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FREEZE-ETCH OF EMULSIFIED CAKE BATTERS DURING BAKING

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Abstract

Cryofixation, freeze-etch techniques were used to study the structure of cake batters made from a lean cake formulation before heating and after heating to temperatures up to 100-102°C. Batters were prepared without added emulsifiers and with saturated and unsaturated monoglycerides replacing 5 and 10% of the oil. Unsaturated monoglycerides were more effective than saturated monoglycerides in dispersing oil droplets through the batter. Saturated monoglycerides formed liquid crystals during baking. The temperature at which starch granules began to swell was slightly higher for saturated monoglyceride containing cakes. The batter matrix between starch granules was more clearly defined in unsaturated monoglyceride containing cakes.

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Introduction

In a study of the effects of variations in the emulsive system on the structural and dynamic properties of cake batters (Cloke, 1981), it was found that the level and type of emulsifier affected heat transfer properties, water loss rates, air incorporation in batter, final cake structure as well as water loss rate upon reheating the cake. The integration of studies of food microstructure with other studies of changes at the molecular level as basis for understanding these macroscopic characteristics is described by Davis and Gordon (1982).

In this paper we report observations made with the freeze-etch technique of batter systems emulsified with saturated monoglycerides (SMG) and unsaturated monoglycerides (USMG).

The freeze-etch technique as applied to batter can be employed to assist in characterizing cake batter structure (Hsieh et al., 1981). It can be used to evaluate physical or structural events as they take place during heating of the batters. As such, it is useful in establishing interrelationships that exist among the components of complex macroemulsive systems. More specifically, changes in starch granule, oil, emulsifier and baking powder morphology as well as the distribution of batter components relative to one another can be observed. The observed physical changes are most likely the result of changes at the molecular level occurring in the system. However, the observations that are reported in this paper are made at the ultrastructural level and, as such, supplement other techniques such as differential scanning calorimetry (DSC) (Cloke, 1981) that document change at the molecular level. These techniques, in turn, can be used to explain the macroscopic changes related to final cake structure and dynamic characteristics related to water loss rates and heating profiles during baking.

Materials and Methods

Test batter formulation

The cake formulation is given in Table 1. Details of the modified two-stage mixing method can be found in Cloke (1981). Specifically, flour and baking powder were sifted together, and the oil (and emulsifier, if part of the

Table 1. Test Formula

Ingredient	Quantity g	%	% (flour basis)
Cake flour[a]	150.0	25.3	100.0
Baking powder[b] (Sodium aluminum sulfate-phosphate)	7.1	1	5.0
Shortening Corn oil[c] and Monoglyceride[d,e]	41.8	7.1	27.9
Sucrose solution			
Sucrose	167.4	28.2	111.6
Distilled water	107.0	38.2	151.0
Additional distilled water	19.5[f] + 100.0		

[a] Softasilk, General Mills

[b] Calumet, General Foods Corporation

[c] Mazola, Best Foods

[d] Dimodan PV, Grinsted Products: Mainly 85-90% glycerol monostearate and 10-15% glycerol monopalmitate (referred to as SMG). When SMG was used, it was heated to 60°C in 19.5 g water and allowed to cool to room temperature before being incorporated into the batter.

[e] Dimodan O, Grinsted Products: Mainly 70% glycerol monooleate (referred to as USMG). When USMG was used, it was heated to 60°C in 19.5 g oil and allowed to cool to room temperature before being incorporated into the batter.

[f] 19.5 g water was added to batters containing oil alone or oil plus USMG, in order to maintain comparable volumes with oil plus SMG systems in which 19.5 g water was added with the SMG.

formulation) and sucrose solution were added. The batter was mixed for 3.5 min with a mixer (Kitchen-Aid Model K45). The additional distilled water was added and the batter was mixed for an additional 3 min. Two-hundred-twenty grams of batter was weighed into an aluminum pan (15.2 cm diam. x 3.2 cm deep). All cakes were baked in a specially designed environmental oven for 25 min at 191°C (± 1°C) and an air flow rate of 10.1 m^3/hr. Details of the construction and design of this oven are given by Godsalve et al. (1977).

The temperature of the batter was monitored by thermocouples placed at the center of the cake and 7 mm above the pan base. The oven door containing the thermocouple setup is shown by Gordon et al. (1979). Batters were removed from the oven once a certain temperature was reached and immediately sampled from the center position. Batters were sampled for freeze-etch procedure at room temperature (i.e., unbaked), 90°C, 95°C and 102°C. Two replications of each batter type and temperature were made.

The choice of pretreatment method for dispersion of emulsifiers was based on the results of preliminary test bakings. Various emulsifier:water:oil ratios and temperatures were used in the test bakings. Phase diagrams of SMG and USMG were used to select the combinations of water that were tested. The pretreatment for each emulsifier that gave the most acceptable cake in terms of volume, symmetry, cell structure and crust characteristics was selected for all further studies (Cloke, 1981).

Freeze-etch technique

The cryofixation freeze-etch procedure has been described by Hsieh et al. (1981). Sucrose, at the high concentration present in our batters, served as the cryoprotectant to prevent ice crystal formation. No additional cryoprotectants were used. Each sample of batter was placed in a specimen support disc, then frozen in liquid Freon 22 at -160°C. The specimens were fractured in a Balzers freeze fracture apparatus at -105°C. Etching took place for 2 min before the specimens were shadowed with platinum and carbon from a Balzers electron beam gun at an angle of 45°. The replicas were strengthened by the evaporation of carbon at a 90° angle. The batter components were dissolved from the replicas by flotation for 5-7 days in a solution containing 50% household chlorine bleach and 50% distilled water. The replicas were placed on formvar-coated slot grids and examined in a Philips 300 TEM microscope at an accelerating voltage of 60 kV.

Results and Discussion

As the first step in the study of the structure of emulsified batters, we examined the appearance of individual components of the system after dispersion in 42% sucrose, which is the concentration of sucrose present in the batters. The morphology of baking powder, starch from flour, and oil when using replicas in TEM, as shown in Hsieh et al. (1981), served as the basis for identifying these components in batters, the appearance and transformations of which is the subject of this paper.

Baking powder in the batters did not undergo an observable morphological change in the 40 to 102°C range. Although some of that originally present may have reacted or dissolved in the batter, recognizable structures were still present at 102°C.

Oil droplets also did not undergo an observable morphological change in the 40 to 102°C range and looked similar in appearance as those seen in Fig. 1. Fractures always occurred through the droplet.

Both the initial size distribution of the oil droplets (Fig. 1) and the changes in size distribution with heating (Fig. 2) were related to the emulsive system present in the batter. Unemulsified and SMG batters initially had a few small oil droplets and tended to form pools of oil (Fig. 1). After heating to 102°C, both the unemulsified and SMG batters showed irregularly shaped oil pools between amorphous starch granules (Figs. 2a, b). USMG batters initially showed both large and small droplets. This type of distribution of oil in the USMG batter persisted up to 102°C (Fig. 2c).

No structures assignable to USMG were

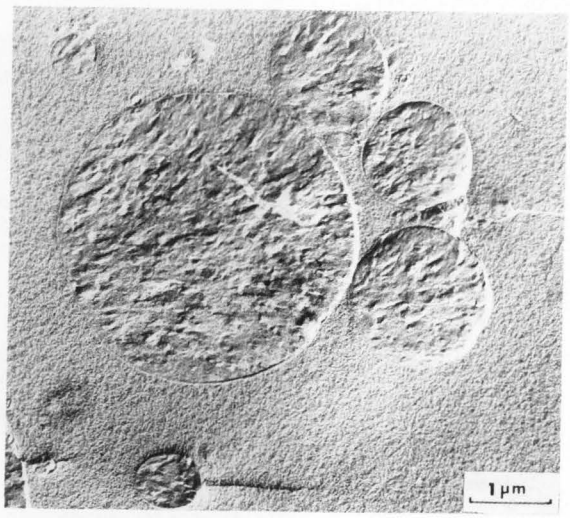


Fig. 1. Freeze-etch micrograph of oil droplets from a 5% saturated batter (unheated).

observed above room temperature. USMG was heated with oil to 60°C before it was added to the batter. It may have become associated with the oil prior to batter formation resulting in the fine dispersion of oil droplets observed in the batter.

SMG, in contrast to USMG, had distinct structural features which could be detected readily. Prior to batter preparation, SMG was dispersed in water and heated to 60°C. While some SMG may have formed mesophases, some appeared crystalline as can be seen in Fig. 3a for 10% SMG batter. Here we can see a surface fracture of an SMG particle. SMG appears to be made of layered sheets. At 89°C (Fig. 3b), a different crystal-like structure appears which is not associated with oil. According to Krog and Lauridsen (1976), a viscous isotropic and water mesophase could exist at this temperature. By 94°C (Fig. 3c), SMG partially encased oil droplets. Furthermore, SMG appears to be in lamellar or layered sheets similar to those present in the unheated batter (Fig. 3a). By the time the batter reached 100°C (Fig. 3d), SMG-oil interactions are once again observed with a variety of lamellar and crystalline forms present. It seems that SMG is present in several mesophase forms.

Thus, the oil/emulsifier/water system can be considered a three-phase system with a significant portion of the emulsifier present in mesophase structures. These micelles constitute a reserve from which emulsifier molecules can move to expanding interfaces to stabilize the interfaces. Furthermore, at some of the oil/water interfaces, the emulsifier is present in multilayers which would be expected to contribute to the stability of the system. The significance of presence and type mesophases in relation to starch transformations will be discussed following presentation of granule transformation.

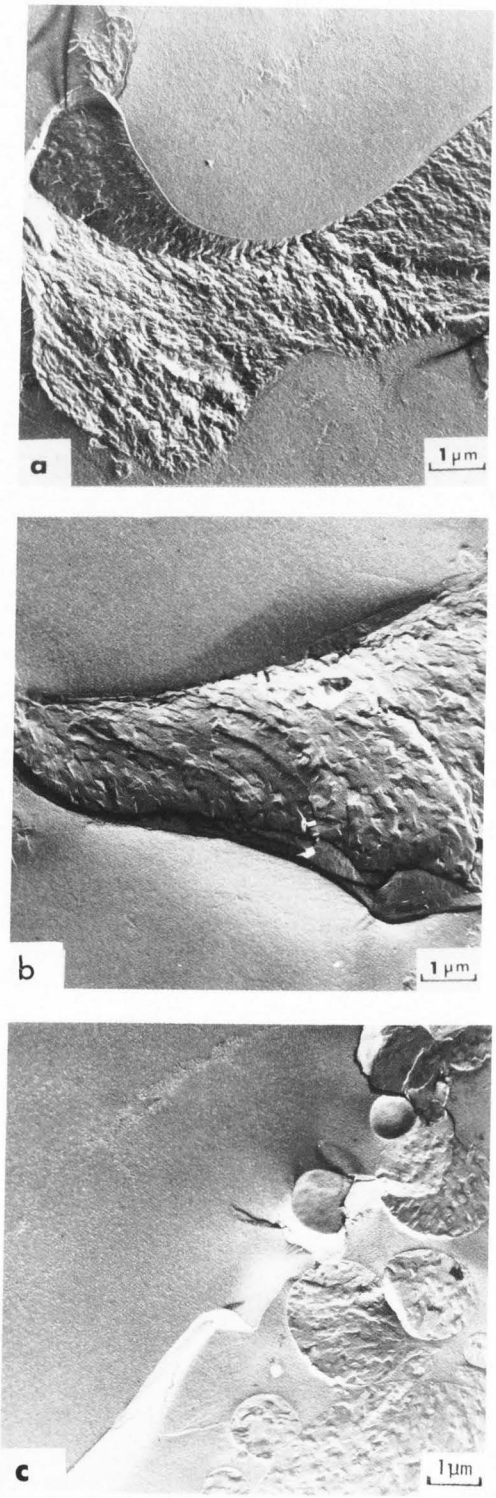


Fig. 2. Freeze-etch micrographs showing oil distribution at the batter setting stage.
(a) Unemulsified batter heated to 102°C
(b) 10% saturated batter heated to 100°C
(c) 10% unsaturated batter heated to 102°C

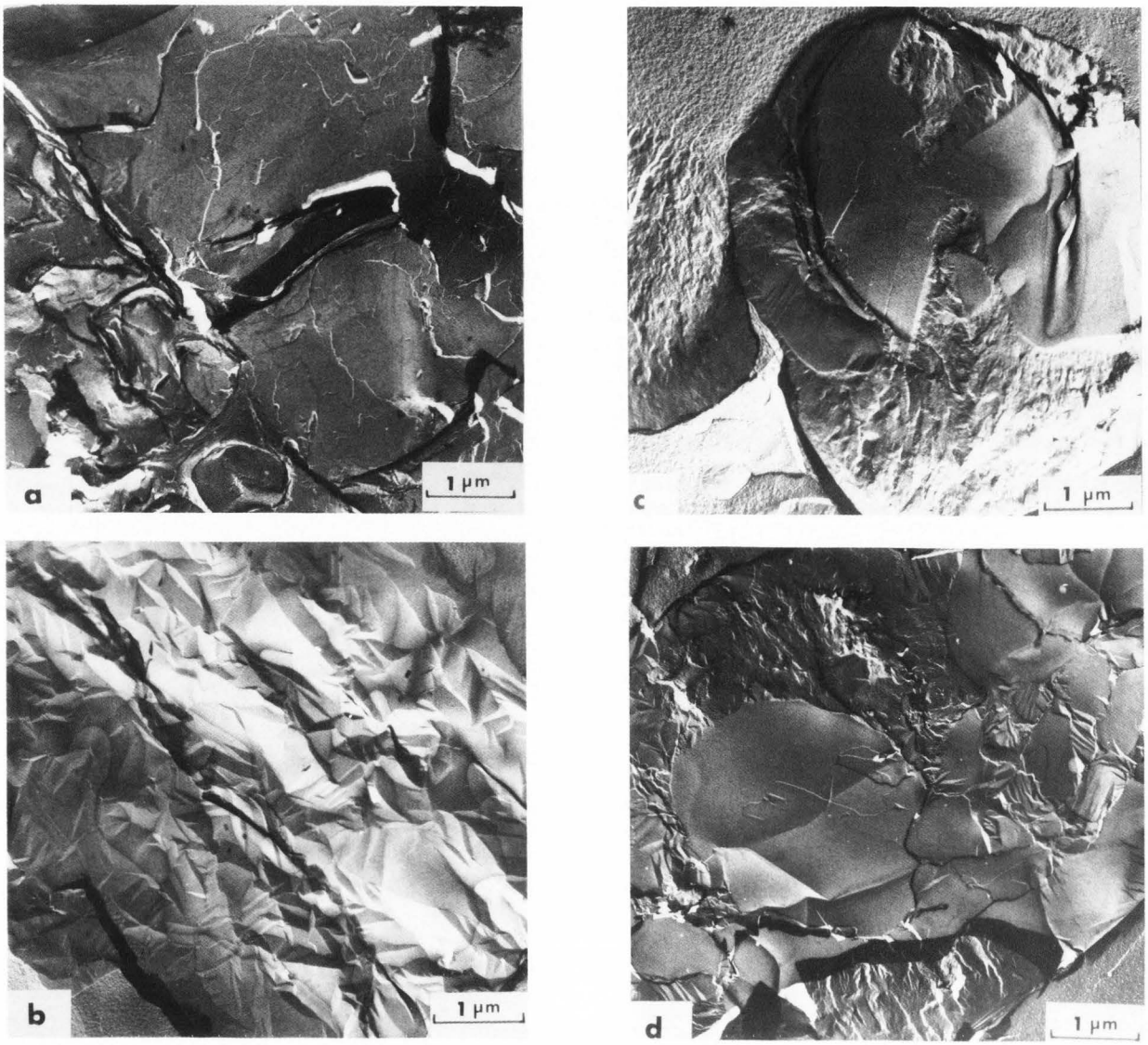
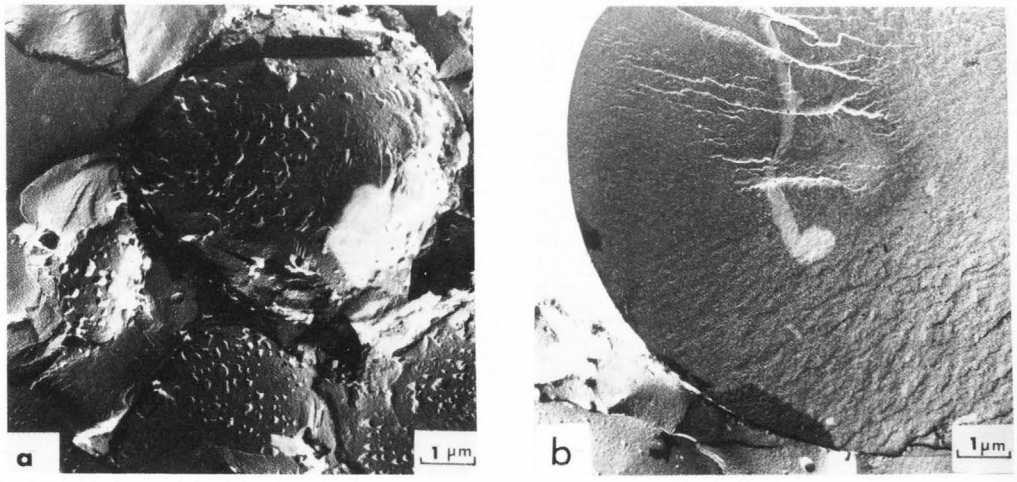


Fig. 3. Freeze-etch micrographs of the saturated emulsifier taken from 10% saturated monoglyceride batters at various stages of heating: (a) Unheated batter; (b), (c) and (d) heated to 89°, 94° and 100°C respectively.

Fig. 4. (a) Surface and (b) through fracture freeze-etch micrographs of starch granules from unheated, unemulsified batters.



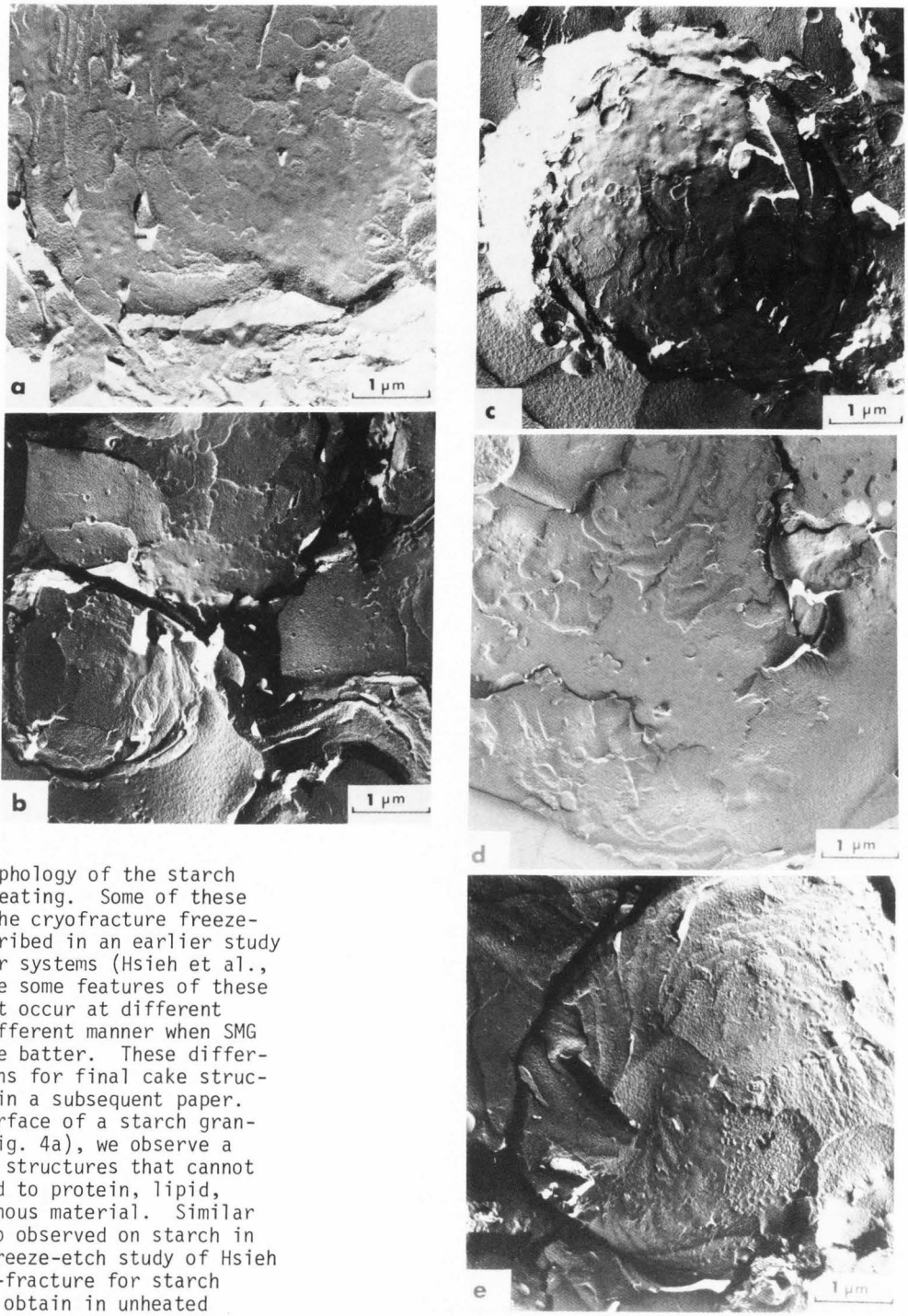


Fig. 5. Freeze-etch micrographs of surface fractures of starch granules from:
(a) Unemulsified batter heated to 90°C
(b) 5% saturated batter heated to 89°C
(c) 10% saturated batter heated to 89°C
(d) 5% unsaturated batter heated to 87°C
(e) 10% unsaturated batter heated to 88°C.

As expected, the morphology of the starch granules changed during heating. Some of these changes, as observed by the cryofracture freeze-etch technique, were described in an earlier study of simplified model batter systems (Hsieh et al., 1981). However, there are some features of these morphological changes that occur at different times or in a slightly different manner when SMG or USMG are present in the batter. These differences may have implications for final cake structure as will be reported in a subsequent paper.

If we look at the surface of a starch granule in unheated batter (Fig. 4a), we observe a non-uniformity of surface structures that cannot be specifically attributed to protein, lipid, sucrose, or starch membranous material. Similar bumpy structures were also observed on starch in sucrose solution in the freeze-etch study of Hsieh et al. (1981). The cross-fracture for starch granules was difficult to obtain in unheated batter. In the example shown in Fig. 4b, the edges are clearly fractured with no evidence of a membrane on this granule. A fine granular appearance is present as described by Hsieh et al. (1981). All unheated batter formulations give similar results.

By 87°C to 91°C, the starch granules began differentiation from those in nonheated batters, and cross-fractures were frequent. By 94°C, almost all starch granules cross-fractured. By 102°C, there are no surface fractures of starch granules.

The temperature at which starch begins to change appearance (87-91°C) is altered by the presence of emulsifier. In Figs. 5 and 6, we show differences between unemulsified and some emulsified batters for surface and cross-fractured starch granules, respectively. We can see that

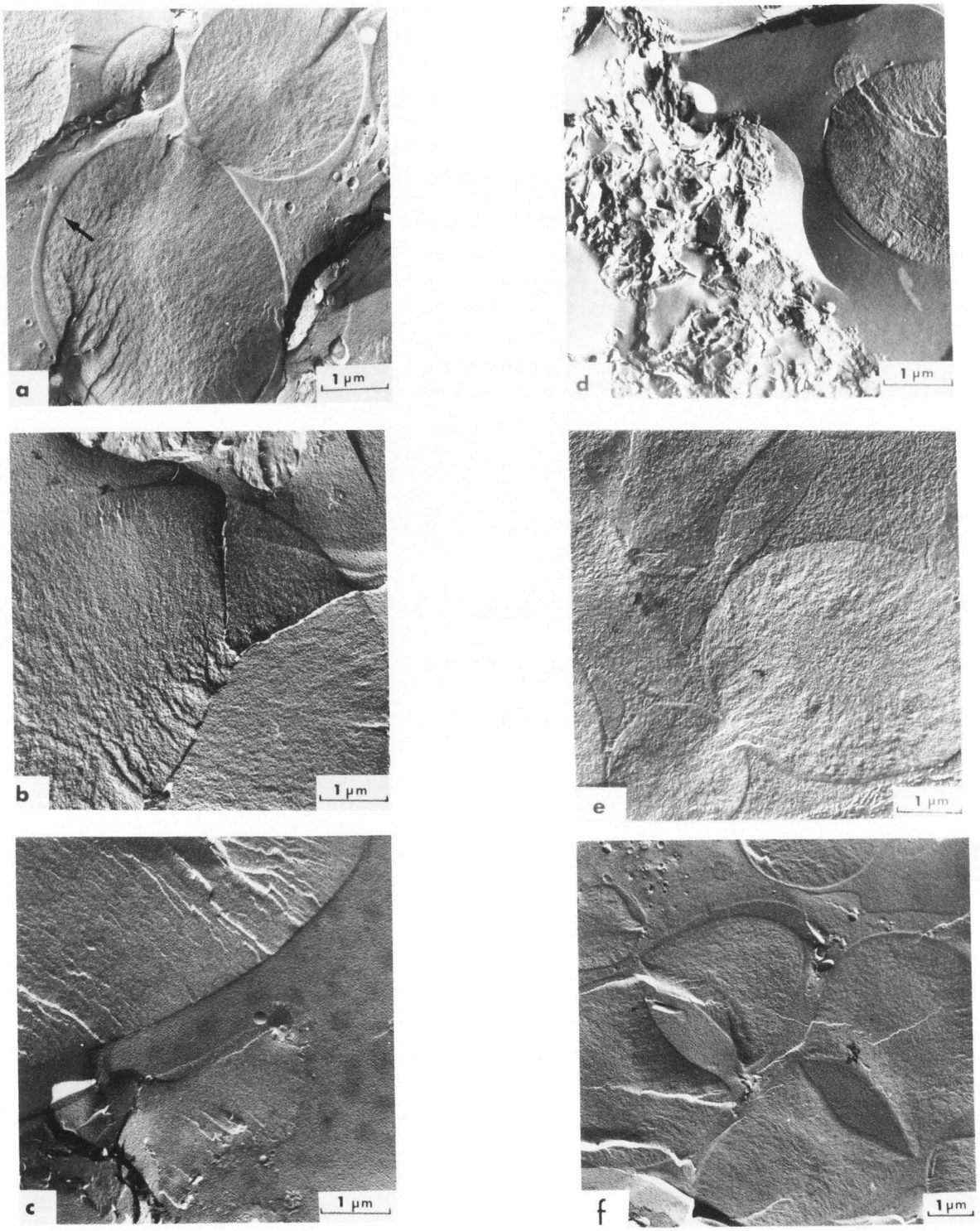


Fig. 6. Freeze-etch micrographs of through fracture of starch granules from batters with different treatments heated to 87-91°C. (a) Unemulsified batter heated to 90°C (arrow points to rim); (b) 5% saturated batter heated to 91°C; (c) 10% saturated batter heated to 89°C; (d) 5% unsaturated batter heated to 87°C (also showing baking powder with sucrose solution); (e) 10% unsaturated batter heated to 89°C; (f) 5% saturated batter heated to 94°C.

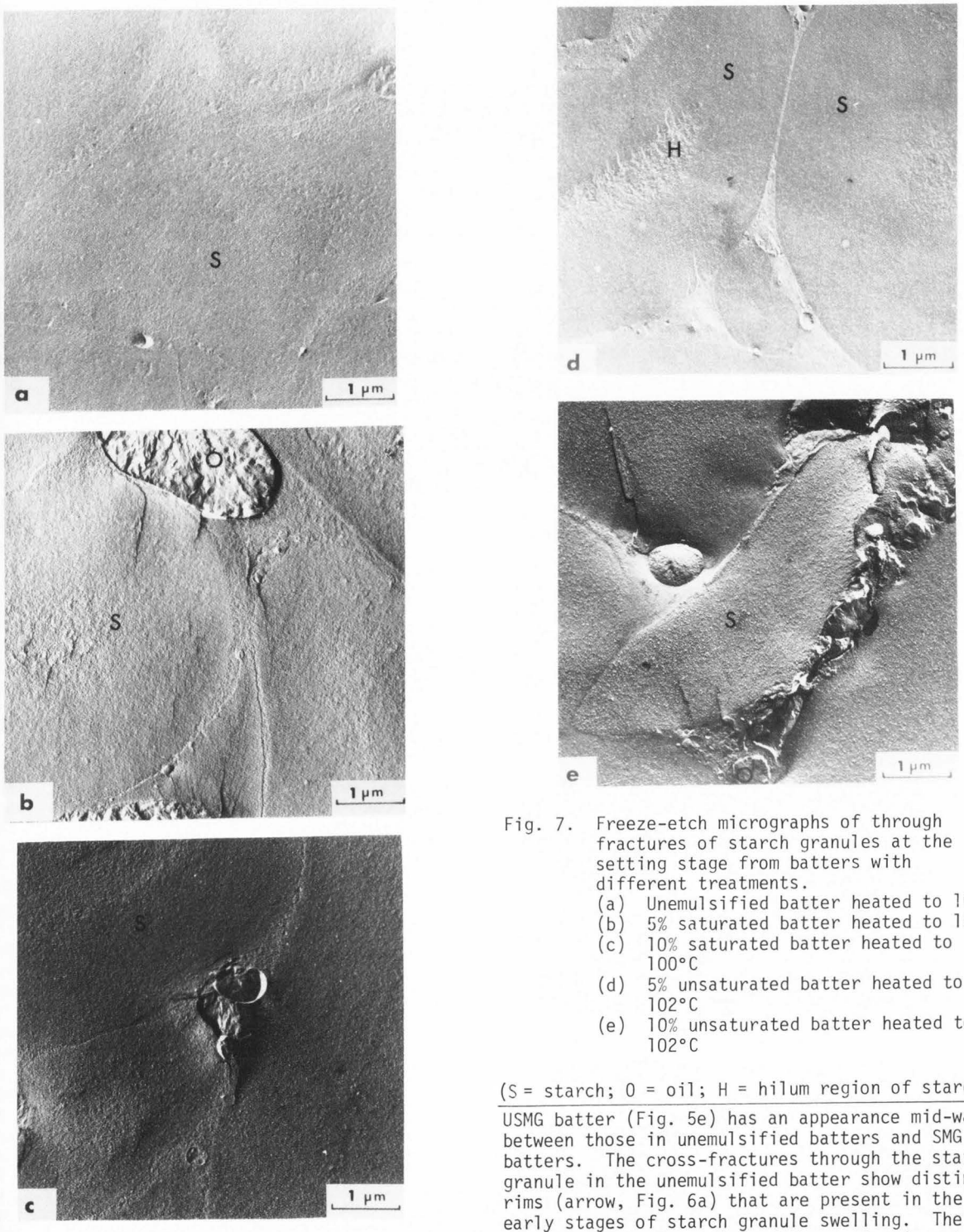


Fig. 7. Freeze-etch micrographs of through fractures of starch granules at the setting stage from batters with different treatments.
(a) Unemulsified batter heated to 102°C
(b) 5% saturated batter heated to 100°C
(c) 10% saturated batter heated to 100°C
(d) 5% unsaturated batter heated to 102°C
(e) 10% unsaturated batter heated to 102°C

(S = starch; O = oil; H = hilum region of starch)

the surface structure of granules in the unemulsified batter (Fig. 5a) is more smooth and layered than that of granules from the 5% and 10% SMG batter (Figs. 5b and 5c), respectively. The 5% USMG batter (Fig. 5d) shows a starch granule surface similar to the unemulsified one, but the 10% USMG batter (Fig. 5e) has an appearance mid-way between those in unemulsified batters and SMG batters. The cross-fractures through the starch granule in the unemulsified batter show distinct rims (arrow, Fig. 6a) that are present in the early stages of starch granule swelling. The reason for the formation of these rims is not known. It may be an initial stage in the plasticization of the granule with concomitant flow toward the edges. It is also possible that release of the soluble components is restrained by a membrane. However, the cross-fractured granules from unheated batters showed no evidence of such a membrane. Furthermore, in a study of granules,

utilizing ultra-low temperature microscopy, no evidence of a membrane was found (Davis and Gordon, 1978). The SMG batters contain starch granules that have few granule changes (Figs. 6b, c). The 5% USMG batter (Fig. 6d) contains starch granules that have a rim similar to those found in the unemulsified batter. The 10% USMG batter has starch granules (Fig. 6e) that have undergone some changes but not to the extent found in the unemulsified batter. Based on the criteria of presence of cross-fractures, granularity of interior, as revealed by cross-fractures, and development of a rim at the edge of the granule, the swelling order at about 90°C is: unemulsified > 5% USMG > 10% USMG > 5% or 10% SMG. Size of granule is not a useful criteria for this purpose because of the initial size variations and the uncertainty as to where the fracture occurs in the granule. It is not until 94°C that the SMG batter contains granules with rims (Fig. 6f) that closely approximate those seen at 90°C for the other systems.

At the time of thermal setting of the batter (100-102°C), all starch granules have swollen and the internal appearance of granularity is different (Fig. 7). All batter preparations contain starch granules with nondescript boundaries, such as those seen for unemulsified batters in Fig. 7a. Batter with 5% SMG has some starch boundaries that were more clearly defined (Fig. 7b). Batter with 10% SMG (Fig. 7c) had less clearly defined starch boundaries. The boundaries between starch granules in USMG batters were also clearly defined, and there was less contact between granules than was the case in SMG batters. The oil appeared to be more finely dispersed throughout the matrix surrounding the granules. In Fig. 7e, the dispersion of the oil at the boundary of a group of overlapping starch granules is shown. Therefore, before the time of thermal setting, USMG disperses through the batter matrix, assuming that it remains closely associated with the oil. SMG, however, must undergo a series of phase changes (Figs. 2 and 3) before it becomes effective in encasing the oil later in the baking process (at about 95°C). Simultaneously, the initial stages of starch granule swelling are developed as shown in the sequences in Figs. 5 and 6. Eventually, all of the granules will undergo similar swelling at a higher temperature. Also, the matrix material between granules is more developed in the USMG batters at the time of swelling.

In interpreting these studies, it should be remembered that all experiments were carried out at the high sucrose concentration typical of cake batters. This has the advantage of studying the transformation as it occurs in batter. It has the further advantage in freeze-etch studies that the sucrose served as the cryoprotectant so that additional cryoprotectants were not required. Inhibition of swelling and elevation of gelatinization temperatures in model systems containing high sucrose concentrations was studied by Bean and Yamazaki (1978).

This, together with the starch:water ratios present in the batter, may account for some of the differences between starch transformation in the batters that we observed and those observed by others working with starch:monoglyceride:water systems in different concentration ranges.

The freeze-etch data presented here do not provide direct evidence of complexing of the emulsifiers with starch at the molecular level. DSC studies of this system (Cloke, 1981) indicated that the enthalpies of the starch transitions up to 120°C are the same, although the onset of the transition was delayed slightly at the 5% level of SMG. This result is supportive of the observations made with the freeze-etch technique which focuses on the changes at the ultrastructural level.

The critical role of water in starch granule transformation has been emphasized by many workers. Marchant and Blanshard (1978), in interpreting their small angle light scattering studies of starch granule transformation, felt that water must enter the starch granule by diffusion in order for molecular changes to occur. Van Lonkhuysen and Blankestijn (1974, 1976) suggested that the monoglyceride micelle may form around the starch granule, or at least adhere to the surface of the granule. In this view, the monoglyceride does not enter the granule, although it may be tightly bound to it even at relatively low temperatures of 30°C. The monoglyceride would then act as a barrier to entry of water as suggested also by Eliasson et al. (1981).

If the monoglyceride does not enter the granule, enthalpies for starch transitions, as measured by DSC, and by implication the changes in molecular conformation of the starch components, would not be affected by the presence of monoglycerides as was, in fact, observed in our earlier study (Cloke, 1981) and by Eliasson et al. (1981) for potato starch.

From our freeze-etch studies of batters at room temperature (e.g., Fig. 3) it appears that much of the SMG remains in discrete particles at room temperature. From the distribution of these particles, it appears that close associations between SMG and the granules did not occur. While detection of monomolecular layers closely associated with the starch granule is beyond the resolution of our method and, therefore, cannot be ruled out, it would appear that SMG would be unable to interact with the starch granule to any great extent in the initial stage. USMG appears to affect the oil droplet distribution, but if it has an effect on the starch in the initially unheated batter, it cannot be seen at this stage of the batter development.

The freeze-etch studies of the transformation of SMG during heating reported here document the phase changes of SMG. If SMG requires mass transport of water into its crystalline structure during these phase changes, starch swelling may be delayed because of decreased availability of water for many of the chemical and physical transformations that precede or accompany swelling. In some of our earlier work with a variety of emulsifiers (Hsu et al., 1980) and in the investigation of the saturated and unsaturated monoglyceride batters (Cloke, 1981) in which water loss rates were monitored during baking, it was shown that, generally, the mass transfer of water out of the cake is delayed during this period of baking in

the presence of an emulsifier. Therefore, the water must be participating in some interactions even if it is blocked from the granule. Participation in emulsifier phase changes and oil micelle effects are possible explanations.

In our DSC studies (Cloke, 1981) SMG phase changes were observed to begin in the range of 57-59°C. Enthalpy changes were noted as oil and water were added, which suggest the formation of an SMG-water mesophase. Freeze-etch data show oil surrounded by SMG structures at 95°C, but similar structures were not found to surround starch granules. Other workers have attributed a surface adsorption role to the emulsifier. For example, Jongh (1961) stated that the adsorption of glycerol monostearate to the surface of the starch granule led to flocculation of previously stable starch suspensions. Thus, our freeze-etch studies do not confirm a surface adsorption role for the monoglycerides either in the initial or later stages of granule transformation.

The potential for complex formation between amylose, and, to a lesser extent, amylopectin and lipids including monoglycerides has been recognized for many years. Many of the studies of complex formation were made with extracted amylose or amylopectin. When the granule is considered, either isolated from its original site or in the presence of other constituents found in its natural environment, as in the case of flour, the site at which complexing occurs (e.g., intra- or ex-granule), the stage in the heat-induced transitions at which it occurs, the consequences of complex formation on other aspects of the heat-induced transitions (most commonly - granule swelling, viscosity, extractability of monoglycerides (Krog, 1981)), as well as effects on overall product quality, have been the subject of much argument. Therefore, care must be taken to compare experiments that are measuring the same phase transitions or properties in starch gelatinization as Donovan (1977) has stated so clearly in the past.

The extent of complex formation with amylose is related to molecular structure of the lipids (Krog, 1981). Conformational differences between saturated and unsaturated monoglycerides are considered to be one basis for these differences. SMG, more than USMG, was observed in our studies to have an inhibitory effect on swelling of starch granules during heating.

For saturated monoglycerides, the nature of the mesophase has also been considered to play a role in the extent of gelatinization (Krog and Nybo-Jensen, 1970). It may be simply that the dispersion state influences the distribution of the monoglycerides throughout the system. Recently, however, Krog (1981) suggested that monoglycerides are adsorbed onto the granule surface in the β-crystal form and then are transformed to a liquid crystalline phase as the active form for complex formation. In his view, reduced granule swelling as a result of complex formation makes more water available for other reactions. As pointed out earlier, we saw no extensive adsorption of SMG on granule surfaces by freeze-etch technique. We suggest also that availability of water may be decreased by mass transport of water into the mesophase.

The stage in starch transformation at which monoglyceride-amylose complexing occurs is not clear, although some DSC studies indicate that complex formation comes after the original conformational changes in the starch. In our DSC studies, we saw no changes in enthalpy of starch transitions in the presence or absence of monoglycerides (Cloke, 1981). However, observations of Kugimiya et al. (1980) and Kugimiya and Donovan (1981) suggest that complexing occurs just after the initial granule transformation and that the complex disorders in the range of 95-104°C. The relationship of this sequence to the mechanism of granular swelling as observed by freeze-etch is not clear, although the overall differences in swelling between SMG and USMG were observed.

Therefore, the observations made with the freeze-etch technique can be explained either by amylose-monoglyceride complex formation or by the effects on water transport of phase changes of monoglycerides. Since there were no morphological changes or differences in thermal requirements in this temperature range, it would tend to support the water transport mechanism. This does not exclude complex formation and/or melt at higher temperatures. Similarly, the decreased effectiveness of USMG in delaying granule swelling may be because USMG does not complex as readily with amylose or that it does not undergo phase changes in that temperature region.

Conclusions

The reactions occurring in cakes are many and complex. This paper examined, by freeze-etch, the role of monoglyceride emulsifiers during baking. In lean formula cakes where the shortening is a corn oil, USMG was more effective than SMG in dispersing oil droplets throughout the batter. SMG formed liquid crystals during baking, during and after which it played an active role in starch swelling due either to complexing ability or water transport involvement. Although monoglycerides do not alter the energy of transitions that the molecules present in starch undergo, they do alter the temperature at which swelling of the granule begins. Evidence from other studies showed that SMG with its better amylose-complexing ability delayed swelling more than USMG. At about 95°C, granules began swelling in SMG and USMG batters. Towards the end of baking, starch granules from SMG batters had swollen and in some batters were virtually indistinguishable from unemulsified batters. Cake batters made with USMG could be differentiated from the others by more evenly distributed oil droplets and by the development of a more clearly-defined matrix between starch granules.

This information on the initial batter structure and the transitions that occur in batters during heating as obtained by freeze-etch techniques can be integrated with other types of information such as heat transfer properties and water loss rates to explain differences in final cake structure (Davis and Gordon, 1982).

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Discussion with Reviewers

J. Holme: The paper suggests one or two mechanisms by which decreases in water availability may result in less starch swelling and/or water loss from batter systems. Could you comment if and how EM might also be of value in demonstrating the role of other normal cake batter constituents, such as egg white and milk, in the thermal setting process of batter systems.

Authors: We have a study of this type in which dry nonfat milk solids additions are added to the lean formula described in this paper. We are measuring the macroscopic properties of the baked cake such as volume, color, cell structure; dynamic properties such as heat transfer and water loss rates and hope to correlate these with the microstructural changes observed with EM. We hope to characterize the changes in the microstructure of the components of the nonfat milk solids such as lactose and casein as well as changes in the components described in this paper such as oil, starch granules, and intergranular matrix. Studies, such as those of Buchheim, of the microstructure of milk products (Buchheim, W. A comparison of the microstructure of dried milk products by freeze-fracturing powder suspensions in non-aqueous media. Scanning Electron Microsc. 1981; III. 493-502), will aid in characterizing the initial structures before heating the batters.

P. S. Pesheck: Have you looked for starch-monoglyceride complexes by X-ray diffraction or tried to measure water activity in the presence of SMG or USMG?

Authors: We are planning to do X-ray diffraction studies in the next phase of our studies. We have determined the water activity of the cake "crumb" after baking. The values were in the range of 0.89 to 0.92 and did not appear to be related to the type of emulsive system being used.

P. S. Pescheck: I'm intrigued by the "bumpy" structure in Figure 4a. Have you seen them in systems which don't contain sucrose? What if you froze a suspension in oil - would you see them there too?

Authors: We have not prepared any samples without sucrose. The sucrose, in addition to its presence in the formulation, served as the cryoprotectant. Whether freezing in a suspension of oil without cryoprotectants would be successful would have to be investigated. Ultra-low temperature microscopy is an alternate approach.

D. D. Christianson: Do you have evidence for amylose solubilization and retrogradation in your batters? See Hoover and Hadziyev. Starch. 10, 1981; 346-355.
Authors: We did not attempt any measures of solubility. If amylose solubilization occurred, the soluble amylose would become part of the intergranule matrix. In the freeze-etch studies, the matrix for USMG appeared to be more developed. It would be tempting to interpret this observation as support for increased solubilization of amylose in presence of USMG as compared to SMG, but further study is needed to support this interpretation. SEM micrographs of starch granules from batters made with several different emulsifiers are given in Hsu et al. (1980). In these cases, a matrix is observed, but it is not fibrous appearing as shown by Hoover and Hadziyev. Ropey structures similar to those shown by Hoover and Hadziyev were observed occasionally in cakes baked in microwave ovens. They were observed in potato starch viewed at ultra-low temperatures (Davis and Gordon, 1978).

D. D. Christianson: Do you think that the SMG actually enters the granule and complexes with amorphous amylose inside the granule? Does this prevent solubilization? Because the thesis is hard to get at for the reader, I feel it would be valuable to include some backup DSC data, especially where oil-water-emulsifier play a key role in starch surface transition.
Authors: As we point out in the text, this question of the site of monoglyceride amylose interaction can only be answered indirectly in studies of this type. The freeze-etch technique can give information on the overall effects on the granule swelling. DSC studies give information on the enthalpies, and, as a result, conclusions about the conformational changes can be drawn. But neither technique unambiguously pinpoints the site of the interaction. Furthermore, it is our view that the question of amorphous amylose regions within the granule needs further investigation. One approach would be to form amylose-iodine complexes and then investigate the binding location of iodine with X-ray microanalysis.

Details of the DSC studies are given by Cloke (1981). As we point out in the text, in the batter formulation we did not see the endothermic peaks for complex formation reported by Kugimiya et al. (1980) and Kugimiya and Donovan (1981). However, almost all DSC studies show that the temperatures of onset of the peaks and enthalpies depend on starch:water ratios among other things. Thus, for our specific formulation we do not observe changes in enthalpy when emulsifiers, either USMG or SMG, are added although the temperatures of onset of peak change slightly.

R. G. Fulcher: Presumably, removal of samples from partially-cooked batters results in significant cooling and physical stress prior to freezing in liquid freon. Does this sampling procedure induce artifacts in the specimen?
Authors: Artifacts are always a possibility, but we tried to minimize the time between sampling and freezing, and to remove the sample with minimum handling. The batter remains quite fluid up to 102°C, so that it is easily sampled. In the 100-102°C range, structure is just beginning to form so, again, the crumb is not subjected to cutting stress.