volume in ice cream as was previously reported (36)

for the model fructose solution. However, the addition of LBG to ice cream reduced the rate of crystal growth during heat shock and constant temperature storage.

Donhowe and Hartel (7) studied recrystallization in ice cream at steady temperatures (-5 , -7 , -10 , and -15°C) and sinusoidal fluctuations (1°C) and reported that accretion was predominant in all cases; however, melt-refreeze recrystallization was apparent during fluctuations. Also, higher amplitude rendered an increased recrystallization rate; low storage temperature (-20°C) did not cause changes in crystal size. Moorty and Balachandran (26) arrived at the same conclusions for storage at low temperature (-15°C) in unstabilized and stabilized low fat ice cream and also concluded that stabilizers exert a minimal effect in crystal growth. Hagiwara and Hartel (17) reported smaller ice crystals in stabilized ice cream for all combinations of sweetener and storage temperature, but inhibition of recrystallization rate was only statistically significant for stabilized samples containing high fructose corn syrup. Another study (24) showed that after storage at -15°C , this effect was negligible compared with that exerted by the different sweeteners. However, after storage at -9.5°C significant differences were observed but only in samples made with sucrose containing carrageenan or LBG. Caldwell et al. (6) reported smaller ice crystals after heat shock in stabilized (carrageenan and guar gum) ice cream. The fusion of crystals was predominant in unstabilized samples, whereas stabilized samples showed a thicker serum phase between crystals, and air was more finely distributed in the sample. More air crevices were observed in unstabilized samples and coincided with shrinkage observed in packages. Therefore, stabilizers seemed to hold the air once the air bubble was broken.

This study focused on the effect of stabilizers on recrystallization of ice cream under storage conditions of constant and fluctuating temperatures. It follows a previous study (10) on the effect of ingredients, processing variables (i.e., overrun and rheology of the mix), and addition of polysaccharide stabilizers on the initial size distribution of ice crystals in ice cream. The previous study reported that polysaccharide stabilizers (**CMC**, guar gum, and xanthan gum) did not affect the initial ice crystal size distribution of model solutions or ice cream dynamically frozen in a batch process.

MATERIALS AND METHODS

Ice cream mixes consisted of 10% milk fat (fresh cream; Gay Lea Foods, Weston, ON, Canada), 11% instant skim milk powder (Gay Lea Foods), 10%

sucrose (Red Path, Toronto, ON, Canada), 5% corn syrup solids with 42 dextrose equivalent (Casco Inc., Etobicoke, ON, Canada), and 0.15% emulsifier blend (80% mono- and diglycerides and 20% polysorbate 80; Food Specialties, Halton Hills, ON, Canada). Stabilizers, when added, were incorporated at a concentration of 0.26% and included CMC, guar gum, and xanthan gum (Germantown Canada Inc., Scarborough, ON, Canada). Mixes were prepared by addition of dry blended ingredients to preheated water and cream (65 to 70°C), batch-pasteurized at 74°C for 15 min, homogenized at 17.2 MPa (2500 psig) and 3.4 MPa (500 psig) second stage on a homogenizer (V15-8T; Gaulin Corporation, Everett, MA), and aged overnight at 4°C. Aliquots of 2 L were frozen (Taylor Batch Freezer, model B733-32; Tekni-Craft, Rockton, IL). The refrigeration system was turned off when the semifrozen slurry reached -5°C, then samples were further whipped for a total of 15 min. Overrun was measured, and samples of approximately 50 g were extruded into plastic cups, covered, and stored at -30°C for the hardening period (24 h).

Samples, after hardening, were stored at -30°C and at -16°C for 4 wk, both of which were considered constant temperature storage, although there is a small, inherent fluctuation due to the refrigeration cycle in the freezer. After constant temperature storage, samples were also subjected to programmed temperature cycles according to the parameters shown in Table 1 (sets 1, 2, 3, and 4). Temperatures were monitored during the cycles by inserting the probe of a thermocouple thermometer (model 8112-10; Cole Parmer Instrument Company, Vernon Hills, IL) into the core of the sample. Cycle times were determined experimentally to allow the core temperature to reach the freezer temperature and hold this temperature for not less than 10 min. Samples previously stored at -30°C were allowed to reach the higher limit of the temperature cycle (freezer setting) before the freezer controller was set to cycle. Additional cycles (sets 5 and 6) were designed for ice cream samples with and without guar gum to study the effect of the cycle time length and prolonged number of cycles as shown in Table 1.

Ice crystals were measured from images taken using cryoscanning electron microscopy (Hitachi S-570 SEM; Hitachi Ltd., Tokyo, Japan; with Emscope SP2000A Sputter-Cryo Cryogenic Preparation System, Emscope Ltd., Kent, United Kingdom), after quenching and fracturing samples under liquid nitrogen, as described previously (10). Digital images were collected using the Voyager Acquisition System (Noran Instruments, Middleton, WI). Sample sizes of not less than 100 crystals were obtained from at least

TABLE 1. Temperature cycle programs for ice cream.

| Ice cream | Previous storage temperature | Temperature cycle | Cycle time length | Cycles |
|--------------------|------------------------------|-------------------|-------------------|--------------|
| | (°C) | (°C) | (h) | (no.) |
| Set 1 | -16 | -15 ± 2 | 3 | 3 |
| Set 2 | -30 | -15 ± 2 | 3 | 3 |
| Set 3 | -30 | -15 ± 5 | 4 | 3 |
| Set 4 | -30 | -15 ± 5 | 4 | 9 |
| Set 5 ¹ | -30 | -15 ± 5 | 4 | 15, 25 |
| Set 6 ¹ | -30 | -15 ± 5 | 8 | 3, 9, 15, 25 |

¹Sets 5 and 6 were performed only for samples without stabilizer or that contained guar gum.

two different locations (fields) of each specimen using magnifications of 150 and 250 times, depending on the sample. The Mocha™ Image Analysis Software (Jandel Scientific, Sausalito, CA) was used to calculate the cross section area and the shape factor (0 to 1, 1 being a circle) of the ice crystals by manual tracing of the perimeter of the sockets. Ice crystal size distributions were characterized by the logistic model with a cumulative distribution of equivalent diameters as previously described by Flores and Goff (10). Parameters used to characterize the distribution were the ice crystal diameter at 50% of the cumulative distribution function of the sample (X_{50}) and the slope of the cumulative distribution at X_{50} . Calculations of ice content of ice cream at different temperatures were performed as previously described (10). For statistical purposes, the different formulations were replicated once, and the measurements of crystal sockets were performed for two specimens of each replicate and treated independently. Statistical analysis of the data was carried out using SAS (32). The ANOVA and the Ryan-Einot-Gabriel-Welsch Multiple F test (REGWF) were used to determine statistical significance ($\alpha = 0.05$) of differences between the means.

RESULTS AND DISCUSSION

Constant Temperature Storage

The reported X_{50} values for the ice creams after storage (Table 2) are smaller than means of ice crystal sizes (~45 to 50 μm) as reported previously (25). This phenomenon may occur because X_{50} values are analogous to median values of the fitted data. As such, X_{50} values are typically lower than mean values when a preponderance of small crystals compared with large ones exists, as probably occurs in fresh ice cream. This class of sizes would be more easily de-

TABLE 2. Ice crystal diameter at 50% of the cumulative distribution function of the sample (X_{50}) and slope at X_{50} for ice cream after hardening and after 4 wk of storage at constant temperatures.

| | After hardening | | After 4 wk at -30°C | | After 4 wk at -16°C | |
|------------------|---------------------|---------------------|-------------------------------------|---------------------|-------------------------------------|---------------------|
| | X_{50} | Slope | X_{50} | Slope | X_{50} | Slope |
| | (μm) | (%/ μm) | (μm) | (%/ μm) | (μm) | (%/ μm) |
| No stabilizer | 9.3 ^{b,A} | 5.7 ^{a,A} | 9.1 ^{b,A} | 5.9 ^{a,A} | 21.5 ^{a,A} | 2.1 ^{b,A} |
| CMC ¹ | 11.8 ^{b,A} | 5.7 ^{a,A} | 11.0 ^{b,A} | 5.0 ^{a,A} | 20.9 ^{a,A} | 2.7 ^{b,A} |
| Guar gum | 10.3 ^{b,A} | 5.8 ^{a,A} | 9.5 ^{b,A} | 5.6 ^{a,A} | 20.3 ^{a,A} | 2.4 ^{b,A} |
| Xanthan gum | 9.5 ^{b,A} | 6.6 ^{a,A} | 10.7 ^{b,A} | 5.6 ^{a,A} | 18.7 ^{a,A} | 3.0 ^{b,A} |

^{a,b}Values for each parameter with the same letter in the same row do not differ ($\alpha = 0.05$).

^AValues with the same letter in the same column do not differ ($\alpha = 0.05$).

¹CMC = Carboxymethyl cellulose.

tected using scanning electron microscopy techniques; however, every effort was made to be quantitative across all of the size classes. Storage at -30°C did not affect ice crystal distribution ($P > 0.05$) when compared with that after hardening (Table 2). The glass transition temperature of ice cream can range from -24 to -43°C according to formulation (13, 21), thus it is not surprising that storage time at this low temperature did not affect ice crystal sizes. Stabilizers do not affect the glass transition temperature of ice cream (13) or the unfrozen phase according to different studies (3, 30) of model solutions of this phase. Although the X_{50} was fairly similar, the shape factor of crystals (data not shown) increased, coinciding with a significant decrease in the slope of the distributions ($P < 0.05$). These changes are most likely due to isomass recrystallization. This recrystallization mechanism at constant storage temperature was also reported by Donhowe and Hartel (7) in ice cream samples. Ostwald ripening (migratory recrystallization at constant temperature) might also be responsible, in part, for these changes, considering the high percentage of smaller crystals present after hardening.

The impact of a higher storage temperature (-16°C) was reflected by an increase in X_{50} and a noticeable increase of span of the crystal distribution (lower slopes) (Table 2). Samples were initially hardened (-30°C , 24 h) and then transferred to the tempering cabinet (-16°C) for the rest of the storage period (4 wk). The reduction of ice content because of different storage temperatures (from 56.2 to 52.7% for -30 and -16°C) would result in smaller crystals disappearing (melting) because of their lower melting points (or greater solubilities) (9), thus increasing the X_{50} . However, the broadening of the distribution (lower slopes) implies that larger crystals also increased in size, ultimately showing evidence of

recrystallization. Migratory recrystallization was most likely the predominant recrystallization mechanism involved during warming (crystal melt-down and probable diffusion) and throughout storage (Ostwald ripening). Samples contained many small crystals after hardening (typically 15% were from 1 to 5 μm), which disappeared after the storage time at -16°C (typically 2% were from 1 to 5 μm). Accretion is another possible mechanism when considering the initial microstructure of the samples (i.e., crystals closely packed in the unfrozen phase with many crystals in contact). According to Sutton et al. (35), the first stages of recrystallization of model solutions at constant storage temperature (-15°C) involved smaller crystals mainly disappearing through this accretive mechanism. Therefore, it is feasible that some of the melting small crystals may have joined larger crystals, which then rounded off.

Stabilizers did not significantly prevent recrystallization in ice cream during constant temperature storage (Table 2), which suggested that stabilizers are not capable of controlling or reducing crystal migration according to the mechanism previously described (i.e., migratory recrystallization of smaller crystals also promoting accretion). As previously shown by proton (^1H) nuclear magnetic resonance (23, 30), water mobility is not hindered by the presence of stabilizers. Accordingly, stabilizers were not capable of reducing diffusion of water melted during warming or diffusion caused by Ostwald ripening during constant temperature storage. Note that there was an uneven growth of certain sizes of the population in unstabilized ice cream and that containing guar gum after high temperature storage (-16°C). In both, there was more damage to the air bubbles (larger crevices) after the storage period (Figure 1). The collapse of a weaker matrix may induce irregular changes in ice crystal sizes by

promoting accretion of the crystals. In such event, a stabilized sample with a high overrun (like guar gum) would apparently have poorer control over recrystallization. However, structure deformation would be responsible for this occurrence rather than a

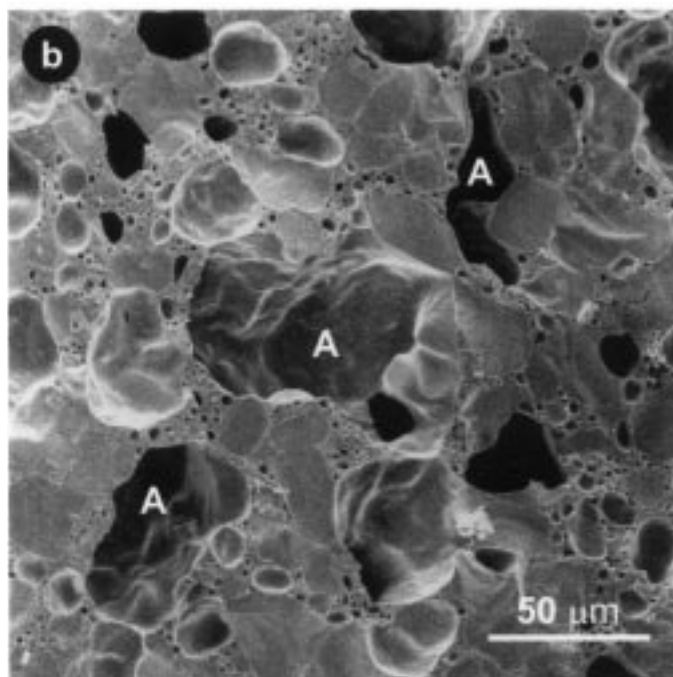
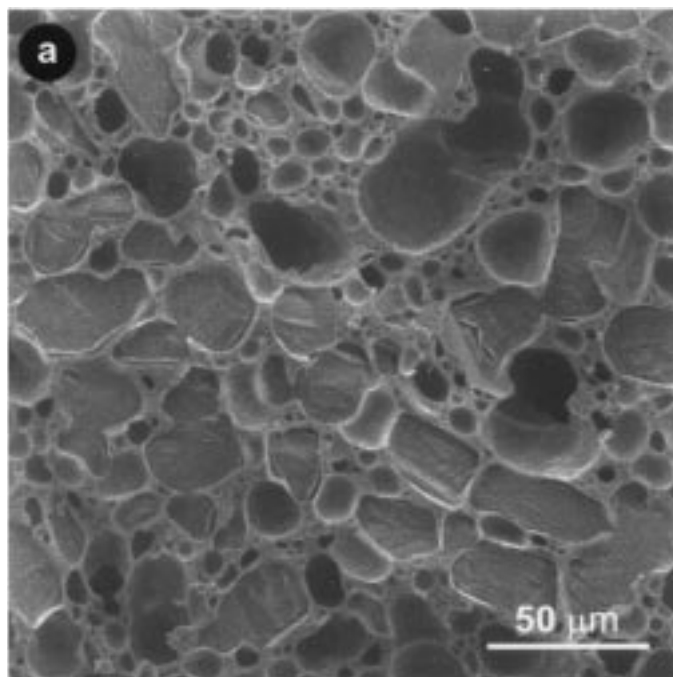


Figure 1. Microstructure of ice cream samples without stabilizer after 4 wk of storage at -30°C (a) and at -16°C (b) showing air crevices (A) caused by air bubble channeling.

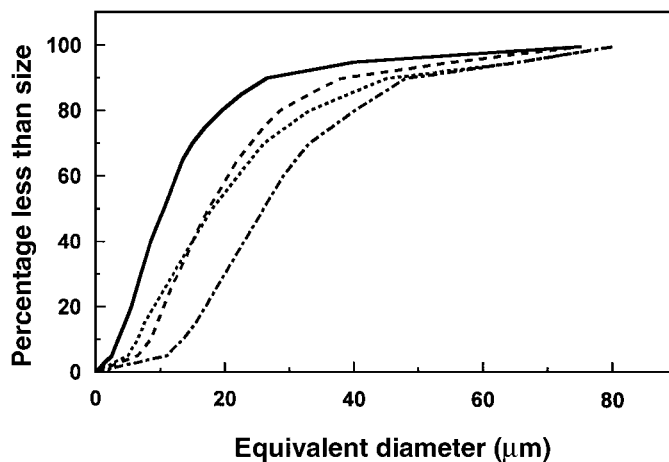


Figure 2. Comparison between cumulative distribution functions after constant storage and cycling temperature conditions for ice cream containing carboxymethyl cellulose. Key: ice cream stored at -30°C before cycling (—), set 1 from Table 1 (.....), sets 2 and 3 from Table 1 (----), set 4 from Table 1 (-·-·-·-·-).

low effectiveness of the stabilizer. According to Goff et al. (16), increased viscosity of the serum contributed by the presence of stabilizers helps to control shrinkage (volume loss) in ice cream during storage. However, as previously mentioned, such effect may be overcome by the impact of a high content of air (high overrun) as observed for the guar gum formulation.

Temperature Cycles

The temperature cycles after a high storage temperature (-16°C , set 1) did not affect ice crystal size distribution when compared with the constant -16°C storage. The amplitude of temperature fluctuation ($\pm 2^{\circ}\text{C}$), length of each cycle (3 h), or number of cycles (3) did not allow for significant recrystallization to occur. This result was probably due to the massive effect induced by the previous high storage temperature, which promoted disappearance of most of the smaller crystals that were more likely to be affected by a temperature fluctuation of such magnitude and time length. No particular effect was observed from the presence of stabilizers. Temperature fluctuations for samples previously stored at -30°C had a greater impact on ice crystal sizes and distributions. A graphical comparison of the distributions for samples containing CMC clearly depicts the changes in distributions that were a result of constant and cycling temperature storage conditions (Figure 2).

The differences between initial distribution parameters (Table 2, column 1) and those for even the less severe set of cycles (set 2) (Table 3, column

TABLE 3. Ice crystal diameter at 50% of the cumulative distribution function of the sample (X_{50}) and slope at X_{50} for ice cream after temperature cycles of samples that were previously stored at -30°C .

| | Set 2 ¹ | | Set 3 ² | | Set 4 ³ | |
|------------------|---------------------|--------------------|---------------------|---------------------|----------------------|--------------------|
| | X_{50} | Slope | X_{50} | Slope | X_{50} | Slope |
| | (μm) | (%/μm) | (μm) | (%/μm) | (μm) | (%/μm) |
| No stabilizer | 20.7 ^{b,A} | 2.8 ^{a,A} | 20.8 ^{b,A} | 3.0 ^{a,B} | 29.8 ^{a,A} | 2.8 ^{a,A} |
| CMC ⁴ | 17.9 ^{b,A} | 3.7 ^{a,A} | 17.4 ^{b,A} | 3.7 ^{a,AB} | 27.1 ^{a,AB} | 3.0 ^{a,A} |
| Guar gum | 17.2 ^{b,A} | 3.9 ^{a,A} | 15.4 ^{b,A} | 2.6 ^{a,B} | 23.4 ^{a,B} | 2.8 ^{a,A} |
| Xanthan gum | 16.4 ^{b,A} | 3.8 ^{a,A} | 15.4 ^{b,A} | 4.2 ^{a,A} | 25.2 ^{a,B} | 3.1 ^{a,A} |

^{a,b}Values for each parameter with the same letter in the same row do not differ ($\alpha = 0.05$).

^{A,B}Values with the same letter in the same column do not differ ($\alpha = 0.05$).

¹ $-15^{\circ}\text{C} \pm 2^{\circ}\text{C}$, 3 h, 3 cycles.

² $-15^{\circ}\text{C} \pm 5^{\circ}\text{C}$, 4 h, 3 cycles.

³ $-15^{\circ}\text{C} \pm 5^{\circ}\text{C}$, 4 h, 9 cycles.

⁴CMC = Carboxymethyl cellulose.

1) were statistically significant ($P < 0.05$). However, no greater effect was found with an increase in the amplitude of the cycle (set 3), hence the increase of ice content fluctuation. Recrystallization of these samples (sets 2 and 3) was most likely caused by the increase of average temperature (lower ice content) rather than the temperature cycle, which would induce complete meltdown and diffusion of smaller crystals combined with accretion as observed for samples stored at -16°C . The X_{50} values of samples stored at this temperature were comparable to those of sets 2 and 3, even though the differences in slopes revealed a greater recrystallization effect of the former (presence of larger crystals in the distribution). An increase in the number of cycles (set 4, 9 cycles) showed a considerable increase in X_{50} and a decrease of slope at X_{50} in most cases (Table 3). Because of the prolonged number of cycles, part of the expected effect of the thermal fluctuations would be due to ice phase changes, thus promoting melt-refreeze of the crystals, considering the overall increase of crystal size (no smaller crystals) (Figure 2).

The results from sets 2 and 3 showed no significant differences between stabilized and unstabilized samples ($P > 0.05$). However, the tendency observed was for the latter to render a consistently higher X_{50} and lower slope, which reflected an overall larger and broader population of crystals. Such results indicate that stabilizers may have a slight control over recrystallization of ice cream under those conditions. Results for an increased number of cycles (set 4) reinforce this statement. In this case, significant differences ($P < 0.05$) were found between the unstabilized sample and the guar and xanthan formulations. Thus, stabilizers had no control over recrystallization when migratory recrystallization (complete

meltdown and diffusion of smaller crystals) and accretion were probably the predominant mechanisms but showed a protective effect after a prolonged temperature fluctuation regime in which melt-refreeze (partial melting of larger crystals) was probably the predominant mechanism.

Donhowe and Hartel (8) concluded that an important factor affecting recrystallization rates during temperature fluctuations is the extent of the fluctuation, (e.g., amplitude and cycle time). An increase in amplitude of the cycle also increases ice phase volume changes and, therefore, the thermal mass and amount of latent heat to be exchanged. Thus, an increase in time of cycle or number of cycles most likely has a greater impact on recrystallization behavior. As shown in Table 4, an increase in time of cycle had a considerably greater impact on recrystallization rate; after 3 cycles X_{50} diameters were comparable with those after 9 cycles for the lower cycle time. In most cases, differences between stabilized and unstabilized samples confirmed the previous results of set 4 (i.e., stabilizers were capable of significantly reducing recrystallization after fluctuation of temperature during cycling). No differences were found after 25 cycles, however samples showed evidence of damage to the structure as most of the air bubbles had channeled, similar to what was observed for the high constant temperature storage (Figure 1). This structural failure was directly related to shrinkage in ice cream and seems to have an important impact on recrystallization rate undermining the effect of the stabilizer.

A feasible mechanism for the preventive effect of stabilizers against partial melt-refreeze recrystallization during temperature fluctuation would be related to the effect of stabilizers on the bulk diffusion

TABLE 4. Ice crystal diameter at 50% of the cumulative distribution function of the sample (X_{50}) and slope at X_{50} for ice cream with and without guar gum after temperature cycles ($-15^{\circ}\text{C} \pm 5^{\circ}\text{C}$) for short- (4 h) or long-time (8 h) cycles.

| Cycles (no.) | Short time cycles | | | | Long time cycles | | | |
|-----------------|-------------------|---------------------|-------------------|---------------------|-------------------|---------------------|-------------------|---------------------|
| | No stabilizer | | Guar gum | | No stabilizer | | Guar gum | |
| | X_{50} | Slope | X_{50} | Slope | X_{50} | Slope | X_{50} | Slope |
| | (μm) | (%/ μm) | (μm) | (%/ μm) | (μm) | (%/ μm) | (μm) | (%/ μm) |
| 3 | 23.5 ^a | 3.3 ^a | 20.7 ^a | 3.3 ^a | 30.4 ^A | 3.4 ^A | 25.1 ^B | 3.5 ^A |
| 9 | 34.0 ^a | 3.0 ^a | 24.1 ^b | 3.2 ^a | 35.7 ^A | 2.2 ^A | 35.1 ^A | 2.9 ^A |
| 15 | 34.3 ^a | 2.9 ^a | 29.0 ^b | 3.0 ^a | 39.3 ^A | 2.3 ^B | 34.4 ^B | 2.8 ^A |
| 25 | 41.2 ^a | 2.4 ^a | 42.1 ^a | 2.3 ^a | 46.3 ^A | 2.6 ^A | 51.5 ^A | 2.2 ^B |

^{a,b}Short time cycles. Values for each parameter with the same letter in the same row do not differ ($\alpha = 0.05$).

^{A,B}Long time cycles. Values for each parameter with the same letter in the same row do not differ ($\alpha = 0.05$).

properties of the unfrozen phase. Because stabilizers do not reduce the diffusivity of water molecules (2, 30) or, particularly, water diffusion in the unfrozen phase (23, 29), changes in diffusion properties of the unfrozen phase would most likely involve a localized effect within close proximity to the ice crystal surface. Recent studies of frozen sucrose and milk protein solutions (14) showed evidence of the formation of a gel-like network in frozen solutions containing LBG. Additionally, LBG in the presence of skim milk powder resulted in the formation of an aggregated, phase-separated protein network in solution. Thus, a protein stabilizer matrix may control recrystallization during melt-refreeze by maintaining close proximity of water molecules to the crystal. This would promote redeposition of water onto the same crystal, rather than diffusion of that water through the unfrozen phase for redeposition onto the largest crystal, which would be thermodynamically favored.

CONCLUSIONS

Constant temperature storage at -30°C did not affect the overall ice crystal size, probably because of the proximity of this temperature to the glass transition temperature of the unfrozen phase. Stabilizers did not affect the ice crystal size distributions because they do not affect the glass transition temperature. Storage at a higher temperature (-16°C) increased the crystal size and span of the distributions showing evidence of recrystallization after the hardening period. The presence of stabilizers also did not affect recrystallization behavior under constant storage temperature at -16°C . However, ice cream without stabilizer or higher overrun (guar gum) was more susceptible to structural failure due to air channeling,

which may promote recrystallization to a certain extent.

Recrystallization behavior caused by temperature fluctuations seemed to be dictated by the predominant mechanism of migratory recrystallization. The overall increase in storage temperature of the first cycles most likely induced smaller crystals to melt (and probably diffuse) and to accrete, which overwhelmed the effect of cycle or amplitude of the fluctuation. An increase in number of cycles or time length of the cycle had greater impact; the temperature fluctuation may have been responsible for the changes in crystal size distributions. Melt-refreeze (partial melting of larger crystals) was most likely the predominant mechanism of recrystallization, and in this case, stabilizers had a measurable effect in controlling ice crystal size. Thus, thermal fluctuations (temperature cycles) initially induced the disappearance of smaller crystals (meltdown and diffusion) and further accretion within the samples. Under these conditions, stabilizers have no measurable effect on recrystallization because they cannot promote renucleation in the unfrozen phase. As the cycling continued, the overall larger population of crystals most likely underwent partial melt-refreeze, and stabilizers exerted an effective control over this recrystallization phenomenon.

REFERENCES

- 1 Blond, G. 1985. Freezing in polymer-water systems and properties of water. Pages 531-542 in *Properties of Water in Foods*. D. Simatos and J. L. Multon, ed. M. Nijhoff, Dordrecht, The Netherlands.
- 2 Blond, G. 1988. Velocity of linear crystallization of ice in macromolecular systems. *Cryobiology* 25:61-66.
- 3 Blond, G. 1994. Mechanical properties of frozen model solutions. *J. Food Eng.* 22:253-269.

- 4 Budieman, E. R., and O. Fennema. 1987. Linear rate of water crystallization as influenced by temperature of hydrocolloid suspensions. *J. Dairy Sci.* 70:534–546.
- 5 Buyong, N., and O. Fennema. 1988. Amount and size of ice crystals in frozen samples as influenced by hydrocolloids. *J. Dairy Sci.* 71:2630–2639.
- 6 Caldwell, K. B., H. D. Goff, and D. W. Stanley. 1992. A low temperature scanning electron microscopy study of ice cream. II. Influence of selected ingredients and processes. *Food Struct.* 11:11–23.
- 7 Donhowe, D. P. and R. W. Hartel. 1996. Recrystallization of ice in ice cream during controlled accelerated storage. *Int. Dairy J.* 6:1191–1208.
- 8 Donhowe, D. P., and R. W. Hartel. 1996. Recrystallization of ice during bulk storage of ice cream. *Int. Dairy J.* 6:1209–1221.
- 9 Fennema, O. R. 1973. Nature of the freezing process. Pages 151–239 in *Low Temperature Preservation of Foods and Living Matter*. O. Fennema, W. D. Powrie, and E. H. Marth, ed. Marcel Dekker Inc., New York, NY.
- 10 Flores, A. A., and H. D. Goff. 1999. Ice crystal size distributions in dynamically frozen model solutions and ice cream as affected by stabilizers. *J. Dairy Sci.* 82:(JDS8318).
- 11 Goff, H. D. 1992. Low-temperature stability and the glassy state in frozen food. *Food Res. Int.* 25:317–325.
- 12 Goff, H. D., and K. B. Caldwell. 1991. Stabilizers in ice cream: how do they work? *Mod. Dairy.* 70(3):14–15.
- 13 Goff, H. D., K. B. Caldwell, D. W. Stanley, and T. J. Maurice. 1993. The influence of polysaccharides on the glass transition in frozen sucrose solution and ice cream. *J. Dairy Sci.* 76:1268–1277.
- 14 Goff, H. D., D. Ferdinando, and C. Schorsch. 1999. Fluorescence microscopy to study galactomannan structure in frozen sucrose and milk protein solutions. *Food Hydrocolloids* 13:353–364.
- 15 Goff, H. D., and M. E. Sahagian. 1996. Glass transitions in aqueous carbohydrate solutions and their relevance to frozen food stability. *Thermochim. Acta* 280/281:449–464.
- 16 Goff, H. D., W. Wiegersma, K. Meyer, and S. Crawford. 1995. Volume expansion and shrinkage in frozen dairy dessert products. *Canadian Dairy.* 74(3):12–13.
- 17 Hagiwara, T., and R. Hartel. 1996. Effect of sweetener, stabilizer and storage temperature on ice recrystallization in ice cream. *J. Dairy Sci.* 79:735–744.
- 18 Harper, E. K., and C. F. Shoemaker. 1983. Effect of locust bean gum and selected sweetening agents on ice crystallization rates. *J. Food Sci.* 48:1801–1803, 1806.
- 19 Hartel, R. W. 1996. Ice crystallization during the manufacture of ice cream. *Trends Food Sci. Technol.* 7:315–321.
- 20 Hartel, R. W. 1998. Mechanisms and kinetics of recrystallization in ice cream. Pages 287–328 in *The Properties of Water in Foods ISOPOW 6*. D. S. Reid, ed. Blackie Acad. Prof., New York, NY.
- 21 Levine, H., and L. Slade. 1990. Cryostabilization technology: thermoanalytical evaluation of food ingredients and systems. Pages 221–305 in *Thermal Analysis of Foods*. V. R. Harwalker and C. Y. Ma, ed. Elsevier Appl. Sci. Publ., New York, NY.
- 22 Marshall, R. T., and W. S. Arbuckle. 1996. Pages 71, 164 in *Ice Cream*. 5th ed. Chapman & Hall, New York, NY.
- 23 Martin, D. R., S. Ablett, A. Darke, R. L. Sutton, and M. E. Sahagian. 1999. An NMR investigation into the effects of locust bean gum on the diffusion properties of aqueous sugar solutions. *J. Food Sci.* 64:46–49.
- 24 Miller-Livney, T., and R. Hartel. 1997. Ice recrystallization in ice cream: interactions between sweeteners and stabilizers. *J. Dairy Sci.* 80:447–456.
- 25 Min, S. G., W. R. Wolf, I. Morton, and W.E.L. Spieß. 1994. Changes in crystal-size distribution during recrystallization of ice in a hydrocolloid matrix. *Food Sci. Technol. Today* 8: 234–242.
- 26 Moorty, P.R.S., and R. Balachandran. 1994. Ultrastructural studies on the effect of different types of stabilizer on size and formation of ice crystals in low fat ice cream mix. *Indian J. Dairy Sci.* 47:496–500.
- 27 Muhr, A. H., and J.M.V. Blanshard. 1984. The effect of polysaccharide stabilizers on ice crystal formation. Pages 321–331 in *Gums and Stabilizers for the Food Industry 2, Application of Hydrocolloids*. G. O. Phillips, D. J. Wedlock and P. A. Williams, ed. Pergamon Press, New York, NY.
- 28 Muhr, A. H., and J.M.V. Blanshard. 1986. Effect of polysaccharide stabilizers on the rate of growth of ice. *J. Food Technol.* 21: 683–710.
- 29 Sahagian, M. E., and H. D. Goff. 1995. Thermal, mechanical and molecular relaxation properties of stabilized sucrose solutions at sub-zero temperatures. *Food Res. Int.* 28:1–8.
- 30 Sahagian, M. E., and H. D. Goff. 1995. Influence of stabilizers and freezing rate on the stress relaxation behaviour of freeze-concentrated sucrose solutions at different temperatures. *Food Hydrocolloids* 9:181–188.
- 31 Sahagian, M. E., and H. D. Goff. 1996. Fundamental aspects of the freezing process. Pages 1–50 in *Freezing Effects Food Quality*. L. E. Jeremiah, ed. Marcel Dekker, Inc., New York, NY.
- 32 SAS® User's Guide: Statistics, Version 6.03 Edition. 1988. SAS Inst., Inc., Cary, NC.
- 33 Shipe, W. F., W. M. Roberts, and L. F. Blanton. 1963. Effect of ice cream stabilizer on the freezing characteristics of various aqueous systems. *J. Dairy Sci.* 46:169–175.
- 34 Sutton, R. L., D. Cooke, and A. Russell. 1997. Recrystallization in sugar/stabilizer solutions as affected by molecular structure. *J. Food Sci.* 62:1145–1149.
- 35 Sutton, R. L., A. Lips, and G. Piccirillo. 1996. Recrystallization in aqueous fructose solutions as affected by locust bean gum. *J. Food Sci.* 61:746–748.
- 36 Sutton, R. L., A. Lips, G. Piccirillo, and A. Sztchlo. 1996. Kinetics of ice recrystallization in aqueous fructose solutions. *J. Food Sci.* 61:741–745.
- 37 Sutton, R. L., and J. Wilcox. 1998. Recrystallization in model ice cream solutions as affected by stabilizer concentration. *J. Food Sci.* 63:9–11.
- 38 Sutton, R. L., and J. Wilcox. 1998. Recrystallization in ice cream as affected by stabilizers. *J. Food Sci.* 63:104–107.