OILS AND FATS IN FOOD APPLICATIONS

Edited by
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ISF

Lipid Technology

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PREFACE

The 22nd Congress of the ISF provided an opportunity to bring together oils & fats scientists and technologists from countries worldwide. The Food Applications session was notable in this respect, and authors of the papers in these Proceedings are from as far afield as Canada, Malaysia, UK, The Netherlands, Singapore, Norway, Denmark, Hungary, USA, Turkey, South Africa and Egypt. A range of fats was covered, including cocoa butter, palm, soya, fish, sunflower, lard and even chicken fat.

We were sad to learn in Kuala Lumpur of the death of Dr M.S.A. Kheiri of Danec SA, Ecuador. Many of us knew Dr Kheiri well and we had looked forward to meeting him again and hearing the paper that he was to present at the Congress. At the request of the conference organizers, Dr Kheiri's paper was replaced by that on palm oil. He was deeply involved in much of the work reported.

The Malaysian Oil Scientists' and Technologists' Association (MOSTA) hosted the ISF Congress in Kuala Lumpur and the administration was provided by the American Oil Chemists Society (AOCS). PJ Barnes & Associates undertook to publish the papers in this session at their own risk with permission from the ISF.

The 23rd ISF Congress will be held in October 1999 with the UK Society of Chemical Industry Oils & Fats Group as the host and we look forward to meeting you then in Brighton, England.

Kurt G. Berger

London,
November 1997

Chapter 1

Crystal networks in margarines and shortenings

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Crystal networks in margarines and shortenings

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Presented at the 22nd ISF World Congress and Exhibition, Kuala Lumpur, Malaysia. September 1997.

Abstract

The solid properties of fats are the results of the presence of a three dimensional network of crystals. Some of the rheological properties of fats have been explained by the assumption of two types of bonds between crystals in the crystal network, primary bonds which are irreversible and reversible secondary bonds. More recently it has been suggested (Heertje *et al.,* 1987) that crystals grow together in a process called sintering. Our investigations have found no evidence for this process. It has been found that in plastic fats the number of crystals is so high that they are tightly packed together. We propose a process of "dynamic entanglement" to account for the properties of the crystal network. Dynamic refers to both mechanical and thermal considerations. Scanning electron micrographs will be presented to show the nature of the entanglement of the crystals. Polymorphic transition of the β′ to β form has an extreme effect on the crystal network, not only because of the crystal morphology but also because of increased melting points.

Introduction

Plastic fats have rheological properties that are characterized by the presence of a yield value and by viscoelastic behaviour. These properties are the result of the presence of a certain percentage of solid fat crystals. To understand the relationship between rheological properties and solid fat content it should be recognized that such fats are not very dilute systems as sometimes proposed. The particular rheological properties of plastic fats are consistent with a tightly packed structure of fat crystals. A plastic fat is workable at room temperature when the solid fat content lies between 20 and 38%. The crystals in margarines and shortenings rang in size between less than 1μm to about 20μm. When crystals form aggregates, spherulites, clusters or aggregates, sizes may reach up to 100μm. The fat then becomes perceptibly grainy, both visually and in the mouth. A recent experiment (1) has demonstrated that margarines start to show a yield value at a solid fat content of about 15% (Fig. 1). Below this level the suspension is sufficiently dilute that the plastic nature is no longer in evidence. It should be well to remember that any hypothesis about the nature of the fat crystal network should be consistent with the observed properties of the fat in question.

The crystallization process

Crystallization involves two processes, nucleation and crystal growth. Both processes are dependent on the degree of supercooling, as indicated in Fig. 2. At low degree of supercooling nucleation is minimal and crystal growth predominates. As the extent of supercooling increases, nucleation predominates resulting in smaller crystals. It should be noted that supercooling is influenced by the melting temperature of the fat fraction that is crystallizing. These crystallization inducing glycerides may be trisaturates or mixed glycerides containing saturated and *trans* fatty acids (Table 1). The rate and extent of crystal formation depends very much on the fatty acid and glyceride composition of the fat. Some fats show a delayed or two step crystallization, undoubtedly caused by two distinct groups of crystallization inducing glycerides. Palm oil is an example of this type of crystallization (Fig. 3). It is important for a discussion of the nature of fat crystal structures to remember that crystallization is a relatively slow process, whereas melting is rapid (Fig. 4). Plastic fats will undergo temperature changes during storage and handling and, therefore, melting and solidification will continue to take place.

At high degrees of supercooling mixed crystal formation may occur. Glycerides with dissimilar melting points may be included in the same crystal lattice, thereby increasing the solid fat content. Such crystals can be made to recrystallize when the fat is tempered below its melting point (Table 2).

Fats may crystallize in a number of polymorphic forms. The most important are the β′ and β forms. These are characterized by their melting points and crystal morphology. Generally, the desirable polymorphic form of plastic fat products is the β′ form. This form is characterized by small needle-like crystals resulting in a smooth texture. When fats undergo transition to the β form, large crystals develop that give the product a grainy structure and undesirable texture. A number of factors influence the likelihood that recrystallization into the β form may occur. Fatty acid uniformity - fats with very high levels of 18C fatty acids are more likely to be β stable, examples are canola and sunflower oils (Table 3). Glyceride composition - glycerides with three fatty acids of equal chain length are most likely to be β formers, such as those with 48 and 54 carbon atoms. Glycerides with 50 and 52 carbons are more likely to remain stable in the β′ form. The situation is never clear cut as fats may contain differing levels of these glycerides. The conversion of β′ to β crystals is also promoted by temperature fluctuations during handling and storage as well as by the level of liquid oil present.

Rheological properties

Plastic fats have a yield value, they behave like a rigid solid until the deforming stress exceeds the yield value and the fat starts to flow like a viscous liquid, this is the plastic viscosity. Fats also have an elastic component. The yield value is demonstrated in Fig. 5, showing the torque vs. time recording of margarine in a recording mixer. The rheogram in Fig. 6 shows another important property of fats, that is the phenomenon of work softening (2). When plastic fats are subjected to mechanical action they become significantly softer, and when left undisturbed thereafter, the fat will slowly regain most of its initial hardness, a process called setting. The rheology of a fat depends on the solid fat content and the size of the crystals. Below the 15% solids level the fat is pourable, between 15 and 35% solids the fat behaves like a plastic substance and at solid levels above 35% or when crystals are very large and mostly in the β polymorphic form the fat will lose its plasticity and become brittle and show fracture instead of flow.

Since most fats contain a range of glycerides with differing melting points, the amount of solids in a fat will change each time the temperature of the product is changed. During the life time of a fat, therefore, it can be expected that melting and solidification will take place frequently.

Nature of the crystal network

The structure of plastic fats has been compared to flocculated emulsions (3) as shown in Fig. 7. It was suggested that the fat crystal network is held together by vanderWaals forces acting between crystals. vandenTempel (4) has proposed a linear chain model for the network structure in plastic fats. According to this model, the network is made up of straight chains oriented in three mutually perpendicular directions, each chain consisting of a linear array of particles held together by two types of bonds. These bonds can be either primary bonds which are irreversible and reversible secondary bonds. According to this theory, the irreversible bonds consist of relatively strong vanderWaals forces between favourably oriented particles, or of a growing together of crystals due to recrystallization processes or polymorphic transitions. Their energy content and contribution to stiffness is supposed to be much higher than those of the secondary bonds. These bonds are disrupted by kneading and do not reform easily, thus causing a high degree of work-softening. We have described this theory in more detail previously (5). The problem with this theory is that it is based on a dilute system as shown in Fig. 7. That kind of representation may be appropriate for gels formed in protein or carbohydrate solutions; such gels can be formed at very low solids contents. Plastic fats are different, they contain high levels of solids. Observation in the polarizing microscope demonstrate this. The observation of fat crystals in the microscope is difficult and only becomes practical after the fat is diluted with mineral oil or similar diluent. Fats are not dilute systems, on the contrary, they are very concentrated. It can be calculated that 1 cm^3 of fat containing 20% solids in the form of cylinders 5μm in length and 0.5μm diameter contains 2 x 10^{11} crystals. These crystals are closely crowded together as can be demonstrated by the following experiment. We have described a method of separating fat crystals from the liquid oil in a fat (6). Isobutanol is miscible with liquid oil but does not dissolve fat crystals. Fig. 8 shows a suspension of a shortening fat in isobutanol. These suspensions initially are in the form of a milky liquid. When allowed to stand for several hours, the crystals will settle to a constant level. This represents the volume they will occupy when loosely packed. The figure shows four levels of fat suspended in 10 ml isobutanol, 100, 200, 500 and 1000 mg. It is obvious that the loosely packed volume of the crystal sediment is many times greater than the original volume of the fat. This demonstrates that in a plastic fat the crystals are very tightly packed. For the kind of structural network in a fat I propose the term entanglement. The crystals fill the volume of a fat completely and are totally intertwined. Electron microscopy provides evidence for this type of structure. Since the entanglement is subject to constant change caused by temperature fluctuations and mechanical action the term "dynamic entanglement" is used. When it is realized how tightly packed the crystals are in a plastic fat, it is probably also unnecessary to use the hypothesis of primary and secondary bonds. After work softening the crystals have been "disentangled" and the hardness reaches its lowest possible value. During subsequent "setting" hardness increases because of increasing entanglement.

An experiment was carried out by deMan and Wood (7) in which a sample of butter was worked. The sample was then split in two parts. The first part was subjected to hardness measurement at 5°C over a three week period (Fig. 13) the second part was stored in the freezer for 3 weeks and then placed at 5°C and hardness measured again. The results show that the setting could be prevented by lowering the temperature to solidify most of the liquid oil. These additional crystals did not in any way alter the structure as it was before freezing.

Recently a process of "sintering" has been postulated (7, 8). Sintering is described as the formation of solid bridges between fat crystals (Fig. 14). According to these authors fat crystals form a network in oil due to mutual adhesion and one source of strong adhesion is the formation of solid bridges (sintering). The term sinter is defined as a porous solid i.e., particles fused together to form a solid. The term is used for the production of sintered metal in which powdered metal is fused together to form a solid porous bloc. In addition, the idea of sintering is again based on the dilute suspension model described earlier. This is simply not applicable to the actual situation in a plastic fat.

Polymorphic changes may completely alter the crystal network for two reason. Firstly, β crystals are much larger than β′ crystals. Often β crystals appear as large spherulites. In addition, the transformation of β′ to β involves a considerable increase in melting point (Table 1) which will result in more solid fat at any one temperature. Such fats then move from the plastic to the brittle stage.

In plastic fats the crystals are present in such large quantity that is unnecessary to postulate that a network will be formed by mutual attraction. The crystals are in such close proximity that they are completely entangled and the entanglement is what provides the rheological properties. Hypotheses based on suspensions with low crystal populations may be valid for pourable suspensions but are not appropriate for plastic fats.

References

1. deMan, L., deMan, J.M. and Blackman, B. (1995) *Fat Sci. Technol.* **97**, 55-60.

2. Davis, S.S. (1973) *J. Texture Stud.* **4**, 15-40.

3. Haighton, A.J. (1963) *Fette-Seifen-Austrichm.* **65**, 479-482.

4. vandenTempel, M. (1961) *J. Colloid Sci.* **16**, 284-296.

5. deMan, J.M. and Beers, A.M. (1988) *J. Texture Stud.* **18**, 303-318.

6. Chawla, P. and deMan, J.M. (1990) *J. Am. Oil Chem. Soc.* **67**, 329-332.

7. deMan, J.M. and Wood, F.W. (1959) *J. Dairy Sci.* **42**, 56-61.

8. Heertje, I., Lennis, M., van Zeyl, W.J.M. and Berendse, E. (1987) *Food Microstructure*, **6**, 1-8.

9. Johansson, D. and Bergenstahl, B. (1995) *J. Am. Oil Chem. Soc.* **72**, 911-920.

Table 1 Melting points of triacylglycerols

TG	CN	β′	β
PPP	48	56.7	66.2
SSS	54	64.2	73.5
PSP	50	68.8	-
POP	50	30.5	35.3

Table 2 Solid fat content of a soft margarine fat measured by AOCS and IUPAC methods

Temp. °C	AOCS	IUPAC
10	22.3	30.7
20	11.7	16.0
30	4.1	6.3
35	2.8	1.9

Table 3 Component fatty acids of some vegetable oils

Oil	Fatty acid (wt %)										
	16:0	18:0	20:0	22:0	16:1	18:1	18:2	18:3	20:1	22:1	Total C18
Cottonseed	29	4	Tr	-	2	24	40	-	-	-	68
Peanut	6	5	2	3	Tr	61	22	-	-	-	88
Sunflower	4	3	-	-	-	34	59	-	-	-	96
Corn	13	4	Tr	Tr	-	29	54	-	-	-	87
Sesame	10	5	-	-	-	40	45	-	-	-	90
Olive	14	2	Tr	-	2	64	16	-	-	-	82
Palm	48	4	-	-	-	38	9	-	-	-	51
Soybean	11	4	Tr	Tr	-	25	51	9	-	-	89
Safflower	8	3	Tr	-	-	13	75	1	-	-	92
Canola	4	2	-	-	-	58	21	11	2	1	93