Microstructure of Shortenings, Margarine and Butter - A Review

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FOOD MICROSTRUCTURE, Vol. 7 (1988), pp. 181-188 0730-5419/88$3.00+.00
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MICROSTRUCTURE OF SHORTENINGS, MARGARINE AND BUTTER - A REVIEW

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Abstract

Fat spreads are composed of liquid oil, fat crystals and water. The fat crystals in these products give the product the required consistency and stabilize the water droplets. Shortenings are water-free products, the rheology of which depends on the solid fat content and interactions between fat crystals. Size and interaction between crystals is influenced by both composition and processing. Crystals form a three-dimensional network. Recrystallization phenomena, especially formation of large beta-crystals, can create product defects like sandiness. Margarines and halvarines are water-in-oil emulsions and have a relatively simple product structure. Because of the wettability of fat crystals, part of the solids are present in the water/oil interface, and influence the stability of the emulsion. Depending on the type of application, tropical margarines, table margarines, halvarines, puff-pastry, creaming margarines, etc., the ratio of solid/liquid and water content can be varied. No essential differences exist in the microstructure of products for different applications. Butter differs in its microstructure from margarines because of different processing and raw materials. Butter still contains a number of fat globules (derived from the cream) in its final product structure. These globules are dispersed in a matrix of fat crystals and oil descending from fat globules that were broken during churning. Also the moisture is present in different forms ranging from droplets to "free moisture". Differences in microstructure can be introduced by different processing regimes.

Initial paper received September 20, 1988
Manuscript received November 30, 1988
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Key words: Fat spreads, shortening, butter, fat crystals, crystal network, fat globule, water droplet, air, microstructure, electron microscopy

Introduction

Microstructural studies in the area of fats and fat-based spreads are becoming increasingly important. Both the dairy and margarine industries are realizing the importance of these studies, since with the knowledge of the product microstructure, a better understanding of the product properties and ways to influence these can be obtained. Initial research focussed on properties like crystal modification and overall product properties, such as product rheology. More recently, the use of new techniques such as electron microscopy (EM) in combination with well established knowledge of margarines and butter has led to a significant improved understanding of structures and their effect on product properties.

From a microstructural point of view, essentially three different structure-types can be distinguished: shortenings (100% fat), margarines and halvarines (80 and 60% fat respectively), and butter (80% fat). Both composition and processing can be used to influence the product microstructure. Margarine and shortenings not only can be composed of a relatively wide range of triacylglycerols but also the aqueous phase may contain different ingredients. The composition of butter is much less subject to change: the only compositional changes result from changes in the milk composition due to, e.g., barn / pasture feeding, level of underfeeding, stage of lactation, breed of cattle, etc. Consequently differences in butter microstructure often result from changes in processing. For margarines and shortenings the many degrees of freedom has led to a diversification of products of 100 to 40% fat, from soft high polyunsaturated fatty acids to hard puff-pastry products.

The present paper reviews the literature on the microstructure of fat spreads. Micrographs used to illustrate the microstructure of fat spreads have been obtained from the investigations by the authors.

Structural elements

Fat crystals

The formation of texture in spreads is the result of crystallization of triacylglycerols with high melting points. The crystals do not behave as single crystals, but show different types of aggregation with formation of a three-dimensional fat crystal network. The strength of this network is influenced by many compositional and processing parameters (6).

Triacylglycerols crystallize in four different modifications: sub-α, α, β' and β (8). The first two modifications, sub-α and α, are unstable and therefore do not exist in spreads. The β' modification is stable but its crystal lattice is less well ordered than the β modification. Of all modifications the β modification has the highest ordering and consequently the highest melting point. In most spreads different raw materials are blended to arrive at the desired overall crystallization and melting behaviour. As a consequence the triacylglycerol composition of the blends is rather complicated. This implies that in spreads the β modification does not occur very often; the β' modification is the predominant one. Fat crystals can be either needles (Fig. 1) or platelets. The β modification is frequently correlated with structural defects: large β crystals are perceived as sandiness (1) (Fig. 2).

Fat globules

Fat globules as found in butter (Fig. 3) (14) originate from the cream. Prior to the churning process, the cream is physically ripened (i.e., the cream is cooled to such an extent that fat crystallization in the oil droplets occurs). Depending on their strength these fat globules will survive the churning process (19).

The fat globule in cream is covered with a fat globule membrane, whereas in butter parts of the membrane may be removed as a result of churning. The outside of this membrane is a hydrophilic, proteinaceous layer of complex composition (14) (Fig. 4). The periphery of the globule is formed by an approximately 0.1 - 0.5 μm thick crystalline shell (15). Different opinions exist about whether this crystalline shell is composed of high melting β crystals (15, 18), which concentrate in the oil/water (O/W) interface as a result of ripening conditions and crystallization at the interface (2). Alternatively a shell would result crystals that are formed randomly in the oil droplet during ripening and subsequently transported to the O/W interface as a result of deformation during churning (24). The average diameter of globules in butter is 3 μm.

Networks

Fat Spreads derive their consistency from interactions between fat crystals which form a three dimensional network (Fig. 5a and 5b). The nature of the interactions between the fat crystals determines the type of network structure and the rheology of the product. Quite a number of publications deal with rheological properties of fat spreads (for a review see reference 3).

Many aspects are related to the amount and the nature of the interaction between fat crystals (6):

- the hardness of a spread depends on the amount of fat crystals;
- blend composition will influence the molecular arrangement in crystals and thus the strength of interactions between crystals;
- slowly crystallizing blends will continue to crystallize after packaging, which favors the formation of a strong network;
- high crystallization speeds give rise to soft and overworked products.

Two types of bonds are assumed for crystal-crystal interactions (5):

- primary bonds, which result from crystals growing together at some points. These bonds are "irreversible", i.e., do not re-form after rupture;
- secondary bonds, which are (weak) London-Van der Walls forces, which are "reversible", i.e., do re-form after rupture.

Primary bonds are considered to be responsible for the hardness of products, whereas secondary bonds contribute little to consistency.

In other works (21) such a distinction between primary and secondary bonds is considered to be arbitrary and it is suggested that a true characterization should be based on the concept of a spectrum of bond strengths. In margarine, weak bonds form only a minor proportion of the bond strength spectrum, strong bonds form the major part. Butter on the other hand contains a small proportion of strong bonds.

Microstructural observations of network structures substantiate such a concept (7, this work).

Water droplets

Margarines and butter roughly contain 16 - 20% water, which is present in the structure as finely dispersed droplets. An impression of the status of the water droplets in spreads can be obtained by using freeze-fracture as the sample preparation technique for EM observation.

Fig. 6 shows the result of this technique for a fat spread, indicating that the sample fractures either over the surface of the water droplets, or that cross fracture of the droplet occurs. Because of their wettability fat crystals can be found in the O/W interface, which stabilizes the water droplets (17). This stabilizing action of the fat crystals strongly depends on the presence of surface-active ingredients like monoacylglycerols, phospholipids and proteins (9).

Emulsifying systems applied in spreads usually are based on monoacylglycerols and lecithins (11). Only in products for other (e.g. bakery) applications sometimes other surfactants are used. Milk protein (O/W emulsifiers), as present in the aqueous phase of spreads, tend to destabilize the emulsion. Water droplets in spreads should be kept small (preferably < 5 μm) to reduce microbiological risks (22, 23). Small droplets induce a greasy taste (see ref. 8, page 221).

Air

In some products (shortenings and margarines) air is introduced to influence either consistency (4, 12) or appearance. Air usually is entrapped in the liquid oil phase of a spread. Small crystals have been described to orientate tangentially to the surface (1). It is not clear whether these fat crystals have a stabilizing effect on the air bubbles. After churning, a similar type of arrangement is observed in fat globules of butter (14). Under polarized light a birefringent layer is observed, also ascribed to tangentially oriented fat crystals in the outer layers

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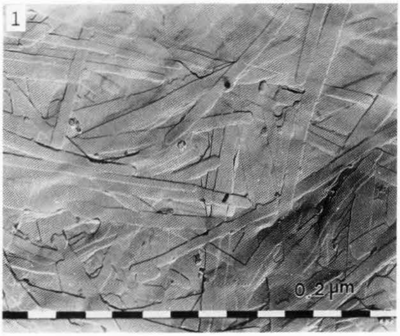
Fig. 1. Typical example of fat crystals (freeze-fracture).

Fig. 2. Spherulites in β-crystal modification, isolated from a fat spread, inducing sandiness.

Fig. 3. Examples of a fat globule as present in butter. The open crystalline shell structure is induced by removing the oil from the inside of the globule during the preparation procedure (reference 7).

Fig. 4. Example of a cross-fractured butter globule. Orientation of fat crystals parallel to the droplet surface (arrow 1); traces of remaining water around the droplet (arrow 2).

Fig. 5. Three dimensional networks of fat crystals in a shortening at (a) low and (b) high magnification.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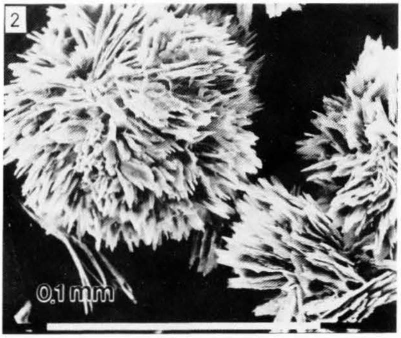
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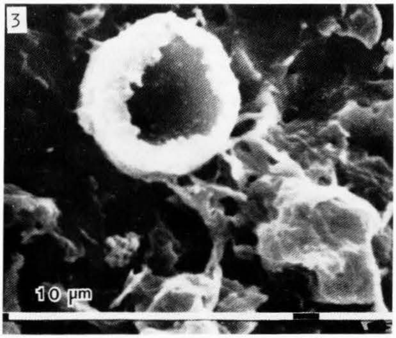
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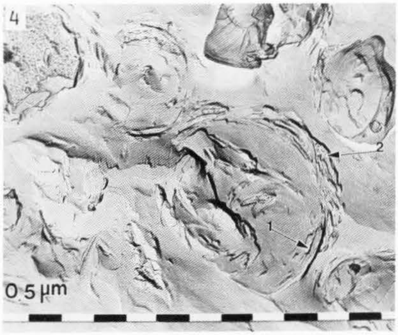
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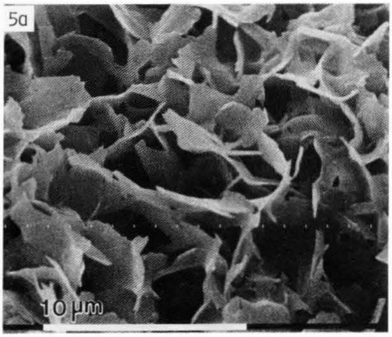
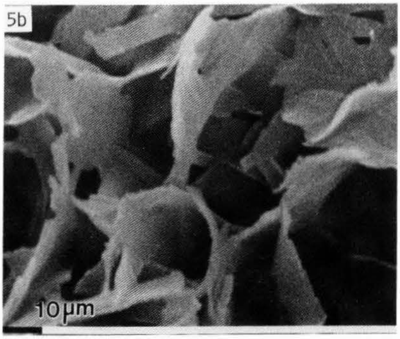

5a
10 µm


5b
10µm

of the fat globules and induced by pressure exerted by air during churning.

Air is present in products in all shapes (Fig. 7), from round bubbles to strongly deformed areas, depending on the way it has been introduced into the product. Smooth round air bubbles are found when introduction is done at low solids levels, e.g., during whipping of margarines or shortenings in cake preparation. Strongly deformed air bubbles are found when high solid contents are present at the moment of air introduction, e.g., during processing or churning. In butter some air (approximately 5 %) is still present as a result of the churning process (14) (Fig. 8).

Product structure

Shortenings

Due to their composition shortenings have the simplest product structure of all fat spreads. These products are composed of liquid oil and fat crystals only. Blending different oils offers a wide range of solid/liquid ratios. Fat crystals usually take the shape of needles or platelets.

The existence of a three-dimensional network of fat crystals has been postulated for many years (5), but only recently sample preparation techniques have developed (7) that could demonstrate the existence of such a network. The nature of the network structure will depend on both composition and processing conditions. In particular, the extent to which individual crystals aggregate, determines the character of the observed network. As an example of this, Fig. 9 shows the microstructure of two shortenings of the same composition. The only difference is found in the processing condition.

For some applications air-containing shortenings are produced. The presence of air does not principally affect the crystal-crystal interactions in the crystal network but it does reduce the number of crystals per unit of volume. The product hardness (g/cm^2) decreases with increasing air contents (5). At higher levels of air, brittleness may occur (4).

Tempering, i.e., storage above ambient for a few days (5) is sometimes applied for shortenings. During this process recrystallization takes place in which mixed crystals (as formed during fast crystallization in a votator) "demix" and form other more stable crystals. This generally leads to larger crystals and a slightly softer products.

Margarine

Like shortening, margarine derives its consistency from a fat crystal network. No essential differences in fat crystal network are found on comparing these two types of products. The most striking difference in structure is the presence of water droplets in margarine. Water droplets of a few µm are formed during intensive mixing of fat and water phase during processing. In this process crystals can orientate at the water droplet surface.

In margarines "shells" of fat crystals can be found (7) (Fig. 10) that surround the water droplets. These "shells" seem to be interconnected with the three-dimensional fat crystal network.

The water droplet size distribution can be influenced by processing: intensive shear during processing results in a finer emulsion (Fig. 11). The main difference in microstructure found in all 80% fat products is the nature of the fat crystalline network, e.g., the size, shape, and aggregation of fat crystals. Depending on the type of product, more or less solids are applied. Over the last two decades the fats industry has diversified the margarine area into products aimed at specific applications such as margarine for tropical countries, halvarines, and products for bakery applications like creaming, cakemaking and puff-pastry products.

In halvarines essentially the same microstructure is found as in margarines: only the ratio water droplets/fat/oil is different. In puff-pastry a finer crystal structure is preferred to a coarse crystal structure (10, 11). The finer crystal structure was found to give a better performance in pastry preparation while the pastry margarine itself showed less work softening.

Butter

In butter a limited number of milk fat globules are still present in the final product. The number of fat globules that survive processing strongly depends on the ripening procedure of the cream (19,20) and on the working conditions during and after processing (20): Cold-warm-cold (CWC) ripening procedures give stable globules with thick surface crystal layers of high melting triacylglycerols, while the interior of the globule contains crystal aggregates and liquid oil. A large number of these globules survive processing in contrast to globules formed during "cold-ripening" (19) which are less stable and break during processing (Fig. 12).

Intensive working destroys fat globules resulting in a more crystalline interglobular phase and consequently a harder consistency. A combination of "C-ripening" and intensive working is applied in the production of summer butter. Winter butter is produced by applying a CWC-ripening (20).

The interglobular phase in butter is a mixture of liquid oil, crystal aggregates and membrane residues. In fresh butter the crystals are slightly curved and sometimes arrange in groups with parallel orientation. The liquid phase often contains ordered structures which are not as distinctly differentiated from amorphous areas as real crystals. Possibly they represent liquid crystals (16). After 10 days storage of fresh butter an increase of uncurved newly formed crystals is observed. This phenomenon is thought to be related to the setting and hardening of butter (16).

Fig. 6. Water droplets in fat spreads. The freeze fracture technique gives rise to two different images of water droplets depending on whether the sample breaks (S) over the surface of the droplet or (C) whether cross-fracture occurs "through" the droplet.

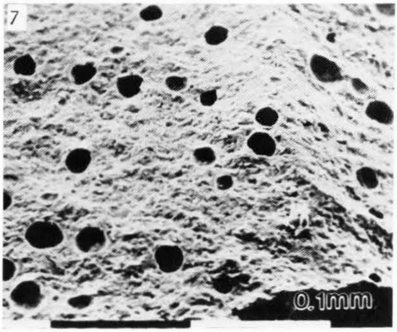
Fig. 7. Example of air cells in a shortening. Air dosed during votator processing.

Fig. 8. Air cell in a churned product. (g) fat globule; (w) water. The air interface is covered with fat globules.

Fig. 9. Partial crystallization in rest shows a structure of interconnected crystal clusters (a), whereas complete crystallization in a votatorline shows a structure of connected plate-like crystals (b).

Fig. 10. Fat crystalline network (f) and water droplet structure (w) showing a crystalline shell, in a margarine.


6
s
s
1µm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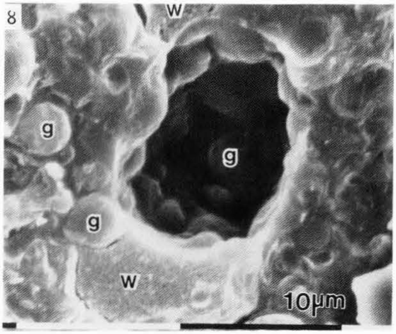
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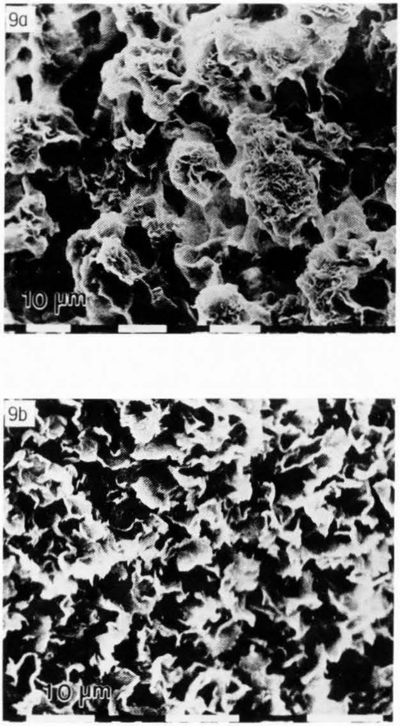
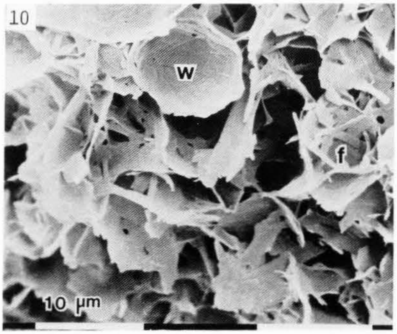
10µm


9a
10 µm
9b
10 µm


10
w
f
10 µm

The emulsion structure of butter has been a subject of much debate, especially the water continuity of the product (13,14). At the start of butter production, water is the continuous phase. During churning and subsequent working, the fat phase becomes the continuous phase. By more intensive working, the water becomes more finely dispersed in the product. Nevertheless, in contrast to margarine, water continuity in butter is still observed. It has been proposed by Mulder (13) that the water containing membranes of many fat globules lie so close to water droplets that a pathway is offered for transport of water molecules (water channels). This type of structural arrangement can indeed be observed by freeze fracture EM (Fig. 13), although water, as such, cannot be detected.

Water droplets in the final products have sizes between 0.25 and 25 µm. Occasionally small fat globules are incorporated in the water phase (17). The presence of fat crystals around the water droplets in butter is a matter of some debate. A dense surface coverage with high melting butterfat crystals has been reported (17). In other work such a shell formation was not observed (7).

Conclusions

Fat spreads have a microstructure composed of liquid oil, fat crystals, water droplets and sometimes air. A wide variety in ingredients and processes influences the product structure:

- the fat composition determines the amount of fat crystals, the speed of crystallization, as well as the size, the shape and the aggregation of the individual crystals into a network.
- water and water-phase ingredients are emulsified in the fat continuous matrix. Some of the water-soluble ingredients, such as milk proteins (O/W emulsifiers), affect the emulsion stability and consequently the efficiency of emulsification of the water in the product;
- emulsifiers also affect the network structure and the emulsion stability during and after processing;
- processing is another instrument to manipulate crystallization and emulsification conditions such that the desired product properties are obtained. It is clear that these conditions strongly affect structural parameters, such as crystal size, crystal-crystal interactions, network formation, and emulsion stability;
- finally, storage can induce changes in product structure, e.g., as a result of recrystallization.

Recent developments, especially in the area of electron microscopy, have led to a major increase in our understanding of the structure of fat spreads. Hypotheses regarding network formation and distribution of water in various spreads, as they were postulated in the past, have been substantiated. The challenge for the future lies in relating composition and processing variables to changes in product structure, i.e., network structure, fat crystals, cream globules, air cells, water droplets, and shell structure.

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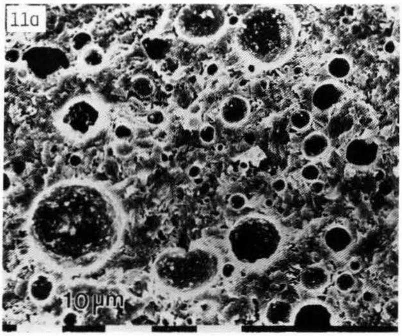
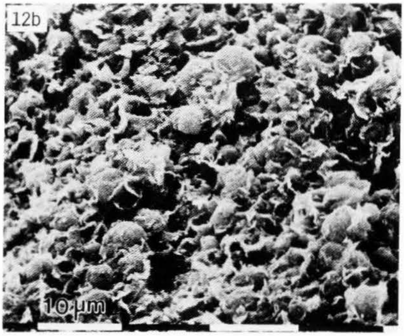
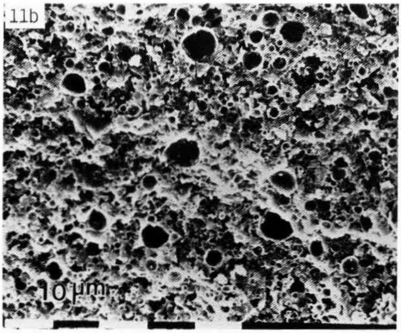
Fig. 11. Differences in water droplet size distribution in margarine as a result of:
(a) low and,
(b) high shear during processing.

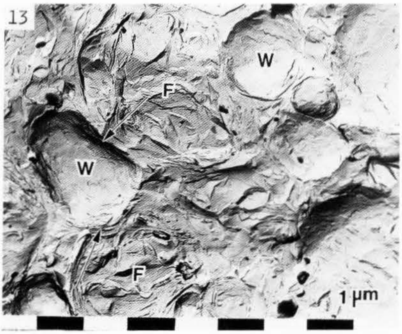
Fig. 12. Differences in the survival of fat globules in butter as a result of differences in the ripening procedure in the cream prior to churning.
(a) CWC-ripened cram;
(b) C-ripened cream.

Fig. 13. Freeze-fracture micrograph of butter showing membranes of fat globules in close contact with water droplets. Arrow indicates position of deformation of the globule surface. (w) Water droplet; (F) fat globule.









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Discussion with Reviewers

D. Precht: Is there clear evidence that only the β'- and β-forms are present in spreads or could also less stable forms like the α-form exist due to certain temperature treatments (e.g., rapid cooling)?

Authors: By X-ray diffraction techniques it is shown that, under normal storage conditions, indeed only the β'- and β- modifications are present. During processing, however, under conditions of strong cooling, first the α-modification is formed, which is in general rapidly converted to the β'-modification.

Preservation of α-modification would require the use of low temperature and storage of the product below the melting points of the most abundant α-forms, i.e., below 0°C.

D. Precht and W. Buchheim: According to our own observations the accumulations of fat crystals around the water droplets of butter, margarine, and low-fat dairy and non-dairy spreads is similar, despite strongly varying amounts of surface-active lipids in these products. Could there be another driving force behind this separation process than the one that the authors have mentioned?

Authors: In our opinion shell formation around water droplets is not the same in different products. It can vary between a clear shell and the mere entrapment of the water in the continuous fat matrix, without a clear shell structure. In butter (text reference 7), as well as in some other products, the latter structure is predominant.

It cannot be excluded that freeze-fracture techniques when applied to products containing oil, may lead to erroneous results. Also in fat systems, freezing velocity appears to be very critical. We found that emulsifiers play an important role in shell formation, but certainly other aspects, such as processing conditions, must also be considered. Working may enhance the possibility for transport of fat crystals to the oil/water interface (Heertje et al., this issue). Such a mechanism would, however, not be valid during churning in the normal processing of butter by phase inversion. Also from this background prominent shell formation in butter is not very likely.

D.P. Dylewski: In your opinion how would a close linkage of microscopy, rheology, and sensory help in the formulation and processing of new oil-based products?

Authors: Examples of how microstructure, rheology and product properties are related have been given in this paper and other articles from our laboratory (e.g., see text reference 7; and Heertje et al., the article following this paper in this issue). In this context, it should be mentioned how:

- the nature of the network structure (e.g., continuous versus granular) influences the hardness of a product;
- the emulsion structure influences other sensorial properties.

By deliberately manipulating the structure by the applied processing, it will be possible to induce desired product properties.