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THERMOTROPIC BEHAVIOR OF COCONUT OIL DURING WHEAT DOUGH MIXING : EVIDENCE FOR A SOLID-LIQUID PHASE SEPARATION ACCORDING TO MIXING TEMPERATURE

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Abstract

Freeze fracture electron microscopy and differential scanning calorimetry were used to study the behavior of coconut oil during cake batter processing. The greatest modifications of fat crystallization are due to the mixing temperature of batter more than the physical state of the fat before its incorporation and the wheat flour hydration. Mixing at a temperature below the melting point of coconut oil involves a liquid/solid fat segregation in the cake batter. The endogenous wheat flour lipids and proteins appear to stabilize this fat partition. These results are likely related to previous observations which correlate loaf volume and mixing temperature of wheat flour dough containing coconut oil.

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Key Words : Coconut oil, fat crystallization, wheat dough, freeze fracture, differential scanning calorimetry.

Introduction

Fats play an important role in the processing of bakery products. In cake-making a 35 to 50% fat content based on flour weight influences : entrapment of air during mixing process, lubrication of protein and starch particles, emulsification and retention of considerable amounts of liquid to increase softness of the cake. In smaller amounts (1-3%) fats can be used in bread-making to increase loaf volume and to improve slicing properties, crumb grain uniformity and tenderness (Chamberlain et al. 1965). These effects depend on the crystalline form (α, β or β') adopted by the fat; for instance, in cake-making the beta prime form has been found the most appropriate to improve volume and texture of cakes (Hoerr et al. 1966). Furthermore, the liquid/solid ratio of the fat at mixing temperature greatly influences bread or cake volume (Tamstorf et al. 1980).

It has been suggested among many hypotheses that the solid components of the fat facilitate the production of oriented structures in cake batters, which may remain even when the temperature exceeds the melting point of the fat; and these structures favour gas retention in the earliest stages of baking (Bell et al. 1977). In addition, microscopic studies of cake batters have shown that during mixing, air cells are incorporated into the fatty phase and during baking the fat quickly melts and releases the suspended air into the flour water phase (Carlin 1944).

However, the reported hypotheses do not provide a very satisfactory explanation for the role of fats in bread-making or cake-making. In fact very few studies concern the behavior of fat during cake batter processing while a number of factors are known to influence fat crystallization especially nonfat components such as amphiphilic lipid molecules (Timms 1984).

In order to clarify the mechanism of fat crystallization in the cake batter, the coconut oil, usually used in cake factories, has been chosen to take advantage of its low melting point (24-27°C) well apart from starch gelatinization. Moreover simple thermal behavior due to predominating beta-prime polymorph (Riiner 1970), was expected to simplify interpretation.

In the present investigation a dual approach of cake batter structure has been used combining freeze fracture microscopic observations for lipid phase identification and differential scanning calorimetry for the characterization of phase transitions.

Experimental

Cake batter formulations and processing conditions are given in Table 1, with 40% or 60% water content on flour weight basis. The doughs were mixed for 15 min in a Farinograph under controlled temperature and with a mixing speed of 61 rpm.

ADDITION ORDER →

Wheat Flour	Water	Coconut oil	Mixing (°C) Temperature
100g	40g	L 30g L 10g SL 10g	15 - 20 or 30
100g	60g	L 30g L 10g SL 10g	15 - 20 or 30
Wheat Flour	**Coconut oil**	**Water**	**Mixing (°C) Temperature**
100g	L 10g L 30g	40g	15 - 20 or 30
100g	L 10g L 30g	60g	15 - 20 or 30

Table 1. Standard cake batter formulation with sequential procedure, 3 min of mixing after the first adding of water or fat to the flour. Physical state of fat before mixing : L liquid, SL solid/liquid.

Polarized light microscopy was performed with an Olympus Vanox microscope to detect starch birefringence in the cake batters.

Cake batter samples incubated between two copper sheets at mixing temperature were rapidly plunged in an liquid N_2 slush. Other freeze-fracture conditions were as previously described (Marion et al. 1987). Replicas were viewed on a Jeol 100S electron microscope operating at 80 kV. For each mixing condition at least ten replicas were observed.

Thermal measurements were carried out on a temperature programmable, differential heat flux microcalorimeter (DSC111, SETARAM). The samples were placed in 150 µl stainless steel pans. The samples were cooled from their mixing temperature to 1°C, at a rate of 5°C/min, and then heated to 150°C at a rate of 1°C/min. Indium was used to check temperature calibration. Data were collected on a HP 86 microcomputer.

The same coconut oil, stored at 4°C, was used during these experiments and care was taken to reproduce identical "thermal history" for all coconut oil aliquots.

Results

Differential Scanning Calorimetry

Figure 1 shows the DSC thermogram of coconut oil. A large endothermic peak is observed with a T_m (temperature of endothermic peak maxima) at 25°C. The onset temperature of endotherm is obviously below 0°C and represents the melting of the solid β' form, according to results of Hannewijk et al. (1958).

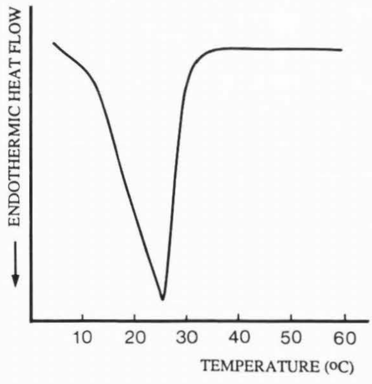

Fig.1 : Representative DSC thermogram of coconut oil. (Heating rate 1°C/min).

The endothermic melting of coconut oil, incorporated in a liquid state into the dough and mixed at 30°C, is not modified (Fig. 2). Furthermore, at a mixing temperature of 30°C, the melting endotherm of coconut oil is not influenced by water or the amount of fat added to wheat flour. In the same way, the melting endotherm does not depend on the order of water or oil addition to the flour.

The two endothermic peaks caused by gelatinization of starch are affected by water content as shown in previous work (Donovan 1979), but not by fat level (Fig. 2).

With cake batter mixing at 30°C the melting coconut endotherm seems to be almost independent of the physical state of the fat added to cake batter (solid-liquid mixture or liquid fat). (Table 2 or Figs. 3 and 4).

After heating to 150°C in the DSC pans, reheating after cooling (5°C/min) restores the initial melting profile of coconut oil. The starch endotherms have disappeared, suggesting complete starch gelatinization.

Studies with polarized light of these cake batters after first heating show the starch granules lose polarization crosses (results not shown). These observations agree with DSC studies, and clearly demonstrate the complete starch gelatinization after a first heating, even at 40% water level.

On the contrary, the endothermic peak shape of coconut oil is greatly modified when cake batter is mixed at 15 or 20°C (Figs. 3 and 4) whatever should be the other processing conditions, such as addition of other ingredients, water content (40% or 60%) and the physical state of fat added to the cake batter (Table 2).

Thus, in regard to the endotherm of coconut oil melting, new peaks appear below and above T_m of coconut oil. This suggests that part of the fat has a higher melting point since a thermal recycling of these cake batters restores the usual pattern of mixture obtained by fat addition at 30°C (Fig. 5).

Mixing Temperature	Water Content			Water Content		
	60% (60g water/100g wheat flour)			40% (40g water/100g wheat flour)		
	Physical state of fat before mixing	1st scan oC	2nd scan oC	Physical state of fat before mixing	1st scan oC	2nd scan oC
15oC	Liquid	13 20 27	22.4	Liquid	N.D. 18.3 26.4	22
	Liq/sol	12 27	22	Liq/sol	N.D.	
20oC	Liquid	18 22.5 29	22.5	Liquid	N.D. 20.7 27	22
	Liq/sol	18.5 23.8 29.6	22.9	Liq/sol	N.D.	
30oC	Liquid	23.2	23	Liquid	23.1	23
	Liq/sol	22.7	23.5	Liq/sol	N.D.	

Table 2. Temperatures of fat melting peak maxima, in the various processing conditions, achieved with DSC.

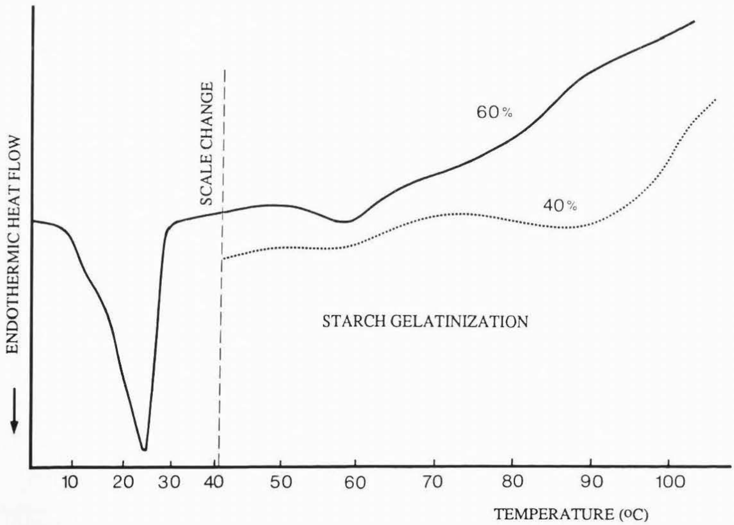

Fig.2 : Representative DSC thermogram of a cake batter (40% and 60% hydration on a wheat flour basis) containing coconut oil, mixed at 30oC.

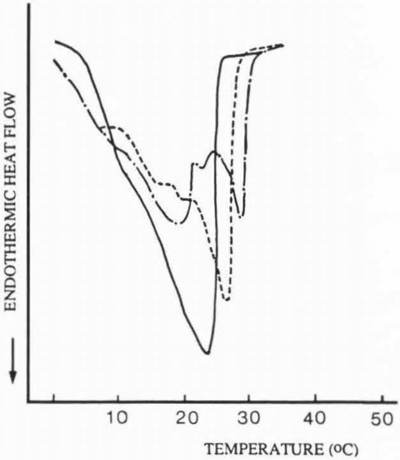

Fig.3 : Representative DSC thermograms of cake batters (60% hydration) containing coconut oil. The fat is incorporated as liquid in the cake batter. Comparison of (—) 30oC, (—·) 20oC, and (- - -) 15oC mixing temperature.

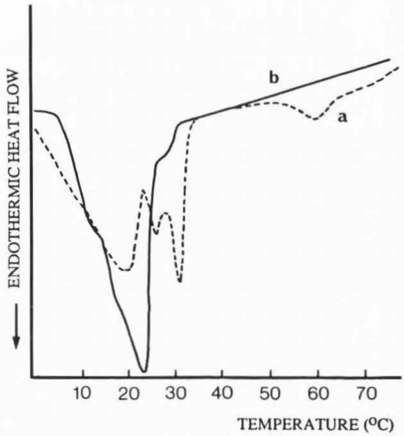

Fig.5 : Representative DSC thermograms of cake batters (60% hydration) containing coconut oil. The fat is incorporated as liquid in the cake batter, with mixing temperature of 20oC. Comparison of (a) the first heating, (b) reheating of this cake batter after a cooling at a rate of 10oC/min.

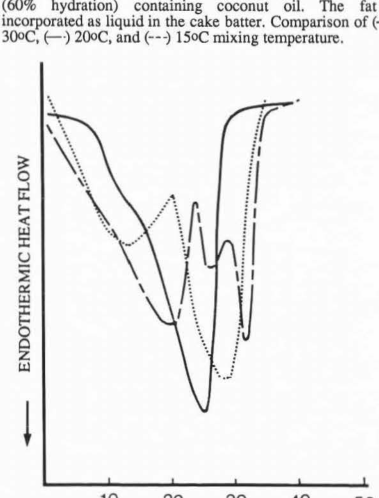

Fig.4 : Representative DSC thermograms of cake batters (60% hydration) containing coconut oil. The fat is incorporated as solid-liquid in the cake batter. Comparison of (—) 30oC, (—) 20oC, and (····) 15oC mixing temperature.

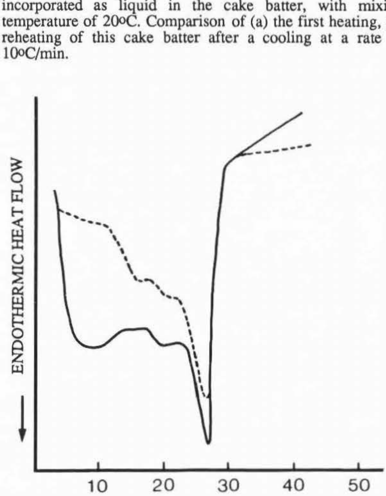

Fig.6 : Representative DSC thermograms of cake batters containing coconut oil. The fat is incorporated as liquid in the cake batter, with mixing temperature of 20oC. Comparison of (—) 40% hydration, and (- - -) 60% hydration.

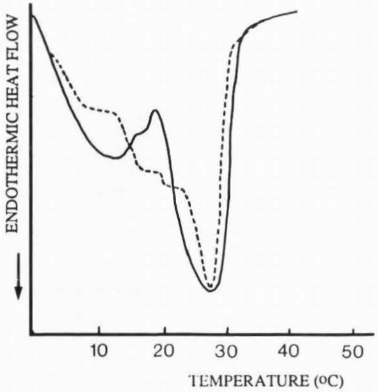

Fig.7 : Representative DSC thermograms of cake batters containing coconut oil, with mixing temperature of 15oC and hydration of 60%. (- - -) Fat incorporated as liquid. (——) Fat incorporated as liquid-solid.

For the mixing temperature of 15 or 20°C, we can even observe the same phenomenon independent of the other processing conditions. This peak is more or less important, depending particularly on water content (Fig. 6), and to some extent on the state of fat (liquid or solid-liquid) incorporated into cake batters (Fig. 7).

Freeze-fracture electron microscopy

Freeze-fracture of the cake batter clearly shows the protein matrix, starch granules and lipids of wheat flour (Fig. 8).

The cake batter with the mixing temperature of 30oC exhibits globular fat droplets with a diameter varying between 0.15 to 2 µm more or less surrounded by the gluten protein network. There are a few small spherical particles (50 to 200 nm in diameter) associated with fat globules (Fig. 9 a-b), which according to previous freeze-fracture studies on wheat flour and gluten (Al Saleh et al. 1986; Marion et al. 1987), could be attributed to endogenous wheat lipids. However DSC studies indicate that these associations do not modify the melting point of coconut oil.

Cake batters mixed at 15 or 20oC exhibit not only comparable fat globules but also irregular crystalline platelet areas (Fig. 9 c-d). These two types of fat structures appear to be more or less separated from each other (Fig. 10 a). It should be mentioned that these crystalline regions are not surrounded by the wheat flour lipidic vesicles, but only by proteic particles. It is noteworthy that less endogenous lipid vesicles are still present in the protein network, suggesting that most of them have been combined with fat droplets (Fig. 10 b).

No distinct changes in the location and structure of fat has been detectable for cake batter mixing temperatures of 15 and 20oC, with fat incorporated either as a solid-liquid mixture or as a liquid. These results are also valid for 40 and 60% water content (Fig. 10 c).

After heating of cake batters mixed below the melting temperature of fat, only globular droplets are observed, suggesting that fusion of fat crystalline structures and oil droplets occured during heating.

Fig.8 : Freeze fracture of a non fat cake batter preparation. S : Starch; L : Lipids of wheat flour; p : Protein network.

Discussion

The results of this study emphasize the importance of mixing temperature at which the cake batter is mixed on fat melting. It is obvious that cake batter mixing at temperatures below 30oC modifies the melting endotherm of coconut oil. This might be explained by changes in fat crystallization implying growth of new crystal structures such as β or α polymorph, or by a separation of solid and liquid fat fraction may then take place inside the dough matrice. In the former hypothesis, it is well known that for a pure triglyceride melting temperature increases from α to β' and to β (Perron et al. 1969); in the latter, few degrees below its melting point, coconut oil is composed of a heterogeneous slurry of crystals in liquid oil. During cake batter mixing, the segregation and stabilization of these two phases, led to the formation of a lower melting solid solution and a higher melting one.

At any rate, freeze-fracture electron microscopy observations indicate that the individual endothermic peaks of thermograms for dough mixing at 15oC and 20oC, are related to a differentiation of at least two distinct fat structures. In addition to fat droplets, there is a peculiar agglomeration of crystalline platelets at 15oC and 20oC. We expect that the highly organized crystalline platelets give the higher melting DSC curves and corresponds to the solid fat while the droplets gives the lower melting curves.

It must be mentioned that both fat fractions are covered by proteins particles, but only fat droplets appear, surrounded by lipid vesicles. Thus, endogenous lipids and proteins appears to stabilize this partition. The fusion of endogenous lipids with exogenous liquid fat implies a loss of lipid vesicles in the protein network. This phenomenon together with the modification of fat crystallization might be

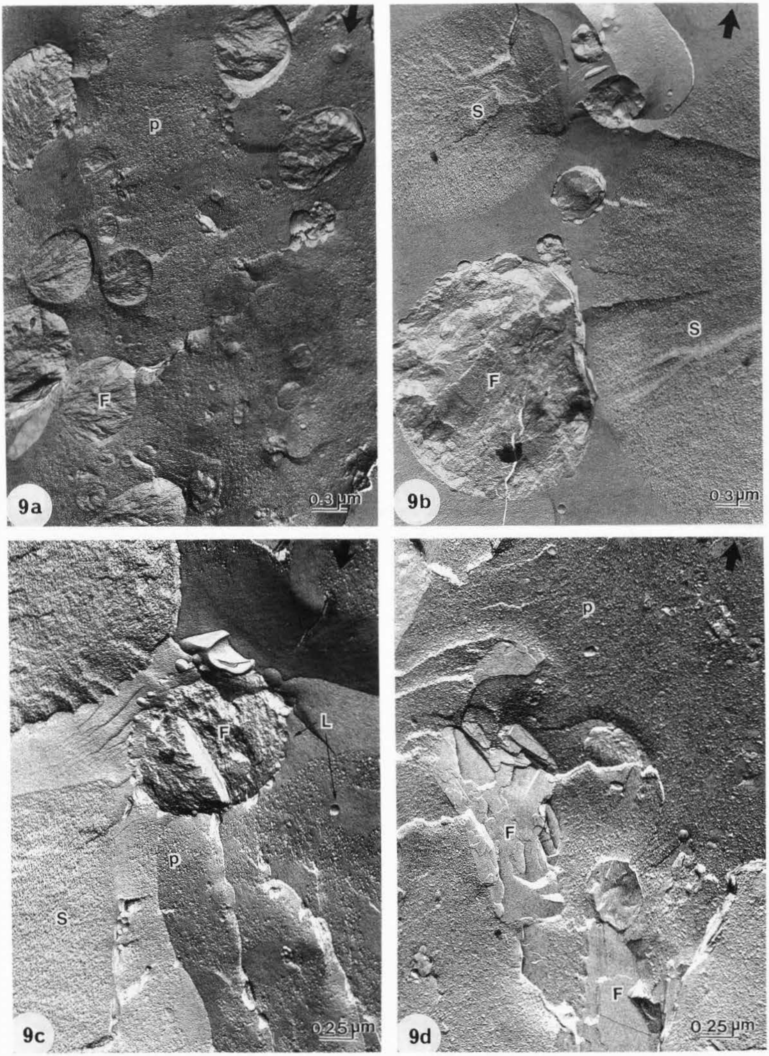

Fig.9 : Freeze fracture of a cake batter preparation (60% water content), containing coconut oil. F : Fat; p : Protein network; L : Lipid vesicle ; S : Starch. a-b : cake batter mixed at 30oC; c-d : Cake batter mixed at 15 or 20oC.

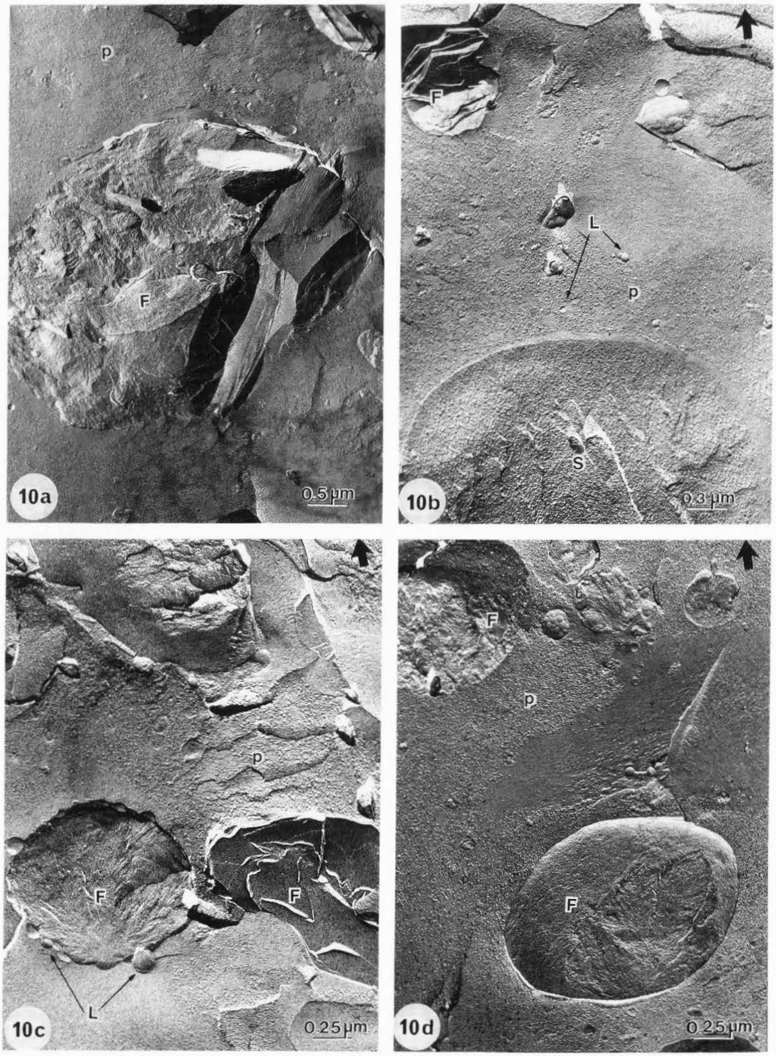

Fig.10 : Freeze fracture of a cake batter preparation containing coconut oil. F : Fat; p : Protein network; L : lipid vesicle; S : Starch. a-b : Cake batter of 60% water content and mixed at 15 or 20oC; c : Cake batter of water content 40% and mixed at 15 or 20oC; d : Cake batter of 60% water content, mixed at 15oC and heated for 30 min at 65oC.

of great importance in relation to the rheological properties of wheat flour cake batters.

In addition, it can be mentioned that the reheating of the cake batters mixed at 15 or 20oC, involves the fusion of the two fat type fractions. This is clearly demonstrated by DSC in which the initial melting endotherm is restored and by freeze-fracture electron microscopy which shows the disappearance of crystalline platelets.

Some slight differences are seen by DSC in peaks between cake batters mixed at 15 and 20oC and according the other processing conditions at these two temperature of mixing (water content, physical state of addition etc...). However, these slight differences are not evidently related to changes in the location and ultrastructure of fat and cake batter.

Concerning starch it is evident that starch gelatinization is not prevented with added fat within the processing conditions studied. These results are in agreement with previous ones (Abboud and Hoseney 1984).

This partition of solid and liquid fat provides an explanation to the results obtained by Baker and Mize (1942) which have shown that dough mixing below the melting point of coconut oil improves bread volume and crumb texture; and this is in agreement with the general idea that fat solid/liquid ratio more than fat source is the determinant on breadmaking technology (Bell et al. 1977).

Furthermore the retention of liquid fat in protein network during gluten washing (Baker and Mize 1942) might be explained by the stabilization of liquid fat droplets at once by endogenous polar lipids and proteins.

Therefore, the results of this work emphasizes the necessity to take into account that fat crystallization may be greatly modified in a dough and thus, that knowledge of fat crystallization before adding to a dough is necessary but not sufficient. Simple DSC tests are sensitive enough to detect changes and can serve as a systematic test to monitored fat segregation as long as sampling problems are overcome.

References

Abboud AM, Hoseney RC. (1984). Differential scanning calorimetry of sugar cookies and cookie doughs. Cereal Chem. **61** (1), 34-37.

Al Saleh A, Marion D, Gallant DJ. (1986). Microstructure of mealy and vitreous wheat endosperms (Triticum durum L.) with special emphasis on location and polymorphic behaviour of lipids. Food Microstruc. **5**, 131-140.

Baker JC, Mize MD. (1942). The relation of fats to texture, crumb, and volume of bread. Cereal Chem. **19**, 84-94.

Bell BM, Daniels DGH, Fisher N. (1977). Physical aspects of the improvment of dough by fat. Food Chem. **2**, 57-70.

Carlin GT. (1944). A microscopic study of the behavior of fats. Cereal Chem. **21**, 189-199.

Chamberlain N, Collins TH, Elton GAH. (1965). The chorleywood bread process : improving effects of fat. Cereal Sci. Today **10**, 415-419, 490.

Donovan JW. (1979). Phase transition of starch-water systems. Biopolymers **18**, 263-275.

Gallant DJ, Guilbot A. (1971). Artefacts au cours de la préparation de coupes de grains d'amidon. Etudes par microscopie photonique et électronique. (Artefacts during the preparation of starch granules sections. Studies under light and electron microscope). Stärke, **23** (7), 244-250.

Hannewijk J, Haighton AJ. (1958). Differential thermal analysis. III. Melting curves of oils and fats. J. Am. Oil Chem. Soc. **35**, 457-461.

Hoerr CW, Moncrieff J, Paulicka FR. (1966). Crystallography of shortenings. Baker's Digest **40** (2), 38-40.

Marion D, Le Roux C, Akoka S, Tellier C, Gallant DJ. (1987). Lipid-protein interactions in wheat gluten : a phosphorus nuclear magnetic resonance spectroscopy and freeze-fracture electron microscopy study. J. Cereal Sci. **5**, 101-115.

Perron R, Petit J, Mathieu A. (1969). Study of palmitic-stearic triglycerides and their binary mixtures by differential thermal analysis (DTA). I. Pure triglycerides. A. Chem. Phys. Lipids **3**, 11-28.

Riiner U. (1970). Investigation of the polymorphism of fats and oils by temperature programmed X-ray diffraction. Lebensm. Wiss. Technol. **3**, 101-106.

Tamstorf S, Jonsson T, Krog N. (1980). The role of fats and emulsifiers in baked products. In : Chemistry and Physics of Baking. J.M.V. Blanshard, P.J. Frazier and T. Galliard (Eds). The Royal Society of Chemistry, London, 75-88.

Timms RE. (1984). Phase behaviour of fats and their mixtures. Prog. Lipid Res. **23**, 1-38.

Discussion with Reviewers

Reviewer II : It is postulated that the native flour lipids are being "dissolved" by the liquid oil fractions and that this may alter the rheological properties. To what extent will this change the finished cake volume and texture? and how?

Authors : Most of the wheat flour lipids have fused with coconut oil so that the polar lipids are no longer available for stabilization of air/water interfaces during cooking and this may affect the cake volume. Furthermore, below the melting point of coconut oil, this phenomenon seems to be associated with a modification of fat crystallisation in cake batter affecting the rheological behavior of fat and therefore cake texture.

Reviewer II : Can the disappearance of the flour lipids be measured quantitatively by electron microscopy and is there enough evidence for this phenomenon?

Authors : In previous work (Marion et al, 1987) we have shown that most of the wheat flour lipids are organized in small vesicles. From analysis of about ten samples for each mixing temperature it is obvious that the quantity of vesicles embedded in the protein network decreases when fat is present.

For applying image analysis on electron micrographs of flour lipids, images need to have sufficient contrast; this contrast enhancement can be achieved by fixation with osmium before embedding and sectioning, so that lipids appear black and are easily distinguished from other structures. The lack of contrast makes quantification in images from freeze-fractured and freeze-etched samples very difficult. The fixation procedure also causes fat extraction which would influence the results of image analysis.

Another kind of measurement could be obtained directly under TEM employing a step by step measurement of different image areas using a special fluorescent screen connected to a sensitive electrometer as already shown by Gallant and Guilbot (1971).

H.C. Hoseney : Coconut oil is a mixture of chemical entities. Would the study be cleaner if pure, sharp melting fats were used?

Authors : Study of binary phase diagrams of some simple triglycerides would give better results but it will be necessary to build a small scale apparatus similar to the Farinograph to control mixing energy and temperature in order to use small amounts of dough and therefore small amounts of pure triglycerides, which are very expensive.

A.E. Blaurock : Walstra's work offers an alternative interpretation of the modification of coconut oil behavior in cake batter. Walstra has demonstrated that, in a finely divided emulsion, some droplets form crystals and others will not, simply as a result of nucleation in some droplets and not others. In addition, the three different curves shown in figure 3 may result simply from the kinetics of crystallization into different mixtures of the polymorphic forms of coconut oil, as a result of the different thermal histories of the three specimens. In this case, no physical separation need have occured in the dough during mixing.

Authors : Nucleation may explain the slight differences observed in individual peaks depending on (1) mainly, whether the fat is added as solid-liquid or liquid (Figs. 3 and 4, respectively), or (2) the water content of the cake batter (Figs. 6 and 7). However the general behavior characterized by individual peaks of low and high temperature endotherms is sensitive to the mixing temperature (Figs. 4 and 5). It is kept even after an overnight resting at 1oC (result not shown) and cannot be explained by nucleation only. Furthermore, it was impossible to obtain such DSC curves whatever the cooling rate (up to 1oC/sec) above the fat melting temperature. This suggests that liquid-solid mixture is necessary to induce modification of the thermal behavior of the coconut oil in cake batter.