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# Texture-structure relationships in foamed dairy emulsions

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Favorable textural qualities of foamed dairy emulsions result from the successful incorporation of air bubbles surrounded by partially coalesced fat globules into a stable product. Stabilizers, usually hydrocolloids, are often added to improve texture by controlling such factors as, in ice cream, the agglomeration of ice crystals and, in whipped cream, protection of the product against excessive drainage during storage. The mechanism of stabilizer action is not yet fully known and a clearer understanding of their role is needed to improve functionality and extend shelf life. This review focuses on recent work employing microstructural and rheological techniques aimed at achieving a better appreciation of the role of stabilizers in foamed dairy emulsions. Results from studies of ice cream and model systems have led to the conclusion that the growth of ice crystals in this product is governed by the kinetic properties of the freeze-concentrated viscoelastic liquid surrounding them and hydrocolloid stabilizers are effective due to their ability to increase viscosity of this liquid, possibly through the interaction of their chains. In whipped cream, preliminary data suggest that structure formation is a result of coated air bubbles surrounded by a viscous matrix of partially coalesced fat globules, perhaps held in place by proteins. Stabilizers increase viscosity of the serum phase leading to lower overrun but greater resistance of the product to drainage. Copyright © 1996 Canadian Institute of Food Science and Technology

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#### INTRODUCTION

Much of what food scientists do is aimed at developing a better understanding of how and why food structures behave as they do under various conditions of processing, storage and mastication. In this undertaking we are at a huge disadvantage since foods are almost always composed of a host of different molecular types that interact in ways we are only now beginning to comprehend. Borrowing from engineering science, it has proven useful to apply some of the concepts used in the field of material science to food materials. For example, food scientists are keenly interested in functional properties of macromolecules and how they can be used to improve the sensory properties of food products. Of these properties, perhaps none is more important than

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texture, by which is meant the way that the mechanical characteristics of food elicit a sensory response. Obviously, the sensory apparatus responds to structural stimuli and, in fact, one definition of texture is "The way in which the structural components of a food are arranged in a micro- and macrostructure and the external manifestations of this structure" (deMan, 1976). Because of the importance of texture to the manufacture, marketing and enjoyment of food, it behooves those interested in this parameter to be aware of how it is related to structure.

Since the goal of food scientists is to improve or at least maintain texture, many texture-forming adjuncts are used in foods. Unfortunately, in quite a few cases, the mechanism of their action is not known and their use is governed by empirical or trial-and-error experimentation. This is due to our lack of knowledge of the relationships between macromolecular structure and functionality. Recent advances in both texture-measuring and structure-measuring instrumentation and improvements in molecular characterization may lead to an improved understanding of texture-structure relationships in foods. It is the intent of this paper to demonstrate why knowledge of food structure must precede any attempt to control texture. Examples will be drawn from recent work on the role of stabilizers in foamed dairy emulsions.

#### FOAMED DAIRY EMULSIONS

Foams are one of the most common ways in which food materials interact to produce a structure. The organization of structural elements into a compound or aggregate construction is a reoccurring theme in foods, and foams can be found in such diverse products as bakery items and extruded starches where rigid cells are filled with air (Aguilera & Stanley, 1993). Foams can be defined as agglomerations of bubbles; these bubbles may be more or less densely packed and filled with either a gas or a liquid, the cell walls may be thick or thin, rigid or flexible, and the cells may contain either a small or a large proportion of filling, but foams are always constructed from bubbles, either made naturally in the form of globules or sacs, or of the frothy type introduced by man (Dickinson, 1992*a*).

Food foams are liked by processors because of the low cost of one of the major ingredients-air. Food foams are liked by consumers because of several desirable sensory characteristics. Air-filled foams are often characterized by brittle textures and reward consumers with a "snap" that is appreciated not only by the mouth but also by the ear. There is also a type of foam in which the cells contain air but the cell walls are constructed from a preexisting emulsion. In such "solid foams" the liquid has changed into a gel or solid phase as a result of processing operations (Jeronimidis, 1988; Walstra, 1989). Those solid foams made from dairy products are designed to be consumed either in the frozen state, ice cream, or in the unfrozen state, whipped cream. In both cases the manufacturing process is aimed at the formation of a stable, co-existing emulsion and foam. As can be imagined, the technological problems associated with such products are numerous and center mainly on production of acceptable foams possessing satisfactory life spans. Bothof these foamed dairy emulsions will be considered in more detail.

## **ICE CREAM**

Ice cream has been described as complex combination of a partially frozen foam and emulsion held together partially by emulsified fat and partially by a network of

ice crystals dispersed in a viscous macromolecular aqueous solution (Dickinson, 1992a). Very roughly, ice cream consists of about 50% incorporated air by volume and 10-15% fat, 10% milk solids, 15% sugars and 60-65% water by weight. Processing of the ingredients involves aeration and freezing. Storage life of this product is most often limited by defects resulting from either fluctuating temperatures or constant storage at a temperature exceeding that needed for stability. It seems now that even under the best conditions of home storage, ice cream is close to the limit of upper temperature allowable for good quality. Abusive temperatures cause a defect that manifests itself in the form of icy or coarse texture or shrinkage of the product resulting from foam collapse. Fortunately, food scientists have developed additives that help to overcome these problems. Commercially-produced ice creams contain small quantities of emulsifiers and stabilizers that improve texture by promoting small air bubbles and ice crystals and increasing viscosity (Arbuckle, 1986; Madden, 1989). While emulsifiers are employed to aid in the controlled destabilization of the emulsion during freezing, leading to a stable foam, polysaccharide stabilizers increase the viscosity of the aqueous phase. Thus, the foamed structure of ice cream is stabilized through the combined action of a fat globule network, ice crystals and a highly viscous aqueous phase (Dickinson, 1992a). Obviously, a successful product must have close attention paid to such factors as number and size of air bubbles, number and size of ice crystals, number and size of fat globules, and rheological properties of the aqueous phase.

A common cause of the temperature-associated textural defects found in stored ice creams is ice crystal growth wherein large agglomerated ice crystals form to a point where they become noticeable by the consumer as a coarse or rough mouthfeel. Stabilizers, most often blends of complex carbohydrates called hydrocolloids or gums, are known to arrest or delay ice crystal formation, but the mechanism of their action has yet to be fully characterized (Goff, 1993). Clearly, an understanding of how stabilizers assert their protective action would aid in designing improved functional ingredients and could lead to an extended shelf life.

It has been difficult to obtain satisfactory structural information about frozen food materials because of the obvious difficulty in making measurements at such low temperatures. Recent advances, as exemplified by the cryo-SEM and other newer techniques, have empowered food scientists to accomplish more detailed examinations of these products (Kaláb, 1985; Wilson, 1989; German & McCarthy, 1989; Heertje *et al.*, 1990; Brooker, 1990*a*; Kaláb & Caric, 1990; Pilhofer *et al.*, 1994). Through work of this type the structure of ice cream can now be described as multi-phasic, consisting of ice crystals, air cells, emulsified fat and a continuous serum phase (Caldwell *et al.*, 1992*a*). Air bubbles are



Fig. 1. A: Cryo-SEM micrograph showing the four phases of ice cream. C: partially etched ice crystal socket; A: air bubble lined with fat globules; S: serum phase. Bar = 30  $\mu$ m. B: Cryo-SEM micrograph showing air bubble (A) lined with fat globules (F) and surrounded by serum phase (S). Bar = 7.5  $\mu$ m. Source: Caldwell *et al.*, 1992*a*.

spherical in form and are lined with numerous fat globules while the ice crystals, or, more accurately, the spaces they occupied prior to ion etching and sublimation, are less regularly shaped (Fig. 1).

As mentioned previously, ice crystals have a tendency to merge during adverse storage of ice cream. An example of this may be seen in Fig. 2; structures of this type are more prevalent in unstabilized than stabilized samples (Caldwell *et al.*, 1992b). A comparison of stabilized and unstabilized ice creams following a thermally abusive storage period shows that while ice crystal size increased for both samples, control samples contained more merged and contiguous crystals (Fig. 3). Through the use of image analysis of cryo-micrographs it was possible to quantitatively estimate the size of ice crystals in stabilized and unstabilized ice creams to provide data that were also reflected by sensory judges (Table 1).

These results strongly suggest the textural benefits accruing from the use of stabilizers can be attributed to structural differences. In order to demonstrate this relationship more fully an objective measurement of texture is required. Recent research on the subject of cryostabilization suggests that molecular mobility is the overriding mechanism in achieving stability (e.g. Levine & Slade, 1990). Thus, it may be that stabilizers act by decreasing the mobility of water in the serum phase surrounding ice crystals so as to prevent its migration to, and recrystallization with, existing ice crystals. Enhanced viscosity of the unfrozen phase, contributed by entangling macromolecules, may be important in this process.



Fig. 2. Cryo-SEM micrograph of four ice crystals surrounded by serum phase (S) that have merged into one (C) as a result of recrystallization. Bar =  $25 \ \mu m$ . Source: Caldwell *et al.*, 1992*b*.

Determining the viscosity of frozen materials is not an easy task, but several recent advances in methodology have made this achievable. The thermomechanical analyzer (TMA) is an instrument capable of measuring mechanical properties of samples while they are undergoing temperature changes. In a recent study (Goff et al., 1993), parallel plate geometry was used to study the deformational properties of stabilized and unstabilized ice cream mixes (ice cream was not studied in the TMA because of the dominant effect of overrun). A flat frozen sample  $\approx 500 \ \mu m$  thick and 1 cm in diameter was loaded into a prechilled quartz stage fitted with a



Fig. 3. Cryo-SEM micrographs of stabilized (A, C) and unstabilized (B, D) ice creams stored under abusive temperature conditions for 0 weeks (A, B) or 24 weeks (C, D). (A, B) Bar = 100  $\mu$ m; (C, D) Bar = 50  $\mu$ m. Source: Caldwell *et al.*, 1992b.

Table 1. Influence of stabilizer (0.15% locust bean gum, 0.02% carrageenan) on ice crystal size and sensory response in thermally abused (daily thermal fluctuation from -25 to  $-10^{\circ}$ C)

ice cream samples <sup>a</sup>	

Treatment	Ice crystal mean maximum diameter (mm)	Sensory iciness score <sup>b</sup>
Unstabilized (0 weeks)	35.4 <sup>•,c</sup>	0.02†
Stabilized (0 weeks)	43.3*	-0.63*
Unstabilized (24 weeks)	113.7‡	0.76 <sup>‡</sup>
Stabilized (24 weeks)	95.4 <sup>†</sup>	-0.11*

<sup>a</sup>Data from Caldwell et al., 1992b; Goff et al., 1993.

<sup>b</sup>Higher numbers correspond to coarser samples.

<sup>c</sup>Means in the same column with the same superscript do not differ at  $P \leq 0.05$ .

thermocouple and the expansion probe lowered onto the sample. The probe was equipped with a linear variable dynamic transducer capable of measuring small changes in sample height as a function of time or temperature. A force of  $\approx 0.1$  N was applied and as the sample between the two plates changed in dimension, results (in  $\mu$ m) were obtained. The stage was covered by a furnace and enclosed in an insulated cage. This cell was attached to a thermal analyzer.

By measuring dimensional changes during warming of ice cream mixes from -70 to  $0^{\circ}$ C it was possible to calculate viscosity:

$$\eta = \frac{4F}{3\Pi r^4} / \frac{\Delta 1/h^2}{\Delta t} \tag{1}$$

where F is the applied force measured in kg m/s<sup>2</sup>, r is the sample radius in meters, h is the height of the sample in meters, and  $\Delta t$  is the time change in seconds.

The presence of stabilizer, in this case 0.6% guar gum, increased resistance to deformation as a function of temperature since the viscosity was higher in the stabilized sample (Fig. 4). It is thought that as guar became more concentrated as a result of freeze concentration, entanglement of the carbohydrate chains occurred, leading to a further increase in viscosity of the unfrozen continuous phase surrounding the ice crystals. Thus, the "micro" viscosity of the unfrozen phase of ice cream increases during freezing as a result of freeze concentration, but in stabilized systems an even higher viscosity results, probably because of polymer entanglement. As freeze concentration progresses during the manufacturing process sugars, proteins and stabilizers are forced into smaller areas surrounding the ice phase, increasing their concentration greatly. Hydrocolloids are high molecular weight carbohydrate compounds in the form of long, straight-chain, or branched polymers capable of considerable interaction at high concentrations. Other data (Goff et al., 1993) have shown that stabilizers have no significant effect on ice melting tem-



Fig. 4. Viscosity of stabilized (○-○-○) and unstabilized (□-□-□) ice cream mixes as calculated from TMA data. Source: Goff *et al.*, 1993.

perature or the amount of ice frozen. However, TMA results indicated that the stabilizers greatly increased the resistance to flow of the serum phase, perhaps as a result of their entanglement due to freeze concentration.

Another possibility exists for measuring the viscous properties of stabilized ice creams. Classical rheology begins with a consideration of two ideal materials, the elastic solid and the viscous liquid. The elastic solid is defined as a material with a definite shape that, when deformed within certain limits by an external force, will return to its original dimensions upon the removal of that force. The viscous liquid has no definite shape and will flow irreversibly upon deformation by an external force. As would be expected, the preponderance of food materials have rheological properties somewhere between these two model representations and are classified as viscoelastic. Traditionally, the firmness of ice cream has been determined by penetrometer tests in which a cone-shaped probe is dropped onto the sample surface and the depth of penetration measured. While such single-point static tests, involving large deformations, have been used widely in food texture studies, mainly due to time constraints and instrument cost, it is now being appreciated that the behaviour of viscoelastic materials cannot be adequately described by these data alone. A one-dimensional approach can only rarely deal with the complex nature of viscoelasticity in nonideal materials.

The development of instrumentation capable of applying a small, dynamic stress makes it possible to obtain a more thorough understanding of viscoelastic behaviour during a reasonably short experimental time. Although a thorough explanation of this methodology is beyond the scope of the present paper, interested readers are directed to several excellent texts and chapters that describe its application to polymeric and food materials (Ferry, 1980; Walters, 1980; Collyer &

Table 2. Effect of stabilizer (0.15% guar gum) on the viscoelastic properties of ice cream mixes frozen to -15°C in the rheometer<sup>a</sup>

G'-storage modulus (N m <sup>-2</sup> )	G"-loss modulus (N m <sup>-2</sup> )	$\tan \delta \left( G''/G' \right)$	$G^{\bullet}$ -complex modulus (N m <sup>-2</sup> )
2300 <sup>*,b</sup> 11 500 <sup>†</sup>	2700* 8000†	1.23* 0.68†	3500* 14 000†
	G <sup>7</sup> -storage modulus (N m <sup>-2</sup> ) 2300 <sup>*,b</sup> 11 500 <sup>†</sup>	G'-storage modulus (N m <sup>-2</sup> )         G''-loss modulus (N m <sup>-2</sup> ) $2300^{*,b}$ $2700^{*}$ $11500^{\dagger}$ $8000^{\dagger}$	G <sup>2</sup> -storage modulus (N m <sup>-2</sup> )         G <sup>n</sup> -loss modulus (N m <sup>-2</sup> )         tan $\delta$ (G <sup>n</sup> /G <sup>r</sup> )           2300 <sup>*,b</sup> 2700 <sup>*</sup> 1.23 <sup>*</sup> 11 500 <sup>†</sup> 8000 <sup>†</sup> 0.68 <sup>†</sup>

<sup>a</sup>Data from Goff et al., 1995.

<sup>b</sup>Means in the same column with the same superscript do not differ at  $P \leq 0.05$ .

Clegg, 1988; Ross-Murphy, 1988; Barnes *et al.*, 1989; Steffe, 1992). In dynamic oscillatory testing, materials are subjected to a controlled sinusoidally oscillating stress or strain. For an ideal viscous liquid there will be a 90° phase difference between the stress-strain applied and the strain-stress observed, whereas for an ideal elastic solid the stress-strain will be in phase with the strain-stress (0° phase angle). If the material is viscoelastic, as is the case for most food materials, the phase angle will be between 0 and 90°.

The storage modulus is the ratio of the in phase stress component to the strain observed while the loss modulus is the ratio of the stress component 90° out of phase to the observed strain. As it turns out, four of the most important rheological characteristics of a viscoelastic material are G', the storage modulus, G", the loss modulus, G<sup>\*</sup>, the complex modulus, a measure of overall rigidity, (stress amplitude strain amplitude, i.e.  $G^* = G'^2 + G''$ ), and the G''/G' ratio or tan  $\delta$ . We can view tan  $\delta$  as the ratio of energy lost to energy stored per stress cycle, it would be expected to decrease in samples with more and stronger elastic components but be higher for more viscous samples. In other words, this parameter is the ratio of viscous characteristics to elastic characteristics of a viscoelastic material.

The influences of stabilizing agents on the rheological properties of ice cream mixes and ice creams were measured using dynamic rheological techniques with a controlled stress rheometer (Goff et al., 1995). A temperature-controlled platen allowed these values to be obtained at low temperatures; also, mixes could be frozen directly in the sample holder. Results from this work (Table 2) show that the addition of stabilizer significantly increased the storage, loss and complex moduli and reduced tan  $\delta$  in frozen ice cream mixes. This suggests an increasing viscosity and the formation of elastic and rigid components, perhaps by the interaction of hydrocolloid chains, that reduce the kinetic ability of ice crystals to unite. These data are consistent with a mechanism of stabilizer action that relies on increased interaction among the structural elements to raise the serum viscosity to a point where ice crystals cannot migrate to each other.

In order to achieve a better understanding of the role of stabilizers in ice cream it is necessary to consider their structure and rheological characteristics. Using guar gum as an example, this hydrocolloid is a naturally occurring gum obtained from a leguminous seed. The active macromolecular component of guar gum is a linear mannan chain with single unit galactose side chains. It exhibits solution properties characteristic of a random-coil polymer (Robinson *et al.*, 1982). In dilute solution, viscosity increases linearly with increasing concentration, but with a further increase in concentration, a point is reached where the viscosity-concentration relationship deviates from linearity. This transition corresponds to the onset of coil overlap between the polymer chains, and the critical concentration  $(c^*)$  at which it occurs depends on the volume occupied by each molecule in isolation (Morris, 1989).

For guar gum the transition from dilute to concentrated solution behaviour is quite distinct; at lower concentrations (c) viscosities are proportional to  $c^{1.3}$ , however at higher concentrations they are proportional to  $c^{5.1}$  (Robinson *et al.*, 1982). This transition is attributed to specific associations ("hyperentanglements") caused by physical contact of individual molecules of a longer time scale than non-specific physical entanglements noted for other polysaccharides (Morris, 1989) that lead to a dramatic change in flow behaviour.

Recent research has demonstrated that freeze concentration of ice cream mixes may cause the effective concentration to exceed  $c^*$ , leading to augmented viscosity effects thought to result from polymer chain overlap (Goff *et al.*, 1995). The relationship between



Fig. 5. Storage modulus versus temperature for frozen ice cream samples. Source: Goff et al., 1995.



Fig. 6. Apparent viscosity of ice cream mix with  $(\bigcirc -\bigcirc -\bigcirc)$ and without  $(\bigcirc -\bigcirc -\bigcirc)$  stabilizer added as a function of percentage of water removed from the original mix formulation. The lower x-axis gives the temperature (°C) at which the percentage water indicated is frozen out, as determined by a calculated equilibrium freezing curve. Source: Goff *et al.*, 1995.

temperature of frozen stabilized ice cream and storage modulus (G') is shown in Fig. 5. There was a very large change in the relationship, as illustrated by the slope of the curve, at  $-6.5^{\circ}$ C. This would result from having achieved the critical concentration of stabilizer as a result of freeze-concentration.

In order to determine the mechanism of this effect, a simulation of freeze-concentration was performed by formulating a series of ice cream mixes containing diminishing quantities of water. It was possible to relate the percentage of water removed from the mixes by the formulation with the equivalent percentage of water removed from ice cream mix by freezing at an equilibrium freezing temperature through calculation of an equilibrium freezing curve.

Apparent viscosity of the formulated mixes with varying percentages of water removed is illustrated in Fig. 6. The relationship between viscosity and concentration of the mix changes dramatically at 60% water removed for the stabilized mix; the unstabilized mix, however, does not show this large discontinuity in the viscosity curve. The relationship between water removed and temperature from the equilibrium freezing curve is also shown below the x-axis. It was evident that the break point in the viscosity-concentration curve was occurring at exactly the same location as the break point in the storage modulus-temperature curve in Fig. 5, at close to 60% of the water frozen or  $-6.5^{\circ}C$ .

In order to isolate this effect, the study was repeated using model solutions composed of only the water, sucrose, and corn syrup solids fractions of the mix. It is



Fig. 7. Apparent viscosity of guar (○-○-○), sugar (□-□-□), and guar/sugar (△-△-△) solutions as a function of the percentage of water removed from the original formulation. Source: Goff *et al.*, 1995.

apparent from Fig. 7 that guar gum is responsible for this change in the viscosity-concentration relationship. These data convincingly demonstrate that the action of polysaccharides in stabilizing frozen desserts results from the removal of water by freezing which leads to concentration of the polysaccharide components of the mix in an unfrozen phase. When the critical concentration is reached, the polysaccharides begin to entangle and can thus greatly reduce the diffusion kinetics of water molecules in the unfrozen phase. This same conclusion has also emerged from other studies involving thermal and kinetic properties of freeze-concentrated polysaccharide solutions (Carrington et al., 1996; Sahagian & Goff, 1995). These structural and textural studies of hydrocolloid stabilizers in ice cream lead to the conclusion that the growth of ice crystals in this product is controlled by the kinetic properties of the freeze-concentrated viscoelastic liquid surrounding them.

#### WHIPPED CREAM

In order to understand the texture-structure relationships involved in whipped cream it is necessary to first review some principles of foam formation in this product. Anderson & Brooker (1988) have defined dairy foams as "structures in which a gas is stabilized in a matrix where a significant proportion of the principal components are of milk origin". Note the emphasis on "structure" and "stabilized"; thus, these authors observe that while milk itself will easily produce a foam, it does not persist. Whipped cream, on the other hand, produces a foam that can be both lasting and rigid. This is a result of the semi-solid fat particles in the cream exerting a stabilizing influence on the foam through a mechanism known as partial coalescence.

Partial coalescence is a consequence of the inherent emulsion instability in dairy creams. As explained by Mulder & Walstra (1974), Darling (1982) and Walstra (1987), when the milk fat globule membrane surrounding each fat particle is disrupted by shear and some of the fat is in the solid form so that crystals are present, the shearing action of whipping causes the colliding globules to partially coalesce as a result of these fat crystals piercing the membranes. A coalesced network results that still retains some globular shape and has the ability to build structure during the whipping operation. That is, this material can trap the air bubbles created by shear, surround them and lead to a stabilized structure. Micrographs of whipped cream show these coalesced globules partially protruding into the bubble surface (Buchheim et al., 1985; Krog et al., 1987). Another result of partial coalescence may be to increase the viscosity of the cream, thus slowing the movement of air bubbles and decreasing their size (Anderson & Brooker, 1988). Thus, the practical consequences of partial coalescence in whipped cream include increased viscosity due to the nonspherical shape of the fat aggregates and the ensuing formation of a continuous structural network (Walstra, 1987).

Proteins also have a role in the whipping process. While fat globules can join together to form linkages between adjacent bubbles, liquid fat from coalesced globules does not seem to occupy all the space between globules at the bubble surface (Anderson & Brooker, 1988). It has been suggested that  $\beta$ -casein (which is dissociated from casein micelles as milk is cooled) and, to a lesser degree, whey proteins initially stabilize air bubbles while proteins derived from disrupted milk fat globule membranes occupy some of the space between globules (Brooker *et al.*, 1986; Anderson *et al.*, 1987; Brooker, 1990b; Needs & Huitson, 1991). One consequence of the whipping process may be an unfolding of protein molecules that improves their foaming characteristics (Dickinson, 1992b).

While few reports on the rheological properties of whipped cream are available, Noda & Shiinoki (1986) have investigated the relationship between rheological properties and microstructure during the whipping of cream. These authors concluded that most of the air bubbles are introduced into the cream in the first stage of whipping, but they do not contribute to the formation of a persistent structure until their diameter is reduced, in agreement with the results of Schmidt & van Hooydonk (1980) who determined that entrapped air bubbles decrease in size until maximum foam strength is achieved. It was also observed that free fat levels increase due to partial coalescence, and these fat globules then aggregate (Fig. 8). Serum viscosity and the elastic modulus both increased during the whipping process following the first stage.

Considering the importance of rheological rigidity and stability to the commercial value of whipped cream foams, it is not surprising that emulsifiers and stabilizers are added to formulations, the former of which migrate to the air-water interface so as to reduce excess surface tension and promote interaction of fat globules, while the latter are intended to increase viscosity of the aqueous phase and slow diffusion of serum from the foam and also perhaps interact with the protein components of the cream (Anderson & Brooker, 1988). As with the previous example of ice cream, a better understanding of the mechanism of stabilizer action could allow the development of an improved product with better textural and stability characteristics, particularly in situations where the elements involved in structure formation have been modified by processing such as pasteurization etc. (Graf & Müller, 1965; Bruhn & Bruhn, 1988).

A preliminary study of stabilizer action in whipped cream was undertaken as follows: raw cream was obtained from a local dairy on three different dates and refrigerated (0–5°C) for 24 h. Fat content, determined by infra-red analysis when the cream was removed from the separator, was normalized to 36% by the addition of skim milk. Half the cream was stabilized with the addition of 0.25% of a commercial hydrocolloid



Fig. 8. Changes in key structure-forming components and rheological indices during the whipping of cream. Total whipping time ( $\approx 5$  min) was divided into four equal stages. Data are given as percentage of maximum value. Source: Redrawn from Noda & Shiinoki, 1986.

stabilizer (Aeratex, Food Specialties, Mississauga, ON) containing a proprietary mixture of mono- and diglycerides, disodium phosphate, sodium citrate, guar gum, carrageenan, locust bean gum and soya lecithin.

High temperature, short-time pasteurization was performed prior to the addition of stabilizer using the No-Bac Unitherm IV processing system (Cherry–Burrell Corp., Cedar Rapids, IA) at 77°C for 18 s. Pasteurized cream was then refrigerated for 24 h. Samples were whipped to maximum overrun, determined on a small aliquot every 10 s, using a commercial mixer. Whipped creams were tested for syneresis following refrigerated storage. A sample was loaded onto nylon mesh in a funnel and drainage volume measured after 24 h at  $0-5^{\circ}$ C. The fat content of the drained liquid was determined by infra-red analysis.

The Carri-Med controlled stress rheometer (Model CSL 100, Carri-Med Ltd, Dorking, Surrey, UK) was used to determine rheological parameters. Oscillation

data were acquired using samples of whipped cream taken from the uppermost area of the foam using a 6 cm acrylic parallel plate measuring system at a gap of 3 mm to minimize damage to the structure. A torque sweep was performed to determine the linear viscoelastic region of the mix and a frequency sweep was performed at the appropriate stress. The viscoelastic parameters of G' (storage modulus), G'' (loss modulus),  $G^*$  (complex modulus), and tan  $\delta$ , the tangent of the loss angle, (G'')G'), as a function of frequency were determined. Three frequency sweeps were conducted for each treatment, 0 and 24 h following whipping, stabilized and unstabilized whipped cream samples, on each of the three different pasteurization dates leading to nine replications in all. Statistical significance level of the treatments was tested using analysis of variance and paired t tests.

Microstructure was monitored using cryo-scanning electron microscopy. Samples of whipped cream taken from the uppermost area of the foam were loaded into



Fig. 9. Influence of stabilizer on overrun and rheological indices during the whipping of cream.

Characteristic	Unstabilized, 0 h	Stabilized, 0 h	Unstabilized 24 h	Stabilized 24 h
Maximum overrun (%)	122	82		
Syneresis (%)			45.8	14.3
Fat in drained volume (%)			6.03	0.89
G' (N m <sup>-2</sup> )	4800 (41) <sup>a</sup>	7160 (104)	7300 (47)	3860 (123)
$G''(N m^{-2})$	1530 (49)	2010 (97)	2180 (56)	1050 (113)
$an \delta$	0.312 (10)	0.308 (14)	0.289 (10)	0.461 (47)
$G^*$ (N m <sup>-2</sup> )	5050 (42)	7440 (104)	7630 (48)	<b>4010</b> (122)

Table 3. Effect of stabilizer on characteristics of whipped creams, n = 9.

<sup>a</sup>Numbers in parenthesis indicate coefficients of variation.

copper holders and quench frozen by plunging into liquid nitrogen slush ( $-207^{\circ}$ C) in the freezing chamber of the SP2000A (EMScope Ashford, Kent, UK) cryopreparation system. Samples were fractured at  $-180^{\circ}$ C in the preparation chamber and sublimated at  $-80^{\circ}$ C for 40 min in the chamber or on the cold stage in the SEM (Hitachi S-570, Tokyo, Japan). Samples were coated with 30 nm of gold and scanned at temperatures below  $-140^{\circ}$ C in the SEM operated at 10 kV.

The whipping process allowed an examination of the structure-forming action taking place and the role of stabilizers (Fig. 9). Overrun built up quickly during the first stage of whipping with unstabilized cream rising to  $\approx 40\%$  higher level. Initially, it may seem incongruous that unstabilized cream can be whipped to a higher overrun than stabilized cream, however, one function of the stabilizer is to increase viscosity and while this

depresses overrun at first, it leads to a much more stable foam, as will be seen from the syneresis data. Both G'and G'' rose more quickly for stabilized than unstabilized cream, but G' increased more rapidly, leading to an overall decrease in tan  $\delta$ .  $G^*$ , an index of rigidity, also increased to a greater degree for stabilized cream, although this was much more pronounced during the last stage of whipping. Thus, it would seem that structure formation involves at least two stages, an initial phase of expanding overrun in which, according to Schmidt & van Hooydonk (1980) and Noda & Shiinoki (1986), all the air is incorporated into the cream, but air bubble distribution is broad, followed by a phase of increasing viscosity and rigidity during which only the small, more uniform bubbles remain and the free fat content of the cream builds up (Fig. 8). It should not be overly contentious to postulate that while the larger air



Fig. 10. (A) General structure of freshly whipped unstabilized cream. Note air bubbles (A) surrounded by matrix of fat globules (Bar =  $100 \ \mu m$ ). (B) Higher magnification showing fat globules (F) protruding into air bubble, partially coalesced fat globules (C), bridges and attachments between adjacent air bubbles (P) (Bar =  $5 \ \mu m$ ).

bubbles coalesce and dissipate and reform, or are disrupted by the shearing action resulting from whipping, smaller ones persist that are coated with fat globules. The partially coalesced fat globules then join in bridges between adjacent air bubbles (Brooker *et al.*, 1986) to form a viscous and rigid matrix with the accompanying release of a portion of fully coalesced fat. Much more speculative is the possibility that the nonlinearity of the  $G^*$  response and its  $\approx 100\%$  higher value in stabilized samples results from a combination of air incorporation, shearing and the accompanying stressing of the air bubbles that induce the hydrocolloid molecules into a localized ordering where *c* exceeds  $c^*$ .

Characteristics of the whipped samples are shown in Table 3. Syneresis data indicate that a large difference was found not only for total volume but also for the amount of fat in the drained liquid. Unstabilized whipped creams were found to sag considerably more than stabilized samples but the liquid phase drained rapidly, leaving a dried foam that did not sag further. The commercial stabilizer used also contained monoand diglycerides and the combined effect of these surface active emulsifiers that migrate to the air-water interface to reduce interfacial tension along with the reduced diffusion rate produced by the hydrocolloids was effective in holding the fat in the whipped structure.

Considerable deviation was seen in the rheological data for the cream samples. ANOVA indicated significant ( $P \le 0.05$ ) differences due to day-to-day variations among the data. This is thought to be a response to variations in cream composition other than total fat content. Brooker (1990b) has attributed variations in whipping characteristics of cream to the degree of fat globule damage during processing. The addition of stabilizer had no significant effect on the initial rheo-

logical properties of whipped cream, however the stabilized sample tended to be more viscous (higher G''), more elastic (higher G') and more rigid (higher  $G^*$ ). After 24 h, paired *t*-tests resulted in significant ( $P \leq 0.05$ ) differences among all these parameters between stabilized and unstabilized creams. The unstabilized cream had drained excessively, leaving behind an overly stiff, dry foam while the stabilized cream had not changed significantly at the upper level from which samples were taken. Thus, it seems that a more stable product results from a fine, cohesive, viscous foam. Recently, Pilhofer et al. (1994) have been able to measure the stratification of foam density using magnetic resonance imaging. Drainage during storage produces a gradient of densities and, hence, the results of these experiments in which samples were taken from the top layer of cream might not be representative of the entire foam.

Microstructural examination of the whipped cream samples illustrated rheological changes. The general appearance of whipped cream using cryo-SEM is shown in Fig. 10. Smooth, rounded air bubbles are seen embedded in a matrix formed from partially coalesced fat globules. Higher magnification of the lamellae area discloses the tendency of fat globules to extend into the air bubbles, to partially coalesce, and to form bridges between adjacent bubbles. Structural comparisons of freshly whipped stabilized and unstabilized creams showed no major changes, but following 24 h at 0-5°C distinct differences were apparent (Fig. 11). It was obvious that the unstabilized sample had drained, leaving behind deformed, irregular air bubbles, some of which had apparently consolidated and were lined with a noticeable layer of what is thought to be a continuous covering of fat. This combination of excess drainage and totally fat-covered air bubbles is expected to



Fig. 11. (A) Unstabilized and (B) stabilized whipped creams following 24 h at  $0-5^{\circ}$ C (Bar = 100  $\mu$ m). Note distorted air bubbles (A) and thickened serum phase (S). (C) Higher magnification of (B) showing fat globule matrix, bridges and attachments between adjacent air bubbles (Bar = 5  $\mu$ m).

contribute to the higher rigidity measured for this sample. Although exhibiting larger air bubbles, these were smoother, rounder, and more evenly distributed in stabilized cream and there was no evidence of a fat layer covering the bubble surface. Perhaps as a result of the joining of air bubbles the lamellae between them were much thicker, leading to a more viscous, less rigid structure. Higher magnification verified that numerous small air bubbles still persisted firmly anchored in the partially coalesced network. It is of interest to note that even when the fat globules were not actually combined they seemed to be joined by way of thread-like organization resembling that seen in heat-set protein gels, perhaps portions of the milk fat globule membrane removed during shearing and globule adsorption (Anderson & Brooker, 1988). These authors also comment that stabilizers can interact with the protein components of the cream, adding to structure building.

The commercial stabilizer used in this study contained hydrocolloids that were effective in increasing the stability of whipped cream through enhanced viscosity that prevented drainage during the storage period. Prins (1988) has suggested that one role of hydrocolloid stabilizers in foams is to provide a yield value in the liquid phase that keeps the bubbles in place. Emulsifiers contained in this preparation function to decrease the surface tension at the air-water interface, thus promoting fat globules to penetrate the interface, adhere to air bubbles, and decrease globule-globule coalescence. Emulsifiers also decrease protein adsorption at the oilwater interface, thereby lowering surface tension excess and allowing the partial coalescence of fat to proceed. Further work is underway to examine whipping of UHT cream, a processing operation known to produce differences in whipping characteristics (Bruhn & Bruhn, 1988), and to attempt a better understanding of such still poorly understood effects as the influence of overrun on rheological parameters and the role of the individual components in the commercial stabilizer.

# CONCLUSIONS

Ice cream and whipped cream are two examples of foamed dairy emulsions that, although similar in containing fat-stabilized air cells, differ since ice cream contains ice  $(25-50 \ \mu\text{m})$  and some lactose  $(20 \ \mu\text{m})$ crystals, bigger air cells but less air and fat. However, both these products require stabilization to prevent bubbles from growing in size and adjacent air bubbles from coalescing. As more becomes known about the action of polysaccharide stabilizers and surfactant emulsifiers it should be possible to improve their effectiveness and perhaps even to design molecules better able to serve this purpose than the natural products employed now.

Some interesting conclusions about the action of

polysaccharides in stabilizing dairy emulsions are beginning to emerge from the experiments summarized in this paper. For ice cream, the data demonstrate that removal of water by freezing leads to concentration of the polysaccharide components of the mix in an unfrozen phase. As soon as the critical concentration is reached, the polysaccharides begin to entangle and can thus greatly reduce the diffusion kinetics of water molecules in the unfrozen phase. In whipped cream, stabilizers serve to thicken the product and, although a lower overrun is obtained initially, a more stable foam is produced. Also, drainage is limited due to changes in the rheological and structural properties of the foam. Hydrocolloid stabilizers contribute to increased viscosity of the serum phase, hence increasing stability and limiting air bubble movement.

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