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Review

Lipid shortenings: a review

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Abstract

A critical introduction to lipid shortening systems is provided. The review covers types, formulations, functionality, and processing conditions required for the production of lipid shortening systems. Furthermore, lipid shortenings and their production are placed within the context of recent advances in the areas of crystallization, structural elucidation, and mechanical modeling of fat crystal networks in general. The various unit operations involved in the production of lipid shortenings are examined in light of the evolution of structure (both at the crystalline and microstructural levels) and derived physical functionality.

Keywords: Fat crystal networks; Lipids; Shortenings; Crystallization; Hydrogenation; Interesterification; Physical properties; Mechanical modeling

Contents

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1. Introduction

The word 'fats' refers to the lipid food group, and is used to mean both fats and oils. More than 50% of our normal fat intake is in the form of 'invisible' fat; i.e. unseparated oil and fats in foods such as grains, nuts, dairy products, eggs, meat, etc. (FAO, 1977). In such natural food products, which include vegetable oils and fats, the lipid content and composition are more or less fixed, with minor variations depending on the season. Therefore, the nutritional and functional properties due to the lipid content of these natural food products are also fixed. Shortenings and margarines are tailored fat systems whose nutritional and functional properties have been manipulated in order to deliver specific consumer needs. In fats such as margarine and shortening, the functional characteristics of natural fat systems have been modified to provide desirable consistency and keeping quality in the end product. These modified fats offer special functional utility to baking, confectionery, and cooking applications. Being one of the most flexible basic food ingredients, it is expected that the use of shortening and margarine will continue to grow.

Such modified fat systems have to satisfy a host of physical functionality and health/nutritional requirements. These types of requirements are sometimes at odds with each other in terms of the ingredients that are required to deliver specific functionality. In this manner, potentially harmful hydrogenated fats are common ingredients required for consistency, whilst those health enhancing triacylglycerols (TAGs) such as oleic acid and other essential fatty acids (Oomah & Mazza, 1999) must also be included (and do not always aid in the consistency requirements).

This review attempts to provide the reader with a comprehensive introduction to shortening systems. The review is organized thus; Section 2 provides a brief chronology of the development of shortenings, Sections 3 and 4 provide the definition and description of the functions of shortening systems, and Section 5 provides an introduction to the many different types of shortenings; their specific functions and typical formulations. The production of shortenings is integrally related to the types of fats and oils used, and to the way in which these fats and oils crystallize and form solid networks. This is due to the fact that the solid crystalline fat networks are responsible for delivering the macroscopic physical functionalities expected from the various types of shortening systems; by the way they melt, the hardness and compliance of the network, and even the consistency and particulate nature of the network. Section 6 of the review provides a number of classification schemes for fats and oils. These range from molecular classification, classification by source, by crystal type or polymorph, and by end use. It has been established for decades, that due to the polymorphic nature of fat crystal networks, and the fact that the various polymorphs formed by the same ensemble of fat molecules can demonstrate significantly different physical properties, that it is important to control the crystal type and habit of shortening systems. Therefore, Section 7 is a short review and description of the polymorphism of fat networks, and the way they may impact shortening functionality. More recently, researchers have accumulated immense evidence which establishes that the microstructure of shortening systems not only play a pivotal role in determining the physical properties of fat crystal networks and therefore shortening systems, but also that the microstructure of a fat crystal network from the same ensemble of molecules can be drastically different due to differences in the way the system is processed and stored. Section 7 therefore also includes a short review of the microstructural level of structure of fat crystal networks. The theory of crystallization is central to an understanding of the reasons why and processing pathways via which the polymorphism and hierarchical structure of the fat network is established. Therefore, Section 8 provides a short introduction to the fundamental phenomena governing crystallization in general, and a short review of the area of fat crystallization in particular. This section hopefully will provide the reader with an appreciation of the complexity of the crystallization process, especially as it applies to fat crystallization and its effect on subsequent network for-

mation at higher levels of structure. Section 9 deals with formulation and blending of shortening systems, whilst Section 10 is a discussion of the processing considerations that are important in producing shortenings. In particular hydrogenation, actual manufacturing parameters, tempering, the effects of emulsifiers, and the use of interesterification techniques are reviewed. No attempt is made to exhaustively examine any of the particular areas as this is neither within the scope nor intent of this review. An exhaustive review of any of the topics covered, for example, interesterification, would take much more space than this entire introductory review, and in fact such works already exist in the literature.

2. History of margarine/shortening production

The following is a brief chronological review of some of the highlights of the development of the shortening/margarine industry. The development of margarines and shortenings are interlinked. Technological development in the production of one greatly influenced the other. Shortenings, as they are known today, gradually evolved as a result of a combination of economic factors, technological developments, and competitive endeavor.

Attempts to produce a replacement product for butter started in Europe during the middle of the nineteenth century, mainly due to the high prices for butter. The first acceptable butter substitute was produced by the French chemist Mege Mouries in 1869, on commission from Emperor Napolean (Andersen & Williams, 1965a; Chrysam, 1985). The tallow fraction he used proved to be a very good raw material in providing desirable consistency and favorable melting behavior in the mouth. Soon after the introduction of the first butter substitute on the market, several inventors patented various modifications of Mouries' process. In the beginning, lard was used as a primary shortening agent owing to the relatively easy processing requirements to produce an acceptable consistency (Bodman, James, & Rini, 1951; Chrysam, 1985; Weiss, 1983). It was not until the middle and later parts of the nineteenth century, when world demand for edible fats increased, that serious attention was given to the development of alternatives for lard. One such substitute was developed in the United States of America by Roudebush in 1873. Roudebush used tallow, softened by adding an edible oil such as cottonseed oil, and churned the melted fat mixture with fresh milk or cream to prepare a substitute to lard (Andersen & Williams, 1965a). Mouries' American patent was granted in December 1873 and was acquired by the *United States Dairy Company* who began shortening manufacture in the United States. After 1873, shortening production reflects mostly American developments. Towards the end of the nineteenth century, techniques for refining fats and oils were developed, and fatty raw materials such as cottonseed oil, corn oil, coconut oil, soybean oil, palm oil and palm kernel oil began to be used. A process for the liquid-phase hydrogenation of oils was patented by Norman in 1903 (Manderstam, 1939) and this title was passed to the British firm *Joseph Crossfield and Sons* (Mattil, 1964b). In 1909, *Procter and Gamble Company* acquired the American rights to the *Crossfield* patents. Soon after that (in 1911) *Procter and Gamble Company* introduced its hydrogenated shortening, 'Crisco', on the market. Since then, hydrogenation was employed by every producer of shortening/margarine (Mattil, 1964b). This technological advancement, in general, can be regarded as the renaissance of the margarine and shortenings industries. Until 1940, margarine carried a negative implication as a cheap butter substitute. The Food and Drug Administration (FDA) of the United States publicized a standard of identity for margarines in 1941. This gave margarine the status of a food substance in its own right. Further innovations in the techniques of processing such as bleaching, deodorization, fractionation, winterization, and refining of raw oils and fats, together with the mechanization of the processing industry, have increased the ability of the industry to meet specific functional and nutritional requirements. In addition to processing techniques, important quality improvements were achieved by genetic engineering of oil crops (e.g. by breeding rapeseed into canola, which is almost free of erucic acid and is also free of undesirable sulfur compounds; El-Shattory, deMan, & deMan, 1981).

3. Shortening

Shortenings are fats formulated from oil and base oil (often with a plasticizer and an emulsifier) (Mattil, 1964a). Shortenings are considered quasi-plastic materials, but this alone is not enough to define shortenings. Their name is derived from the 'shortness' they impart to the food products they are contained within. The term 'shortening' refers to the ability of a fat to lubricate, weaken, or shorten the structure of food components so that they function in a characteristic way to provide desirable textural properties to a food product. In a baked product, without shortening, gluten and starch particles adhere to each other and give the sensation of hardness and toughness when chewed (Mattil, 1964a). However, if shortening is present, the fat breaks the continuity of the protein and starch structure. This enables the lubrication of gluten particles, which produces a tender and well-aerated bakery product (Chrysam, 1985; Mattil, 1964a). In frying applications, shortenings allow for quick, uniform heat transfer during cooking, and aids in the formation of a moisture barrier (Chrysam, 1985).

4. Functions of shortening

Shortenings induce a number of desirable functions in bakery foods (Andersen & Williams, 1965b; Chrysam, 1985; Pyler, 1952; Weiss, 1983). These are as follows:

- tenderness and texture;
- mouth feel;
- structural integrity;
- lubrication;
- incorporation of air;
- heat transfer; and
- extended shelf life.

Three factors have traditionally been attributed with the determination of the ability of a particular fat or oil shortening to perform one or more of the previous functions. These are:

1. The ratio of the solid phase to the liquid phase of the shortening.
2. The plasticity of the shortening.
3. The oxidative stability of the shortening.

However, in this review article it will be discussed that a host of additional variables combine in a complex manner to define the solid/liquid ratios and plasticity of shortenings. For example, the size and shape of the aggregates of microstructural elements, the shape of crystal aggregates (microstructural elements), the spatial distribution of the solid phase, and the crystallization kinetics under a particular set of processing conditions are all important variables that can affect solid/liquid ratios and plasticity. The nomenclature mentioned earlier have previously been developed (Narine & Marangoni, 1999b), but the reader will be introduced to fat nomenclature as part of this review.

5. Types of shortening

'Shortening' when classified by its end use, may also refer to products that are not 100% fat. In some applications, such as puff pastry manufacturing, water-in-oil emulsions are the shortening agents of choice. Shortenings fall into a number of categories which are determined by the functional requirements of the product. Many shortening functions are described by the industry in terms of the solid fat content (SFC) profiles. Typical SFC profiles of shortening systems are summarized in Table 1.

5.1. All-purpose shortening

These are manufactured with or without emulsifiers. The unemulsified shortenings are especially suitable for cookies, crackers, and frying. All purpose emulsified shortenings contain five to eight percent of mono- and di-glycerides of intermediate Iodine Value (I.V.) (Weiss, 1983). Iodine value measures the degree of unsaturation in fats). These shortenings are used primarily for icing, cakes, etc. where creaming performance (i.e. the incorporation of air into the shortening system) is most desired. This type of shortening may be prepared by partial hydrogenation of a base oil to an I.V. of between 65 and 80. It may also be prepared by blending oils that have been hydrogenated to a low SFI and low I.V., added to approximately 10% long chain saturated fats (such as stearins) or flakes (highly hydrogenated base oil; e.g. fully hydrogenated soybean) (Chrysam, 1985).

Table 1
Typical SFC values for US margarines

Types of shortening	Solids % at 10 °C	Solids % at 21.1 °C	Solids % at 26.7 °C	Solids % at 33.3 °C	Solids % at 37.8 °C	Solids % at 40 °C
Stick margarine[5]	28	16	12	2–3	0	NR
Soft tub products[5]	13	8	6	2	0	NR
Liquid oil + 5% hard fat[5]	7	6	6	5.4	4.8	NR
Baker's margarine[5]	27	18	16	12	8	NR
Roll-in margarines[5]	29	24	22	16	12	NR
All purpose shortening[2]	23	19	NR	14	NR	11
	26	19	NR	13	NR	7
Modified lard[1]	25	11	9	6	3	NR
Lard[1]	25	20	12	4	2	NR
Icing shortening[6]	34	28	27	22	18	NR
Pie crust shortening[4]	23	20	18	12	NR	4
Fluid shortening[7]	8	8	NR	7	NR	6
Frying fats[2]	42	29	NR	13	NR	3
Filler fat[3]	44	30	25	13	NR	2.5
Puff pastry[5]	26	24	23	22	21	NR
	NR	21	20	16	15	NR

NR = Not Reported. [1]Weiss, 1983; [2]Chrysam, 1985; [3]Chrysam, 1985; [4]Cochran, 1981; [5]Wiedermann, 1978; [6]Chrysam, 1985; [7]Gawrilow, 1980.

The melting point of any fat system employed as a shortening should be below body temperature to prevent a greasy mouth feel (as in the case of table margarines). Monoglycerides, lactylated monoglycerides, propylene glycol esters, lecithin, polyglycerol esters, polysorbate 60, and sodium stearoyl lactylate are the most commonly used emulsifiers in shortenings (Chrysam, 1985; Weiss, 1983). Fig. 1 shows the chemical structure of some of these common emulsifiers (Wan, 1990). Gawrilow (1973) provided the formulation for a typical multipurpose shortening (Table 2).

5.2. Fluid shortenings

Because of the significant convenience in storing, pumping, and metering fluid shortening, there is a constantly increasing demand for the production of these liquid-shortening systems. Fluid shortenings comprise a relatively small (less than or equal to 15 micron) and stable *beta* crystalline phase in a fat network (more on crystalline classification and characteristics are included later in this review). A typical formulation is comprised of a hard fat (e.g. lard) and an emulsifier (e.g. lecithin) and is processed through slow cooling of the melted fat accompanied by slow agitation (Chrysam, 1985; Gutcho, 1979). The product formed retains its fluid state for extended periods. Lecithin in the formulation acts as a crystal inhibitor. It prevents co-crystallization between liquid and solid triglyceride components when the system is subjected to slow cooling. Examples of the types of crystal inhibitors effective in preventing co-crystallization include oxidized polymerized oils (brown oils), fatty acid esters of dextrin, fatty acid esters of disaccharides (such as sucrose esters), fatty acid esters of polyglycols, and sorbitol (higher alcohols). Air incorporation in this type of shortening should be minimized for good performance; since small air bubbles will associate with the crystals present and cause these to rise towards the surface resulting in a non-homogenous product (Chrysam, 1985; Gillies, 1974).

5.3. Cake shortening

Cakes with enhanced physical functionality are made by the use of super glycerinated shortenings (Chrysam, 1985). These contain added mono- and di-glycerides as emulsifiers. Mono- and di-glycerides possess marked surface activity due to their content of both oil loving (lipophilic) and water loving (hydrophilic) groups. Saturated monoglycerides are preferred for cakes because these form complexes with the amylose fraction of starch; which lead to softer crumbs and longer shelf life (Krog, 1977). If the original batter contains many small air cells, the final cake will have a larger volume and a fine (close) grain. If the original air bubbles are fewer and larger, the final cake will have a smaller volume and a coarse (open) grain. The cake shortening plays a large role in determining the degree of distribution of the air in batter.

In cake shortening, the fat system, typically composed of soybean oil base stock and cottonseed oil hard stock (fully hydrogenated or partially hydrogenated), undergoes

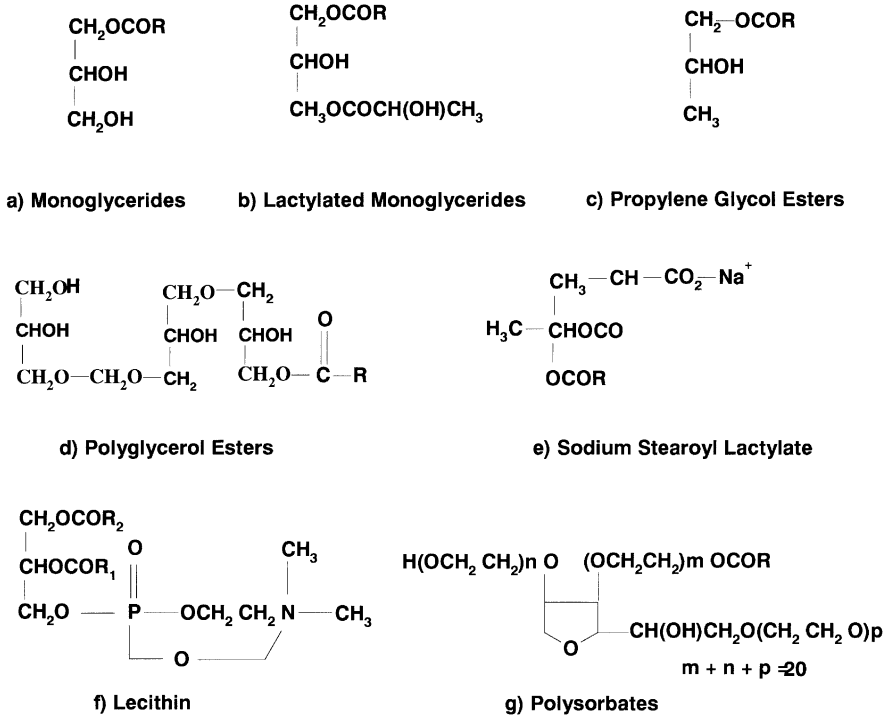


Fig. 1. Chemical structures of common emulsifiers (Wan, 1990).

Table 2
Formulaton for a multipurpose shortening (Gawrilow, 1973)

Tallow	65.6%
Cottonseed oil	21.9%
Monoglycerides & diglycerides	6.2%
Triglycerol monostearate	4%
Lecithin	1%
Polyoxyethylene (20) sorbitan monostearate	1.3%

a crystalline phase change from *beta-prime* to *beta* crystals under widely fluctuating temperature conditions. A reduction in cake baking performance results from such changes. This happens because the large plates of solid fat, associated with*beta* crystals, are much less effective in entrapping dispersed air. Plastic shortenings, in the unstable *beta-prime* phase when prepared, are more desirable over those plastic shortenings which are in the stable *beta* phase.

Canola oil has successfully replaced hydrogenated shortening in layer cakes when used with appropriate levels of water and an emulsifier system of monoglycerides, polysorbate 60, and sodium stearoyl lactylate (Vaisey-Genser, Ylimaki, & Johnston, 1987). In recent years, emulsifier research has enabled the production of cake shortenings that depend very little on structure or Solid Fat Content (SFC) of the TAG portion (Gillies, 1974). A typical formulation for such a shortening has been reported in the literature (Gillies, 1974; Matsui, Tomita et al., 1971) and shown in Table 3. The liquid TAG used in the formulation was soybean oil, cottonseed oil, rapeseed oil, or a mixture of any of these. The solid TAG used in the formulation was obtained by hydrogenating soybean oil, cottonseed oil, rapeseed oil, corn oil, or an animal oil or fat. The product obtained from such a formulation has favorable baking properties for use in any cake-making process. In addition, the shortening has considerable fluidity which makes it easy to handle even at lower working temperatures such as 5 °C.

5.4. Icing shortening

Cream icings contain sugar, water, and up to 40% shortening. These icings are dependent on the SFC in the shortening for their consistency. It is important to use a *beta-prime* stable shortening for producing smoothness and aeration. High melting fats are used in icing shortening in order to impart body over an extended temperature range (Chrysam, 1985). For good aeration and stability, mono- and di-glycerides are added (2–4% w/w of the shortening). Improvement in aeration is observed by the addition of hydrophilic emulsifiers such as polysorbates or polyglycerol esters to icing shortenings (Chrysam, 1985). These hydrophilic emulsifiers also improve melt-in-the-mouth characteristic (Chrysam, 1985).

5.5. Filler fat shortenings

Filler is a name given to the composition used in bakery products where one layer of a filler mixture is inserted between two horizontal pieces of cookies or wafers in a sandwich fashion. A filler fat is one of the ingredients present in the formulation of a filler mixture. Filler fats should be quite firm in order to provide support for the fragile cookies. At the same time, it should not snap or squeeze out when pressed or broken (Chrysam, 1985). For this reason, filler shortenings must have a high solid content at room temperature so that it does not slide when the cookie is eaten. The fat must melt completely at mouth temperature so as not to induce a waxy mouth feel. The SFC profile of a good filler fat is significantly steeper than the SFC profile of an all-purpose bakery shortening (as shown in Fig. 2). The steeper curve represents a good filler fat. A good filler fat has a short plastic range with high SFC at low temperature and approximately zero SFC at 40 °C. A small percentage of hard fat is sometimes added to ensure quick set after the filler mixture is deposited on the cookie (Weiss, 1983). Another requirement for a good filler fat is stability at higher temperatures without oiling out or sticking; since this makes the products unappealing (Gillies, 1974). A typical filler fat has a formulation containing partially hydrogenated fat (lard and tallow) with a high content of carbon-18 fatty acids and a vegetable oil (coconut oil and palm kernel oil) containing high proportions of lauric acid (Kidger, 1966). Typically, a ratio of 60:40 of partially hydrogenated fat to vegetable oil is used. Weiss (1966) reported that addition of 1–5% emulsifier (higher fatty acids esters of polyglycerols) based on the shortening composition imparts good properties to the filler shortening.

Table 3
Formulation for a cake shortening (Gillies, 1974; Matsui et al., 1971)

Vegetable liquid triglyceride	80–90%
Solid triglycerides	0.5–4%
Glyceride mono- &/or di-fatty acid esters	0–3%
Propylene glycol mono & di-fatty acid esters	8–16%
Lecithin	0.1–2%
Polyoxyethyelene glycol mono-% & or di-fatty acid esters	0–5%
Cane sugar fatty acid ester	0–5%
Glyceryl lactic mono- &/or di-fatty acid esters	0–5%

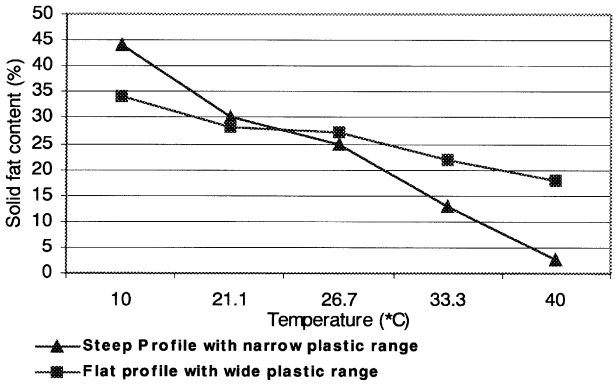


Fig. 2. Steep and flat SFC profiles [Steeper curve represents a filler fat (data plotted from Chrysam (1985)]. [Flat curve represents an icing fat (data plotted from Chrysam (1985)].

5.6. Bread shortening

These shortenings have a wide plastic range at room temperature. The term 'plastic' implies a solid, non-fluid, non-pourable, and non-pumpable shortening at room temperature. A typical formulation of a plastic shortening is shown in Table 4 (Gillies, 1974; Nelson, 1969).

The average shortening content in a bread formulation is about 3% based on flour weight. Bread dough is formed after mixing flour, shortening, yeast, water, salt, and other ingredients of importance. The bread dough is then mixed, and the mixing results in aeration of the bread dough due to the viscoelastic nature of the dough (Elmehdi, 2001). Shortening has the function of providing lubrication in the process of dough mixing. Doughs are then molded, and panned (sheeted), then placed in a proofing cabinet for 'proofing'. Proofing increases the volume of the dough by allowing the gluten to regain its elasticity and the yeast to produce gas. It is during proofing that dough rises. The proofing is done at 37.5 °C for 70 min (Elmehdi, 2001). Presence of sufficient SFC in the shortening is necessary to strengthen the dough and therefore provide gas retention during these initial stages of baking. Too much fat can inhibit rising of dough during proofing.

5.7. Frying shortening

An increase in temperature dramatically raises the rate at which fatty acids react with oxygen, promoting rancidity, and therefore raising the peroxide value. (Peroxide value measures the extent of oxidation undergone by a fat or oil.) Fats and oils from different sources have different levels of stability under such conditions. A large number of factors influence the deterioration of frying fat (Paul & Mittal, 1996; Sinram & Hartman, 1989):

1. The turnover rate of the fat. (Defined as the number of times the same oil is used for food frying purposes).
2. The type of the food material (e.g. its moisture content).
3. The type of the frying process.
4. The operating condition of a frying process (e.g. exposure to moisture, oxygen, etc.).
5. Temperature.
6. Degree of unsaturation of the frying fat.

The most important characteristics for a good frying shortening are flavor stability, frying stability, and oxidative stability (Covington & Unger, 1999). Unhydrogenated oil may be used if the turnover rate is high. Shortening containing significant levels of linoleic acid (as in unhydrogenated soybean oil) should not be used for frying purposes. Unsaturated fatty acids are very unstable in terms of oxidation and their incorporation in food decreases the shelf life of the fried product. Corn, sunflower, and cottonseed oils are the most suitable oils for frying purposes (Chrysam, 1985). Somewhat higher stability is achieved by using less polyunsaturated liquid oils such as peanut, palm-olein, or low linoleic sunflower oil. High smoke point is another prerequisite for frying fats (Black & Mattil, 1951). (Smoke point is defined as the temperature at which a fat gives off thin continuous wisps of smoke when heated under specified conditions.) Hydrogenated lauric fats are also used for frying but are only suitable for low moisture and low temperature frying. The extent to which the solid fat content of the shortening affects the palatability of the food depends on the temperature range over which food is to be consumed and the amount of fat normally absorbed by the food. Because deep frying shortenings are present on the surface of foods, a high melting point can cause a greasy or waxy taste in the mouth. Due to this reason, snack food should be fried in a low-melting point fat (Chrysam, 1985). Chrysam (1985) also stated that use of coconut oil results in a thin and non-greasy texture in a fried food. For this reason, coconut fat is a good frying fat.

Table 4
Formulation of a plastic shortening (Gillies, 1974; Nelson, 1969)

Partially hydrogenated blend of soybean (85%) & cottonseed (15%) oils (I.V. 75)	93.5%
Monoglyceride of vegetable oil containing fatty acid group	4.2%
Propylene glycol monostearate	1.8%
Polyoxyethylene (20), sorbitan monostearate (PH 7.0)	0.5%

Potato chips should be fried in oil containing low solids since fat comprises almost half of the weight of the finished chip. Coated doughnuts require a high stability, high melting frying fat. If the SFC is too high, there will be poor adhesion of powdered sugar coatings. If the SFC is too low, glazes will not stick and there will be too much adhesion of powdered sugar; which may fall off in clumps or become oil soaked (Weiss, 1983).

5.8. Pie crust shortening

In pie manufacturing, the function of the shortening is not to provide aeration but rather to provide lubricity and tenderness without seriously affecting the water absorbing properties of the flour. Lard (with or without hydrogenated lard flakes) has been used for piecrust. Flakiness of the piecrust is attributed to the grainy crystal structure of the fat. The function of the fat is to tenderize and shorten the crust as well as to prevent sogginess (Chrysam, 1985). Emulsifiers are detrimental to flakiness as they cause uniform fat dispersion. So, the SFC profile of a pie crust shortening is similar to an all-purpose shortening for good performance.

5.9. Pastry shortening

Pastry fats must be highly structured fats with a fat crystal matrix; which provides required spreading characteristic yet retain moisture under the conditions encountered during its extrusion onto dough. The shear force generated in extrusion tends to break fat/water emulsions. In a puff pastry, the shortening is layered between sheets of dough. The shortening is not mixed into the unleavened flour or dough but is placed on top of the dough and folded to form several alternating layers of dough and fat. The fat keeps the layers of dough separate and flaky and the moisture contributes the 'puff' as it turns to steam during the baking process (Chrysam, 1985). A continuous process for forming a pastry shortening has been developed (Gutcho, 1979; Kriz & Oszlanyi, 1976). A mixture of 70% prime steam lard (obtained by injecting steam during rendering of hogs' fat in a closed vessel) and 30% hydrogenated soybean oil (I.V. 82 & melting point 26.7 °C) is used in the formulation. The resulting mixture of fat is rearranged by interesterification. This shortening has a very good functionality for roll-in pastry applications while providing good mouth feel in the finished baked product.

5.10. Confectioner's fat

These fats have a short plastic range. In addition to cocoa butter, hard butter replacements (such as Kaomel, Temcote, and fractionated palm kernel oil) and cocoa butter substitutes are extensively used in confectionary and imitation dairy products. The crystallization behavior of cocoa butter is complex and attempts to describe it are plentiful in the literature (for a good review, see Bricknell & Hartel, 1998). Cookies and other snack items are frequently coated with chocolate. Cocoa butter is the fat of choice used for this purpose. The SFC profile of cocoa butter is unique being very high at room temperature with a sharp melting point at about 32–35 °C (as shown in Fig. 3 and Table 5). Careful tempering of chocolate is necessary to obtain a covering that is smooth and glossy. If the cocoa butter in the covering undergoes crystal transformation (because of temperature fluctuation), it takes on a dusky look referred to as chocolate bloom (Bricknell & Hartel, 1998; Schlichter-Aronhime & Garti, 1988; Seguine, 1991; Willie & Lutton, 1966). Interestingly, acetoglycerides, due to their crystal habit can also be used for coating purposes (Feuge, 1955). A process for making confectioners fat involves an interesterification between a lauric fat (palm kernel oil, coconut oil, etc.) and one or more esters of monohydric alcohols and fatty acids having 12, 14, and 16 carbon atoms. These fatty acids are desirable as confectioners fat as they impart brittleness or snap in confections (Brown, Gooding, & Knight, 1970; Gillies, 1974).

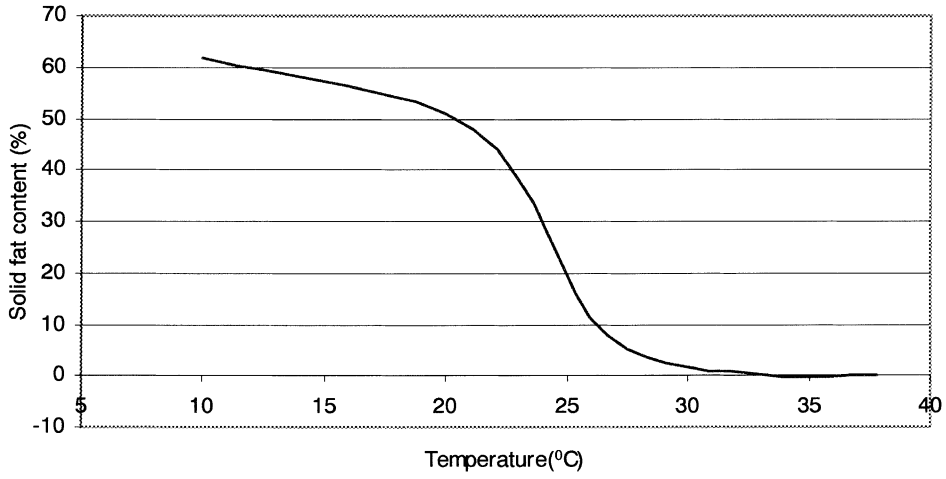
5.11. Dry shortenings

Three kinds of dry shortenings have been reported (Gillies, 1974). These are pelletized fat, powdered fat, and free flowing starch-shortenings. The pellets have a center of soft fat surrounded by a coherent coating of a harder fat (Davies & Worstall, 1966). Such products are relatively easy to store and distribute. The powdered fat is non-greasy. Hayashi and Takama (1968) gave a process to manufacture powdered fat by mixing fat with microcrystalline cellulose and water-soluble protein. After that, the resulting mixture is emulsified and spray dried.

Free flowing starch-shortening compositions are called dry baking mixes. These are used for sweet dough, biscuits, cake, and piecrust mixes. Dry baking mixes are made by incorporating shortening into flour, sugar, non-fat milk solids, emulsifiers, and salt. Piecrust, for example, should contain about 35–45% shortening on a dry basis. The resulting mixture should be dry to the touch and the shortening should not exude from the mix.

6. Classification of oils and fats

There are many methods that may be used to place fats and oils into classes. As a result, the classification of fats and oils vary according to their end use. For shortenings and margarines, fats may be classified by fatty



acid chain lengths, degree of unsaturation, dominant polymorphic form, source, consumption, and those fatty acid species which dominate that particular fat. Vegetable oils and solid fats are not alike. Solid fats come from both animal and plants sources and are usually solid at room temperature. Oils are produced mainly from plants and are liquid at room temperature. The most common oils are extracted from seeds (safflower, sunflower, sesame, canola, flaxseed), beans (peanut, soy), grains (corn, wheat germ), fruits (avocado, olive), and nuts (almond, coconut, walnut, palm kernel).

Fats and oils contain mainly TAG molecules. TAGs are formed if all of the OH groups of a glycerol molecule [$C_3H_5(OH)_3$] are esterified by fatty acid moieties (R_1, R_2, and R_3) as shown in Fig. 4.

The essential elements of fatty acid structure are simple. There are two essential features (Fig. 5):

1. A hydrocarbon chain
   The chain length ranges from 4 to 30 carbons; 12–24 is most common.
   The chain is typically linear and usually contains an even number of carbons. However, in the presence of a double bond or double bonds the chain becomes kinked.
2. A carboxylic acid group
   Natural oils exhibit a wide range of physical properties which are influenced by the degree of unsaturation, the length of the carbon chain, the isomeric form of the fatty acids, the molecular configurations of the TAG molecules, and the polymorphic state of the fat (Dziezak, 1989; Formo, Jungermann, Norris, & Sonntag, 1979b).

Table 5
Melting point (°C) and SFC values of natural fats (Weiss, 1983)

Fat	Melting point (°C)	SFC value (°C)				
		10	21.1	26.7	33.3	37.8
Butter	36	32	12	9	3	0
Cocoa butter	29	62	48	8	0	0
Coconut oil	26	55	27	0	0	0
Lard	43	25	20	12	4	2
Palm oil	39	34	12	9	6	4
Palm kernel oil	29	49	33	13	0	0
Tallow	48	39	30	28	23	18

Fats and oils are alike in that both are made up of fatty acid molecules. These can broadly be discussed under four basic types, as shown in Fig. 6. Because these fatty acids differ in their molecular structure, they differ in their behavior during processing and in the body after consumption. Saturated fatty acids are shaped like a straight line (as shown in Fig. 7). Triacylglycerides consisting of saturated fatty acids can easily align themselves in a close packing to form a compact mass (Charley, 1982). For instance a saturated fat is one that

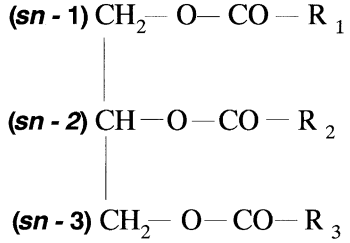


Fig. 4. General chemical structure of a TAG.

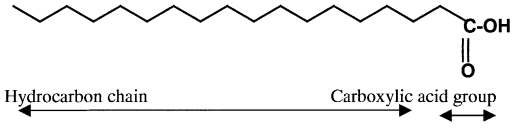


Fig. 5. Chemical structure of a saturated fatty acid.

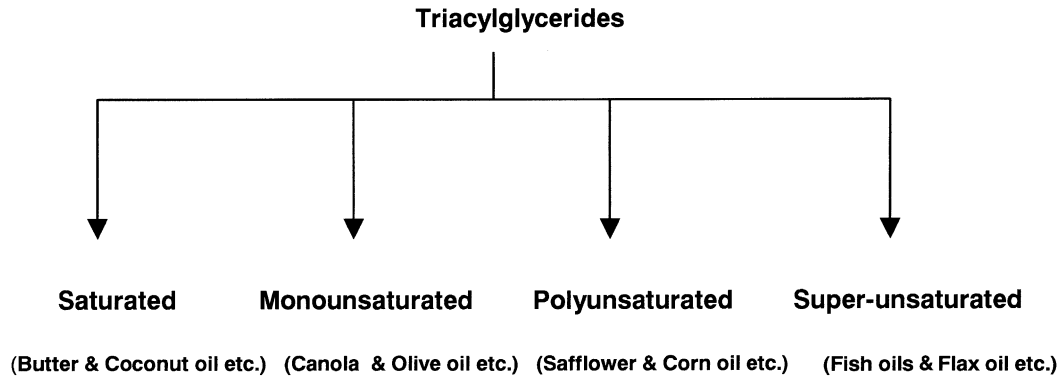


Fig. 6. Classification of triacylglycerides.

stays hard at room temperature and is not easily oxidized. Palm kernel oil and coconut are good examples of the saturated fats. Monounsaturated fatty acids have a single 'kink' in their molecular strand (as shown in Fig. 7). Unsaturated fatty acids on the central (*sn*-2) or on the terminal (*sn*-3) carbon atoms of glycerol molecule interfere with the close packing of triacylglycerides. Such disrupted packing of triacylglycerides makes crystal formation more difficult, thereby lowering their melting point and increasing their susceptibility to oxidative deterioration (Charley, 1982). Olive and canola oils are rich in monounsaturated fatty acids. Polyunsaturated fatty acids have two kinks (as shown in the Fig. 7) and this makes the resulting TAGs more reactive than the TAGs comprising monounsaturated fatty acids. Safflower and corn oil are well known poly-

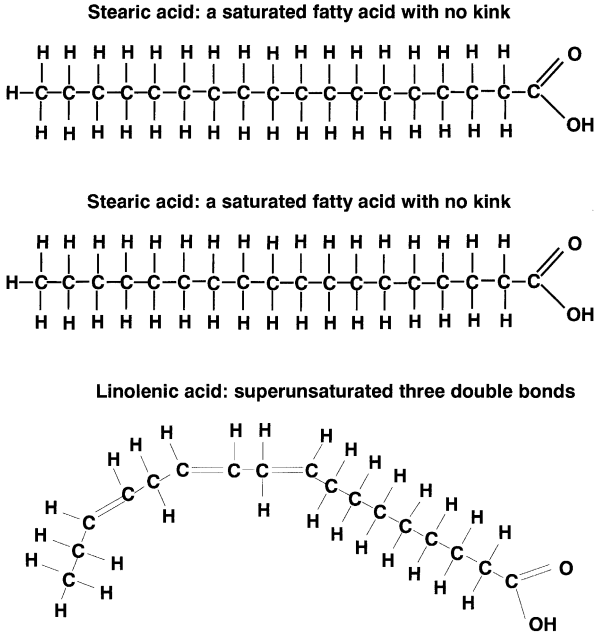


Fig. 7. Chemical structure of a saturated, monounsaturated, polyunsaturated, and superunsaturated fatty acid.

unsaturated oils. Both require careful handling to prevent rancidity due to oxidation. The super-unsaturated fatty acids are molecules with three kinks (Fig. 7). These are found mostly in fish tissue and in the seeds of black currant, evening primrose, and flax plants. These must be carefully protected to preserve their nutritional qualities.

Fats consisting of highly saturated or long chain fatty acids will generally have a higher melting point than those possessing a high content of unsaturated or short chain fatty acids. Unsaturated fatty acids can have different isomeric forms which have different melting points. They naturally exist in the *cis*-form, but can be converted into the *trans*-form during partial hydrogenation (Dziezak, 1989). Crystalline forms in which fats may exist may be categorized as *alpha*-, *beta*-, and *beta-prime*. This classification will be dealt with below. Weiss (Weiss, 1983) classified a number of fats according to their crystallizing nature as shown in Table 6. A large number of oils and fats are available which are classified based on their source and consumption (Dziezak, 1989; Formo, Jungermann, Norris, & Sonntag, 1979a). Below are a number of fatty acids types by which fats are also characterized, as well as source and consumption classifications.

1. Linolenic acid group
   Oils of this group contain appreciable amounts of linolenic acid but may also contain oleic acid and linoleic acid. Flaxseed oil and soybean oil, with its 7% linolenic acid content, is the best example of this group.

2. Oleic-linoleic acid group
   The examples of this group are cottonseed, olive oil, palm, peanut, sunflower, and safflower oil. Cottonseed oil consists of 73% of unsaturated fatty acids. The oil palm (*Elaeis guineensis*) is a native of West Africa. Palm oil contains equal amounts of saturated and unsaturated fatty acids.

Table 6
Classification of fats and oils according to crystal habit (Weiss, 1983)

Beta type	Beta-prime type	Alpha
Soybean	Cottonseed	Acetoglycerides
Safflower	Palm	
Sunflower	Tallow	
Sesame	Herring	
Peanut	Menhaden	
Corn	Whale	
Canbra	Rapeseed	
Olive	Milk fat (butter)	
Coconut	Modified lard	
Palm kernel	Sardine	
Lard		
Cocoa butter		

3. Lauric acid group
These are the least unsaturated of all the edible oils. The typical example for this group is coconut oil (*Cocos nucifera*) which consists of 94% of saturated fatty acids. Palm kernel oil is an example of an oil which is less saturated compared to coconut oil.

4. Erucic acid group
The important members of this group are mustard oil, ravison oil, and rapeseed oil. All are characterized by high erucic acid (an unsaturated 22-carbon fatty acid) content (40–50%). Of the erucic acid group, canola, a derivative of rapeseed oil, is important to the shortening industry. Canola oil is obtained from the seed of a genetically modified relative of the mustard family called the low-erucic acid rapeseed (LEAR) or canola (EI-Shattory et al., 1981; Vaisey-Genser & Yalimaki, 1989). The major differences between canola and original rapeseed oil are reduced levels of both glucosinolates (which contribute to the sharp taste in mustard and rapeseed) and licosenic and erucic acids (two fatty acids not essential for human growth) in canola (EI-Shattory et al., 1981). 'Canola' is a combination of two words, Canadian and oil. In the 1970s, Canadian plant breeders produced canola through traditional plant breeding techniques. Canola-based shortenings have been used in cakes, yeast breads, pastries, and cookies (Vaisey-Genser & Yalimaki, 1989).

5. Vegetable butters
These are highly saturated fats. A typical example is cocoa butter. It has a pleasant chocolate flavor and odor (Dziezak, 1989) and is used principally in chocolate confections and candies.

6. Milk fat
Wide varieties of short chain fatty acids distinguish butterfat from other fats. It comprises 500 separate fatty acids of which 20 are major components and the remainder occur in trace quantities (Dziezak, 1989; Formo et al., 1979a).

7. Animal depot fats
These include lard (rendered from the fatty tissues of hog) and tallow (rendered from fatty beef tissues). Tallow is more saturated than lard and crystallizes in *beta-prime* phase (Weiss, 1970).

8. Marine oils
Marine oils include those from manheden, herring, sardine, and whale. These are highly unsaturated oils.

7. Polymorphism and microstructure

Another important way to characterize fats and oils is through the predominant crystalline phase, or polymorph, that tend to form upon crystallization. Scientists have been aware of the existence of two or more distinct crystalline forms of the same substance since the 1820s. When the same ensemble of molecules can pack in different arrangements on crystallization, depending on the processing conditions, the substance is said to demonstrate polymorphism. The different polymorphic states of a particular substance often demonstrate quite different physical properties (such as melting behavior and hardness), but on melting yield identical liquids. In fact, the first indicator ($\sim$1849) that and acylglycerides exist in different polymorphs was that these compounds demonstrate multiple melting behavior (Chapman, 1962; Hagemann, 1989).

The elucidation of the predominant packing arrangements demonstrated by TAG molecules through primarily X-ray diffraction is perhaps the most important advancement in the academic pursuit of an understanding of the structure of fat crystal networks, and therefore the structure and physical properties of shortening and margarine systems. Therefore, it is of importance to acknowledge the pioneering work of Malkin and co-workers; the first group to utilize powder X-ray diffraction to demonstrate conclusively that the multiple melting behavior of glycerides were due to polymorphism (Clarkson & Malkin, 1934). Since then, it has extensively been reported that fats crystallize in different polymorphic forms (Filer, Sidhu, Daubert, & Longenecker, 1946; Garti, Wellner, & Sarig, 1981; Garti, Welliner, & Sarig, 1982; Haighton, 1959, 1976; Hoerr, 1960; Krog, 1977; Kuroda & Sato, 1987; Lutton 1945,

1950; Lutton & Jackson, 1950; Riiner, 1970, 1971a, 1971b; Rivarola, Segura, Anon, & Calvelo, 1987; Schlichter-Aronhime & Garti, 1988; Thomas III, 1978; Wiedermann, 1978; Wilton & Wode, 1963). Malkin and co-workers worked with tristearin and assigned nomenclature to the four forms they detected. However, later work by other researchers, mainly by Lutton (1945, 1950) and Filer and co-workers (Filer et al., 1946) contested Malkin and co-workers assignation of the different polymorphic forms. Over the years, many researchers have used different terminology for describing the identical polymorphic forms (Chapman, 1955; Chapman, Akehust, & Wright, 1971; Kellens, Meeussen, & Reynaers, 1992; Lovergren, Gray, & Feuge, 1976; Riiner, 1970; Willie & Lutton, 1966). Presently, the nomenclature suggested by Lutton & Lutton, 1950) is used extensively. The basis of this nomenclature stems from short spacing structural data observed in powder X-ray diffraction of triacylglyceride crystals.

Well-described reviews of the Lutton scheme of nomenclature has appeared in the literature (Larsson, 1966; Lutton, 1950; Yano, 1998). The main structural factors used to characterize the different polymorphic forms are the subcell structure and the layered structure of a TAG crystal. The subcell structure refers to the packing mode of the hydrocarbon chains of the triacylglyceride molecules and the layered structure arises out of the repetitive sequence of the acyl chains which form a unit lamella along the hydrocarbon axis. The subcell and layered structures give rise to the short and long Bragg spacings referred to in X-ray diffraction studies of fat polymorphism. The long spacings are observed around 1–15° 2-θ (referring to the position of the X-ray detector with respect to the direction of incidence of the X-rays), and the short spacings are observed around the 2-θ region of 16–25° (Gibon, Durant et al., 1986). The long spacings are dependent on the chain length and angle of tilt of the component fatty acids present in the triacylglyceride molecules. The short spacings are independent of the chain length (Jacobsberg & Ho, 1976). The short spacings are used to characterize the polymorphic forms and the long spacings are used by some authors to signify polytypism. The three main polymorphic forms based on observations of subcell packing are the *alpha* (α), *beta-prime* (β') and *beta* (β) forms; and are listed here in order of increasing thermodynamic stability or, in order of decreasing free energy. It is interesting to note that Ostwald's law of intermediate stages governs the formation of polymorphic phases of a substance during crystallization. This law states that the first crystal formed during crystallization possesses the highest free energy with the least thermodynamic stability. The polymorphic forms then go through successive modifications until the most stable stage is reached (Albanese, 1985). The *alpha* form refers to a hexagonal subcell and demonstrates a Bragg short spacing at 0.42 nm, the *beta-prime* form refers to a orthorhombic perpendicular subcell, with Bragg short spacings of 0.42–0.43 and 0.37–0.40 nm, and the *beta* form refers to a triclinic parallel subcell with a Bragg short spacing of 0.46 nm. Fig. 8(a), (b), and (c) shows diagrammatic representations of the various subcell and layered structures.

In addition to X-ray diffraction, a number of other techniques are employed in the identification of the different polymorphic forms. Vibrational spectroscopy has been used as early as the 1950s to determine fat polymorphism (Amey & Chapman, 1984; Chapman, 1960a, 1964; Freeman, 1968; O'Connor, DuPre, & Feuge, 1955; Yano, 1998; Yano, Kaneko, Kobayashi, Kodali, Small, & Sata, 1997a; Yano, Kaneko, Kobayashi, & Sata, 1997b). Nuclear magnetic resonance (NMR) measurements have also been used since at least the 1960s to study molecular mobility in polymorphs (Arishima, Sugimoto, Kiwata, Mori, & Sato, 1996; Boceik, Ablett, & Norton, 1985; Calaghan & Jolly, 1977; Chapman, 1960a, 1960b; Eads, Blaurock, Bryant, Roy, & Croasman, 1992; Hagemann & Rothfus, 1983; Norton, Lee-Tuffnel, Ablett, & Bociek, 1985). Atomic force microscopy has also been used as a tool to study the structure of TAGs (Birker & Blonk, 1993).

The polymorphic phase of the fat portion of a shortening or margarine system affects the macroscopic physical properties of the system tremendously. The melting behavior of the fat is determined by the polymorph present. The melting points of *beta* and *beta-prime* polymorphs of some common TAGs are compared in Table 7 (deMan & deMan, 2001). In the case of tristearin, the melting point of the α polymorph is 53.5 °C, whilst that of the *beta* form is 73.0 °C.

The shape and sizes of the crystals and crystal aggregates (microstructural elements) found in a shortening or margarine network is affected by the polymorphic form of the crystals to a different extent in different fats (Berger, Jewel, & Pollitt, 1979; Hoerr, 1960; Hoerr & Waugh, 1955; Kellens et al., 1992). The level of graininess of the shortening product may therefore be attributed in part to the polymorphic form, however, the same polymorph may have widely different microstructures (Kellens et al., 1992), leading to coarser aggregates of crystals and therefore increased graininess. The *beta-prime* polymorph is usually the most functional in fat products, due to its small crystal size ($\sim$1μm) and thin, needle shaped morphology. The shapes and sizes of crystals and crystal aggregates (microstructural elements) greatly affects the macroscopic elastic constant and hardness of the fat network and therefore the shortening product (Cornily & leMeste, 1985; Marangoni, 2000; Marangoni & Narine, 2001; Narine, 2000; Narine & Marangoni, 1999a, 1999b, 1999c, 1999d, 1999e, 1999f, 2000, 2002a, 2002b, submitted for publication)

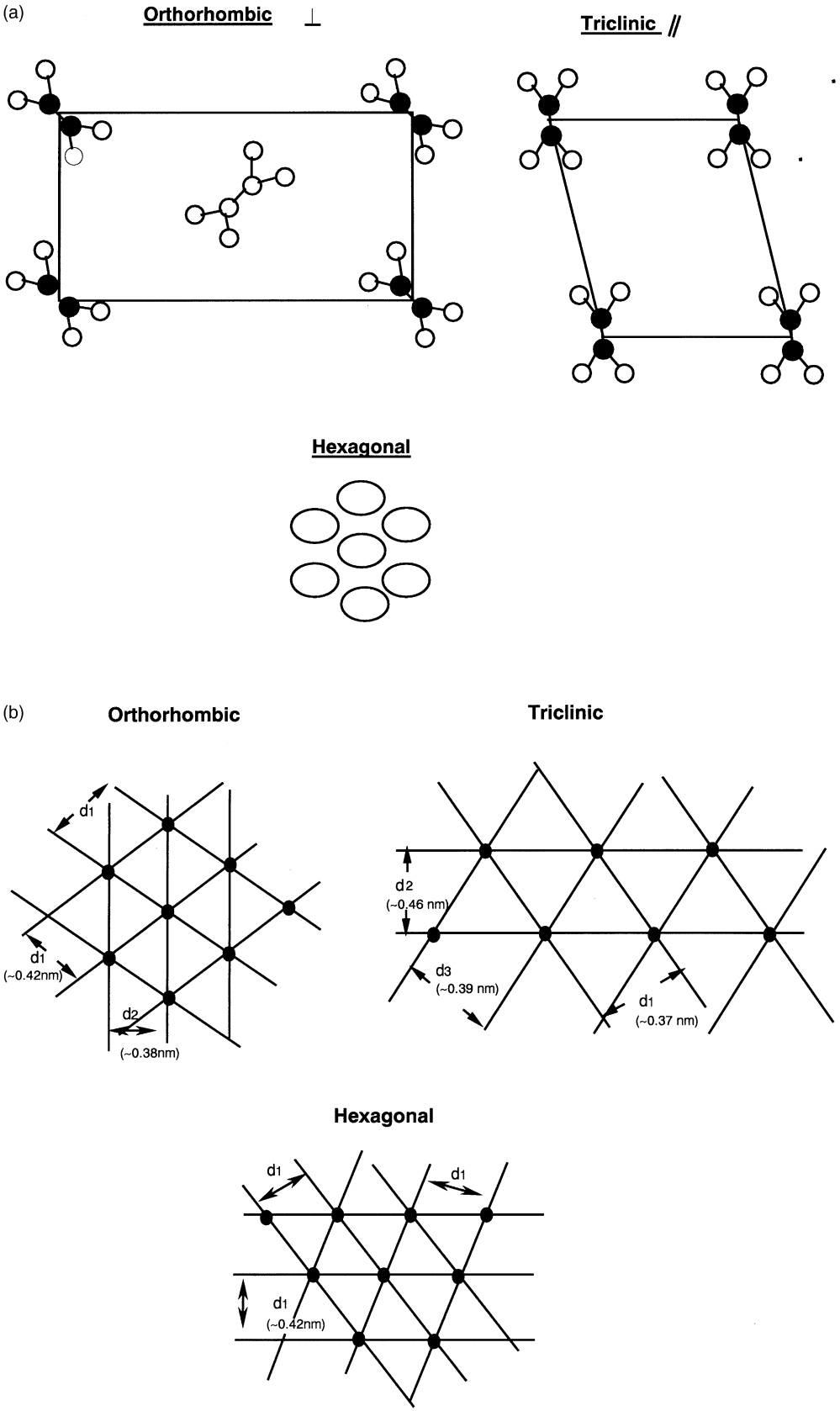


Fig. 8. Typical subcell and layered structures.

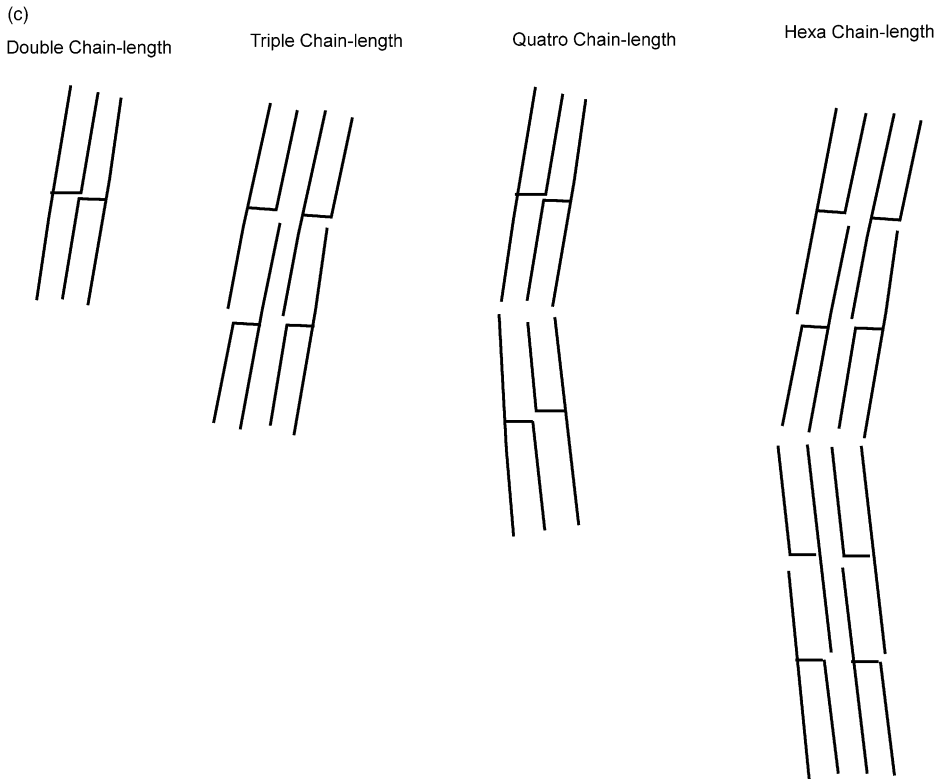


Fig. 8. (*continued*).

The factors which influence the stability of a *beta-prime* polymorph have been listed by deMan (deMan & deMan, 2001):

1. Fatty acid chain length and diversity.
2. TAG carbon number and diversity.
3. TAG structure.
4. Presence of a specific TAG.
5. Level of liquid oil present in a fat system.
6. Temperature fluctuation during storage.

All of the factors, in conjunction with the processing history, affect the polymorphic behavior in general of a fat system. It has been reported that the addition of palm oil has a beneficial effect on the polymorphic stability of margarines and shortenings. Addition of palm oil delays or prevents conversion of *beta-prime* crystals into the *beta* form (Persmark, Melin, & Stahl, 1976). Lutton (1950) investigated the polymorphism of C16–C18 mixed TAGs. According to Lutton, Palmitic–Stearic–Palmitic (PSP) exists in a *beta-prime* form, whereas Stearic–Palmitic–Palmitic (SPP) and Palmitic–Stearic–Stearic (PSS) exhibit both *beta* and *beta-prime* characteristics. Conversion of the *beta-prime* form to the *beta* form results in the formation of large crystals (deMan & deMan, 2001). The polymorphic tendency of some major solid TAGs in margarine and shortenings are summarized in Table 8 (deMan & deMan, 2001). Hydrogenated soybean oil exhibits a *beta* form as well as several intermediate forms of crystals (deMan, deMan, & Blackman, 1989). DeMan and coworkers (deMan et al., 1989) observed the polymorphic behavior of hard fats dissolved in canola oil at the levels of 20%, 50% and 80%. All of the hard fat mixtures resulted in the *beta* form of crystal except palm which showed stability of the *beta-prime* crystal form. The palmitic acid content of some fats and oils are tabulated in Table 9 (deMan & deMan, 2001; Kamel, 1992).

The polymorphism, crystallization, formulation, and processing of palm oil has been commented upon and studied extensively (Duns, 1985; Kawamura, 1979; Riiner, 1971a; Timms, 1985; Yap, deMan, & deMan, 1989).

Table 7
Melting points of *beta* and *beta-prime* polymorphs of some common TAGs

TAG	Beta-prime polymorph in °C	Beta polymorph in °C
PPP	56.7	66.2
SSS	64.2	73.5
PSP	68.8	–
POP	30.5	45.3
SOS	36.7	41.2
SOO	8.8	23.7
OOO	−11.8	5.1
LOO	−28.3	−23.3
LLO	3.02	25.2

Table 8
Polymorphic tendency of major solid TAGs in margarines and shortenings

Number of carbon atoms	TAG	Polymorphic from
48	PPP	Beta
50	PSP	Beta-prime
52	PSS	Beta-prime
54	SSS	Beta

Palm oil is incorporated into canola margarines to increase the diversity of fatty acids thereby preventing or delaying the formation of *beta* crystals (Ward, 1988; Yap, & de Man, 1989). The TAG composition of palm oil is shown in Table 10 (deMan & deMan, 2001). When palm oil is mixed with canola oil, the homogeneity of the fatty acid chain length is reduced and this promotes *beta-prime* crystal formation and stability (Shen, deMan, & deMan 1990). The major TAG in palm oil is POP, which, on hydrogenation, yields PSP. The PSP is responsible for the exceptional *beta-prime* stability (deMan & deMan, 2001). The techniques that are commonly used to stabilize *beta-prime* crystal in fats are summarized in Table 11.

Much interest has been recently focused on the microstructural level of structure of fat crystal networks, especially since the work of the Marangoni group at the University of Guelph beginning in the late 1990s (references to follow). Of course, the fact that the macroscopic physical properties of the network (particularly hardness, elastic modulus and texture) is significantly influenced by the microstructure has been known for decades (e.g. reviewed by deMan & Beers, 1987), but work by the Marangoni group established means via which to quantify the microstructure and to quantitatively link the microstructure to the rheological behavior of the network. The microstructure is so named because one can observe this level of structure under a light microscope, typically from length ranges greater than 0.5 μm. It is generally accepted that when one refers to the microstructure of fat crystal networks, one is referring to the length range bounded by 0.5 and 200 μm. The fact that the microstructure of fat crystal networks are easily changed by modification of the processing conditions under which the network is formed, and the importance of the microstructure to the rheological properties of the network have been noted by a number of researchers (Heertje, Leunis, van Zeyl, & Berends, 1987; Heertje, van Eendenburg, Gornelissen, & Juriaanse, 1988; Marangoni & Rousseau, 1996; Shukla, & Rizvi, 1996). The relationship of microstructure to rheology, in particular, has been the subject of much study, and this area has been reviewed by Narine and Marangoni (1999c, 2002). In particular, a number of models have been developed by Marangoni (2000), Narine and Marangoni (1999b), Nederveen (1963), and Van den Tempel (1961), and to relate the structure of the fat network to its rheological properties. Furthermore, it has been well-demonstrated that although other parameters of importance such as the solid fat content and polymorphism of networks may not change with changes in processing conditions, that large changes in physical properties may still be noted with concomitant changes in microstructure.

The quantification of microstructure has been a difficult task, mainly due to the difficulties in imaging microstructure, and as well to the complexity of this level of structure. Light microscopy has perhaps been the most utilized method for imaging the microstructure of fat and shortening networks (Flint, 1984, 1991; Inoe, 1987; Yiu, 1985). In particular, polarized light microscopy has been the most utilized since the anisotropy of the crystalline phase of the fat network is birefringent, allowing the network to be viewed under cross polarizers. However, this form of microscopy introduces some errors. Firstly, not all of the crystalline entities are viewed under cross polarizers, so that any such pictures are 'missing mass'. Furthermore, for structures to be

Table 9
Palmitic acid content (%) of some fats and oils (Kamel, 1992)

Type of oil	Palmitic acid content (%)
Canola	4
Soybean	11
Olive	14
Cottonseed	29
Palm	44
Lard	24

Table 10
TAG composition of palm oil

TAG	Carbon number	%
PPP	48	6.0
PPS	50	0.0
PSP	50	0.5
POP	50	26.0
PPO	50	6.0
PLP	50	7.0
POO	52	19.0
POS	52	3.0
PLO	52	4.0
OOO	54	3.0

Table 11
Techniques commonly used to stabilize *beta-prime* crystals

1.	Addition of beta-prime tending fat to a beta tending fat
2.	Incorporation of palm oil in a blend to disrupt its homogeneity
3.	Incorporation of a selectively hydrogenated fat
4.	Incorporation of diglycerides and sorbitan esters
5.	Chemical interesterification

resolved, glass slides must be made of the material, and the materials must be sufficiently thin so as not to significantly attenuate the transmitted light. This results in the structure being constrained to grow with one of its dimensions (the thickness dimension) being severely limited. However, if these limitations are taken under consideration, valuable information may be gleaned from polarized light micrographs. For example, Narine and Marangoni developed a method to quantify microstructures of fat crystal networks using polarized light micrographs (Narine & Marangoni, 1999a). This method involves calculating a mass fractal dimension and a number of other methods have been developed or are under development by the Marangoni group (personal correspondence with Dr. Marangoni).

Electron microscopy has also been used extensively to study the structure of fat crystal networks (Brooker, 1990; Buchheim, 1982; deMan, 1982; Heertje, Leunis et al., 1987; Heertje, van der Vlist, Blonk, Hendrickx, & Brakenhof, 1987; Kalab, 1983; Sargeant, 1988). However, this method also has some limitations; the sample usually has to be frozen, leading to much of the normally liquid oil becoming solid. Furthermore, it is difficult to get an idea of the bulk structure as one observes the structure along a fracture line. Confocal laser scanning microscopy has also been used to image fat networks (Heertje, van der Vlist et al., 1987), as has multiple photon microscopy (Marangoni & Hartel, 1998; Xu, Zipfel, Shear, Williams, & Webb, 1996), and atomic force microscopy (Narine & Marangoni, 1999c).

Narine and Marangoni developed nomenclature for the microstructure of statically crystallized fat networks (Narine & Marangoni, 1999a, 1999b, 1999c, 1999d). In a typical confectionery fat or shortening system which has been cooled statically, one can observe individual crystals (e.g. needle shaped *beta-prime* crystals) at the lower range of the microstructural level of structure. Additionally, in such systems one can observe clusters of the individual crystals. Narine and Marangoni, in the references cited earlier, suggested that such clusters be referred to as microstructural elements. The microstructural elements are typically in the order of two to six microns in length. In some systems, and particularly in cocoa butter that has been statically crystallized, one can observe large clusters, made up of aggregations of microstructural elements. Narine and Marangoni suggested that these larger structures be referred to as microstructures. Microstructures in statically crystallized cocoa butter, tallow, palm, and lard have been observed, ranging from 40 microns to 200 microns.

8. Crystallization

The crystalline state may be defined as one that diffracts X-rays and exhibits the first order transition known as melting. Crystallization may be defined as a first order transition of an ensemble of molecules from the liquid state to the solid state in such a manner that the molecules within the solid state pack in a regular repeating manner to form a solid lattice. The main feature of crystallinity is long-range order. The ensemble of molecules constituting a crystalline substance is in regular array over extended regions within each individual crystal. The type of bonding that is present in a crystal determines the nature of the crystalline state. Therefore, if the type of bonding is due to Van der Waals/London forces, the bond strength is weak, and results in a crystalline state that is characterized by close packing of weakly attracted molecules. If the bonding is due to ionic forces, the crystalline state is characterized by giant aggregates of positive and negative ions clearly packed in a way consistent with a net neutral charge. Covalent bonding results in giant molecules with directed bonds, where packing is determined by valency number and directions. In the crystals of TAG molecules that one would expect to find in shortening and margarine systems, the bonding is due to Van der Waals forces, and therefore the corresponding crystalline state is characterized by close-packed weakly attracting TAG molecules. Furthermore, the length and flexibility of these molecules, coupled with the weakness of the bonding, results in many different possible packing arrangements, or polymorphs. In addition, the variety of molecular species typically found in natural fats and oils results in a significant percentage of the total ensemble of molecules remaining in the liquid or liquid crystalline state, i.e. a significant percentage of the more unsaturated triglyceride molecules will remain in the liquid or liquid crystalline state. Furthermore, there can be a variety of crystalline sizes and shapes, as well as sintering in between crystals. Therefore, it is not surprising that instead of the sharp melting points that is associated with crystalline materials, fat crystal networks such as those encountered in most shortening systems demonstrate melting ranges rather than melting points.

The crystallization process may be divided into individual events of nucleation, crystal growth, and crystal ripening. However, these events are not necessarily, and in fats not usually, chronological; once primary nucleation has been achieved. Therefore, after primary nucleation and subsequent growth, one can encounter secondary nucleation whilst growth continues, and crystal ripening during growth. Therefore, the process can be very difficult to model theoretically.

Nucleation can only be achieved via supersaturation or supercooling. These terms are used to describe what amounts to thermodynamic driving forces; which are required to form the smallest stable solid entity from a liquid phase, since there is a free energy barrier opposed to the formation of the solid phase. The thermodynamic

driving force essentially allows the molecules in the liquid phase to form some sort of liquid lamellar structure which grows to a critical size before forming a solid nucleus.

A solution is supersaturated if it contains more of a component than can be theoretically dissolved within it at a particular temperature. The supersaturation of a solution is measured as the quantity $\ln\beta$, and is given by the ratio of the fraction of solute in the supersaturated solution (C_s) to the amount of solute in a saturated solution (C), at the particular temperature:

$$\ln\beta = \ln\frac{C}{C_s}. \tag{1}$$

The driving force for crystallization in a supersaturated solution is the difference in chemical potential, $\Delta\mu$, between a supersaturated solution and a saturated solution, and is given by (for ideal solutions):

$$\Delta\mu_{sol} = R_g T.\ln\beta, \tag{2}$$

where R_g is the universal gas constant and T is the temperature. It should be noted that unless the phase behavior of the many TAG families usually present in a typical fat is known and supports it, making an assumption of ideal solution behavior is not necessarily valid.

Relative supercooling refers to the degree to which the sample has been cooled, T, with respect to the melting temperature, T_M, of the crystallized sample and is given by:

$$\Delta T = (T - T_M). \tag{3}$$

Supercooling is usually required for the crystallization of one or more components from a melt; as opposed to a solution. The supercooling of the sample also provides a thermodynamic driving force for the formation of nuclei, and a chemical potential that drives nucleation may be defined as:

$$\Delta\mu_{melt} = \Delta H\frac{T_M - T}{T_M}, \tag{4}$$

where ΔH is the enthalpy of fusion.

Nucleation (via the chemical potentials provided by either supercooling, supersaturation, or a combination) occurs via bimolecular reactions which lead to the formation of ordered domains (Kloek, 1998). Beyond a certain size, further addition of molecules to such ordered domains result in a decrease in the Gibbs free energy of the system, and therefore when such ordered domains grow beyond a critical size, r^*, a nucleus is formed. As described by Kloek (1998) and Lyklema (1991), the classical nucleation theory described by Volmer (1939) has a number of shortcomings. Firstly, a macroscopic model is applied to the microscopic ordered domains. Furthermore, Gibbs free energy changes generated from equilibrium thermodynamics is used in the classical theory as a measure of the activation Gibbs energy; which is strictly a kinetic parameter. Regardless, the classical nucleation theory is used in the lipid area extensively, and is therefore reproduced here.

The Gibbs free energy change due to the formation of an ordered domain is given by:

$$\Delta G = \Delta G_S S + \Delta G_V V, \tag{5}$$

where ΔG_S is the change in the surface free energy (due to surface tension), ΔG_V is the change in free energy of the system per unit volume (due to the enthalpy of fusion), and V is the volume of the ordered domain.

$$\Delta G = \sigma, \tag{6}$$

where σ is the surface energy and S is the surface area of the ordered domain. Therefore, for an ordered domain considered spherical, with radius r:

$$\Delta G_S S = 4\pi r^2\sigma, \tag{7}$$
$$S = 4\pi r^2$$

and

$$V = \frac{4}{3}\pi r^3. \tag{8}$$

Therefore,

$$\Delta G = 4\pi r^2\sigma + \frac{4}{3}\pi r^3\Delta G_V. \tag{9}$$

For there to be a net decrease in the free energy of the system, the ordered domain must attain a critical size of r^*, where ΔG is maximum and is referred to as the activation energy of nucleation, ΔG^* (as mentioned before, this is a kinetic parameter). One can calculate this value of r^* by differentiating Eq. (9) with respect to r, and equating to zero:

$$8\pi r^* 3\sigma + 4\pi r^* 4\Delta G_V = 0, \tag{10}$$

therefore

$$4\pi r^* 3[2\sigma + r^*\Delta G_V] = 0, \tag{11}$$

and

$$r^* = \frac{-2\sigma}{\Delta G_V}. \tag{12}$$

Therefore, the activation free energy for nucleation is given by:

$$\Delta G^* = 4\pi\left(\frac{-2\sigma}{\Delta G_V}\right)^2\sigma + \frac{4}{3}\pi\left(\frac{-2\sigma}{\Delta G_V}\right)^3\Delta G_V \tag{13}$$

$$\rightarrow \qquad \Delta G^* = \frac{16\pi\sigma^3}{\Delta G_V^2} - \frac{32}{3}\frac{\pi\sigma^3}{\Delta G_V^2} \tag{14}$$

$$\rightarrow \qquad \Delta G^* = \frac{16}{3}\frac{\pi\sigma^3}{\Delta G_V^2}. \tag{15}$$

If the molar volume of the ordered domain (or corresponding crystal lattice) is given by V_M, then the free energy change per unit volume of the system may be written in terms of the chemical potential of the system:

$$\Delta G_V = \frac{-\Delta\mu}{V_M}. \tag{16}$$

For solutions, where the chemical potential is provided by supersaturation [and recalling Eq. (2)]:

$$\Delta G_{V,sol} = \frac{-R_g T \ln\beta}{V_M}, \tag{17}$$

and for melts, where the chemical potential is provided by supercooling [and recalling Eq. (4)]:

$$\Delta G_{V,melt} = -\Delta H\frac{\Delta T}{T_M V_M}. \tag{18}$$

From the above the activation free energy for nucleation for solutions and melts may be respectively be given by Eqs. (19), and (20):

$$\Delta G^*_{sol} = \frac{16}{3}\frac{\pi\sigma^3 V_M^2}{R_g^2 T^2(\ln\beta)^2}. \tag{19}$$

$$\Delta G^*_{melt} = \frac{16}{3}\frac{\pi\sigma^3 T_M^2 V_M^2}{(\Delta H\Delta T)^2}. \tag{20}$$

Therefore, the activation free energy for nucleation is lowered by increases in both supersaturation and supercooling. Furthermore, from Eqs. (12) and (16), increases in these two parameters also may result in the decrease of the critical size of the nucleus.

From the foregoing discussion, the concepts of supersaturation and supercooling are both connected with the lowering of the activation free energy for nucleation. Clearly one is more applicable for solutions, whilst the other is applicable for melts. However, the situation becomes more complex when one considers that a melt may often be a solution of one or more components, and as one or more components may be crystallized or nucleated due to supercooling. This may result in saturation or supersaturation of the other component or components. Clearly both of these phenomena should be considered for the formation of nuclei, through the formation of liquid lamellae in the liquid phase; which then subsequently leads to the formation of a stable nuclei (Boistelle, 1988; Larsson, 1994). The activation free energy for nucleation of a stable critical nucleus and the critical size of the nucleus both decrease on increase of supersaturation or supercooling. It is however very difficult to determine both parameters of supersaturation and supercooling for a crystallizing system, and therefore, as a good approximation, in practice only supercooling is usually considered for crystallization of TAG molecules from the melt. Toro-Vazquez and coworkers (Toro-Vazquez, Dibildox-Alvarado, Herrera-Coronado, & Charo-Alonso, 2001) makes the case that supercooling is the important parameter to consider for crystallization from the melt by pointing out that the bulk surrounding the surface of a growing crystal in the melt does not change as drastically as in crystallization from solution.

The number of nuclei formed per unit time and volume is referred to as the nucleation rate, J. This rate depends on the maximum molecular collision frequency, given by $\frac{kT}{h}$, with h being Planck's constant. It is important to note that the rate will also depend on the configuration of the colliding molecules (more on this to follow). The rate of nucleation per mole of molecules can then be written as an Arrhenius-like activation energy equation, with the previously derived expressions for the activation energy for nucleation, ΔG^*, being used in its appropriate form:

$$J = \frac{N\mathrm{k}T}{\mathrm{h}}\mathrm{e}^{\left(\frac{-\Delta G^*}{kT}\right)}. \tag{21}$$

In Eq. (21) N is Avagadro's number and K stands for Boltzman's constant. However, it should be noted that there are some barriers to nucleation that are inherent and some that arise as a function of the crystallization process itself. These barriers are related to the diffusion of molecules with the appropriate configuration to the interface between the bulk and the growing nucleus. Therefore there is a diffusive term and an entropy term, as the molecule that has diffused to the interface must also be in the right conformation to participate in the growing surface of the nucleus. A decrease in temperature to provide supercooling results in an increase in viscosity and a concomitant decrease in molecular diffusion. Additionally, the crystallization process itself increases the viscosity of the medium. For the long, flexible TAG molecules, the entropy term can become important. The loss of entropy on incorporation into a nucleus is given by $\Delta H/T_M$. The probability that a fraction, α, of the molecules in the melt is in the correct

conformation for participation in the surface of the nuclei is given by $e^{\left(\frac{-\alpha\Delta S}{R}\right)}$. Although it is strictly not correct, since viscosity is a function of time and temperature, both of which change over the crystallization process, one may assume that the fraction of molecules given by α also takes into consideration viscosity barriers. Scaling this probability by the maximum collision frequency, and defining the activation free energy for molecular diffusion of a mole of molecules in the correct conformation to the growing surface of the nucleus as ΔG_D, leads to the Fischer–Turnbull Equation:

$$J = \frac{N\mathrm{k}T}{\mathrm{h}} e^{\left(\frac{-\Delta G^*}{kT}\right)} \mathrm{e}^{\left(\frac{-\Delta G_D}{kT}\right)}. \tag{22}$$

It is important to note that Turnbull and Fischer developed Eq. (22) from the expressions derived above (Turnbull & Fischer, 1949), and from studies on the germination of drops of a liquid in a gas (Becker & Doering, 1940; Volmer & Weber, 1926) for the homogenous nucleation of a solid in a liquid. Throughout the treatment before, with the given assumptions, only homogenous nucleation was considered.

Heterogenous nucleation occurs when there are impurities which act as catalytic nucleation sites for crystal growth. Solid impurities which are larger in size than the ordered domains formed in the bulk liquid are necessary for heterogenous nucleation. The walls of the containing vessels, blades of impellers, emulsifiers, native mono- and di-glycerides, minor polar lipids, and even dust particles can provide catalytic nucleation surfaces. These impurities act as catalysts by lowering the activation free energy for nucleation. Therefore, the activation free energy for heterogenous nucleation is smaller than that for homogenous nucleation; resulting in reduced demands for supersaturation or supercooling for nucleation to occur when there are suitably large impurities present. The activation free energy for heterogenous nucleation depends on the wetting angle, θ, between the nucleus, the foreign substrate, and the liquid phase (refer to Fig. 9). If we assume that the surface of the foreign catalyst is flat and that the nucleus is a semi-sphere, we can express the activation free energy for heterogenous nucleation as a function of the activation free energy for homogenous nucleation:

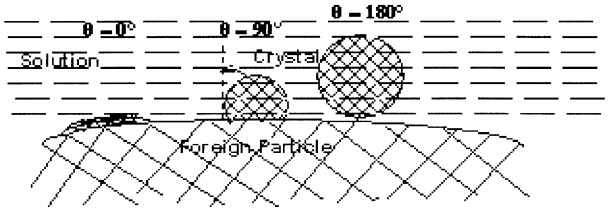


Fig. 9. Heterogeneous nucleation.

$$\Delta G^*_{\mathrm{het}} = f(\theta)\Delta G^*, \tag{23}$$

where

$$f(\theta) = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2, \tag{24}$$

and therefore

$$> 0 \leqslant f(\theta) \leqslant 1. \tag{25}$$

Shortening and margarine systems almost exclusively undergo heterogenous nucleation. Furthermore, the situation is rarely as straightforward as presented above. The surfaces providing nucleation sites are rarely well characterized flat surfaces, and the evaluation of such surfaces and their wettability is inaccessible in the complex systems crystallized in shortenings and margarines.

The nucleation processes described up until this point have been primary nucleation. Margarine and shortening systems also can undergo secondary nucleation; which is defined as nucleation occurring due to the presence of growing crystals in the melt or solution. According to Kloek (1998) and Garside (1987), there are three different types of secondary nucleation: apparent, true, and contact. Apparent secondary nucleation occurs due to fragments of crystals from growing crystals acting as new nuclei. True secondary nucleation occurs when ordered domains (liquid lamellae), which are smaller than the critical nucleus size, are induced by the presence of growing crystal lattices. These ordered domains disturb the steady state of liquid lamellae, and can lead to the enhancement of nucleation. Contact secondary nucleation results from collisions of crystals with other crystals, with the walls of the containing vessel, or with the impeller blades, etc. Clearly the phenomenon of secondary nucleation adds yet another layer of complexity to a very complex process.

Crystal growth on the established nuclei in a supersaturated solution or melt which is below the melting temperature, T_M, is governed mainly by the efficient removal of the heat of crystallization. The attachment of TAG molecules to the surface of growing nuclei is the next limiting factor to the kinetics of growth, since as pointed out by Ovsienko and Alfintsev (1980), the entropy of fusion of triglycerides is quite high ($\frac{\Delta H}{\mathrm{k}T_M} \approx 60$). It should also be noted here that increases in viscosity (a function of both the progress of crystallization as well as supercooling) can also significantly affect the mass transfer of molecules to growing surfaces; a point that has been convincingly raised by Toro-Vazquez and co-workers (Toro-Vazquez, Briceno-Montelongo, Dibildox-Alvarado, Charo-Alonso, & Reyes-Hernandez, 2000; Toro-Vazquez et al., 2001).

Boistelle (1988) and Garside (1987) have both provided excellent in-depth reviews of crystal growth.

The growth mode via which the crystal grows is a function of the smoothness of the growing surface. As explained by Sloan and McGhie (1988), the smoothness of the growing surface is a function of the entropy factor, $\frac{\Delta H}{kT_M}$. For materials with low entropy of fusion the planes of the growing surface are rough, and initiation of new growth layers is relatively easy. For materials with high entropy of fusion, such as TAGs, the densely packed planes forming the growing surface are smooth, and initiation of new layers are relatively difficult. However, planes which are not as densely packed may exhibit intermediate roughness for materials with high entropy of fusion. For the purposes of this review article, it is sufficient to say that for less densely packed planes of TAG crystals, which may imply a rough surface, the growth rate is approximately proportional to the local supersaturation. This may be explained qualitatively by considering that ordered domains necessary for growth can easily attach to kinks on the surface, resulting in continuous growth. Typically, this type of continuous growth occurs at high levels of supersaturation or supercooling. For densely packed crystal planes, which present a smooth growing surface, the crystals grow via a 'layer-by-layer' progression through secondary nucleation events on the smooth surface. Therefore, on the smooth surface, for growth to occur a nucleus of critical size must be formed; to which molecules will then attach to form another layer of the smooth surface. Consequently, the growth kinetics may be modeled in a similar manner to that used to model nucleation kinetics in the bulk and described before. The growth rate is proportional to the rate of nucleation on the surface, and one can therefore define an activation free energy of nucleation for the surface. Therefore, the crystal growth rate is an exponential function of supersaturation or supercooling (based on the development given before of homogenous volume nucleation). Ovsienko and Alfintsev (1980), and Rousset (2002), provided an equation for the crystal growth rate, ν_C:

$$\nu_C = K_1 e^{\frac{-\pi a_o T_M \sigma^2 V_M}{3kT\Delta H \Delta T}}, \tag{26}$$

where K_1 is a constant that depends on the characteristics of the crystal and a_o is the radius of the molecules. However, it must be pointed out here that the crystal growth rate is dependent on many other factors besides the smoothness of the growth surface and secondary nucleation of a surface nucleus of critical size. Other factors such as viscosity, diffusive mass transfer, molecular conformation, surface defects, microscopic and macroscopic shear rates, impurities, and the molecular diversity of the fats encountered in shortening systems, all play a role in influencing the rate of crystallization.

It should be mentioned that if the rates of nucleation and crystal growth are known as a function of supercooling or supersaturation; it would be possible to model the crystal size distribution as a function of time (Kloek, 1998). In the special case of constant rates of nucleation and growth, and assuming spherical crystals, the Avrami equation formulates the volume fraction of solids, Φ, as a function of time (Avrami, 1939a, 1939b; Kloek, 1998):

$$\Phi = \frac{1}{3}\pi \nu_C^3 J t^4, \tag{27}$$

where it is assumed that no impingement or aggregation of crystals occur. Much has been written in the literature on the use, misuse, and manipulation of the Avrami equation in its application to fat crystallization, and the reader is referred to this literature (Khanna & Taylor, 1988; Long, Shanks, & Stachurski, 1995; Marangoni, 1998; Supaphol & Spruiell, 2000; Toro-Vazquez, 2001; Toro-Vazquez, et al., 2000; Toro-Vazquez & Dibildox-Alvarado, 1997; Wright, Hartel, Narine, & Marangoni, 2000; Wright, Narine, & Marangoni, 2001).

The overall crystallization rate is affected by the following factors (Best, 1988; deMan, 2000; Toro-Vazquez et al., 2001):

1. Heat transfer rate.
2. Mechanical agitation rate.
3. Additives and impurities.
4. Bulk viscosity.
5. Formulation of fat systems.

Crystal growth continues until the individual molecular fat aggregates begin to touch. At a low degree of supercooling, crystal growth predominates whereas nucleation predominates at high supercooling (deMan, 2000). As the degree of supercooling increases, the size of fat crystals will be smaller because of the formation of a larger number of nuclei. This, in turn, has an important effect on the texture of a fat system (deMan, 2000). During post crystallization processes an increase in hardness has been noticed (deMan, 2000). This increase in hardness is known as 'sintering'. Sintering is described as the formation of solid bridges between fat crystals. Due to sintering, fat crystals form a network in oil due to mutual forces of adhesion (deMan, 2000).

Controlling formation of crystalline microstructure in shortenings and margarines is critical to obtain desired texture and quality. However, undesirable changes in crystalline structure can lead to total loss of quality. Controlling crystallization involves careful choice of the ingredients to promote desired structure, proper processing

conditions, and storage conditions. Such an approach maintains the desired crystalline structure and prevents undesired crystallization. Controlling crystallization is not an easy task since our understanding of how parameters influence crystal formation and growth is limited, and even the theories presented here are hampered by being simplistic and fraught with sometimes unreasonable assumptions.

9. Formulation and blending

The choice of different fats and oils in a blend used for manufacturing shortening is more a function of empirical experience as opposed to scientific choice. Not much is predictively known about the cumulative effect of different physical and chemical properties of fats/oils present in a blend. The physical properties typically monitored are melting profiles, SFC, and polymorphism/polytypism. The chemical properties monitored are the composition of fat/oils, diversity of fatty acids, length of carbon chain, etc. It is important to relate changes in chemical properties, due to blending, to predictive changes in physical properties. This is important for optimizing a perfect blend to suit individual applications. Of course, the situation is even more challenging when one considers that the processing conditions used for manufacturing the shortening also plays a significant role in determining the physical properties of the product.

The melting point and the SFC values of some major natural fats are shown in Table 5 (Weiss, 1983). The fatty acid composition of some major fats and oils are shown in Table 12 (deMan & deMan, 2001; Kamel, 1992) and the properties of the TAGs of some major fats and oils are shown in Table 13 (Wiedermann, 1978). Table 13 groups the TAGs into four groups which demonstrate similar physical properties. The diversity of palmitic acid in some major fats is shown in Table 9. The palmitic acid content plays an important role in promoting polymorphic stability as has been discussed before. The compositional differences of TAGs can promote very different physical properties. For example, through modification of crystal structure. The shortening industry has learned, albeit empirically, how to manipulate these differences in the compositions of TAGs in order to satisfy the product needs. Wiedermann (1978) has related the physical properties of a number of TAGs in shortening systems to desirable functional properties.

The distribution of fatty acids on each TAG molecule, the quantity of each TAG species, and the proportions and types of each fatty acid depends on the fat source as well as on the processing history. From Table 13, it can be observed that trisaturated TAG (Group I) can provide structure (by virtue of being solid at room temperature and therefore providing a fat crystal network) while the di-saturated and mono-saturated TAGs (Group II) provide both lubricity and structure (Wiedermann, 1978). That is, they are solid at room temperature and melt at body temperature. The lower melting, more unsaturated TAGs (Group III and IV) can provide lubricity.

Group I is used to formulate fluid margarines by blending a high proportion of unsaturated TAGs and a low proportion of trisaturated TAGs. Group II TAGs provide both lubricity and structure. Groups III and IV are used to prepare soft tub products and all hydrogenated stick products, (Wiedermann, 1978).

The effects on the polymorphic stability of the final product due to the addition of palm oil to hydrogenated oils have been studied in detail in literature (deMan, Shen et al., 1991; Shen et al., 1990; Ward, 1988; Yap, 1988; Yap et al., 1989). Though palm oil is a *beta-prime* tending fat (Wiedermann, 1978) and rapid cooling of palm oil results in the formation of *beta-prime* crystals, slow cooling tends to favor *beta* crystal formation. Hydrogenated canola and soybean oils tend to crystallize in the *beta* form because of their low diversity in fatty acid content (Wiedermann, 1978). Canola contains about 95% of C-18 fatty acids (deMan & deMan, 2001). Vegetable fats containing 10% of palmitic acid tend to crystallize in the *beta* form (Wiedermann, 1978). Whereas those having 20% of palmitic acid have the tendency to crystallize in the *beta-prime* form (Wiedermann, 1978). Lard and cocoa butter are the exception to this statement (Weiss, 1970, 1983). Canola and soybean oil contain 5 and 11% palmitic acid, respectively. The palmitic acid content of palm oil is 40%. Palm oil (hydrogenated and unhydrogenated) crystallizes in the *beta-prime* form because of greater diversity of fatty acid content. Palm is therefore incorporated into shortening formulations that contain hydrogenated canola and soybean oils in order to prevent or delay crystallization into the unwanted *beta* form (Ward, 1988; Yap et al., 1989). Yap (1988) studied the behavior of canola oil upon the addition of palm oil. Palm oil was added up to fifteen percent of total blend, to the canola oil before and after hydrogenation. It was observed that this addition changes the crystallizing behavior of the whole blend from *beta* to *beta-prime* character (Yap, 1988). It can be concluded that palm oil has the potential to change the crystalline behavior of the product (i.e. from *beta* to *beta-prime*).

Both beef tallow and lard are obtained from animal sources. However, the polymorphic behavior of these fats differ widely. Beef tallow crystallizes in the *beta-prime* form whereas lard crystallizes in the *beta*-form. The *beta-prime* form of beef tallow is due to the presence of Palmitic–Stearic–Palmitic (PSP) and Palmitic–Stearic–Stearic (PSS) whereas the *beta*-form is attributed to the Palmitic–Oleic–Palmitic/Palmitic–Palmitic–Oleic (POP/PPO) compound (Timms, 1979).

Table 12
Fatty acid composition

Fatty acid	Canola[a] (%)	Rapeseed[a] (%)	Sunflower[a] (%)	Palm oil[b] (%)	Soya oil[b] (%)
Palmitic acid (P)	4	3	4	46	11
Stearic acid (S)	2	1	3	5	4
Oleic acid (O)	58	17	34	39	23
Linoleic acid (L)	21	14	59	9	54
Linolenic	11	9	–	0.5	8
Gadoleic acid	2	11	–	–	–
Erucic acid	<1	45	–	–	–

Values in percentages of total fatty acid present.
[a] deMan and deMan, 2001.
[b] Kamel, 1992.

10. Processing

The macroscopic physical functionality of shortening and margarine fat systems is dependent on a number of factors:

1. relative percentages of individual oils and fats present in a formulation (Wiedermann, 1972, 1978; Weiss, 1983)
2. processing conditions such as rate and degree of cooling, mechanical working, and final product temperature (Haighton, 1965, 1976; Moziar, deMan et al., 1989; Rivarola et al., 1987; Thomas III, 1978; Wiedermann, 1978), and
3. presence of emulsifiers as additives (Garti et al., 1982; Krog, 1977).

Table 13
Compositional/functional relationships (Wiedermann, 1978)

Groups	Melting point (°C)	TAG
I	65	SSS
	61.1	SSP
	60	SPP
	56.1	PPP
II	41.6	SSO
	37.7	SPO
	35	PPO
	32.7	SSL
	30	SPL
	27.2	PPL
III	22.7	SOO
	15.5	OOP
	6.1	SOL
	5.5	OOO
IV	1.1	SLL
	−1.1	OOL
	−2.7	PLO
	−4.2	PLL
	−6.6	OLL
	−13.3	LLL

S, stearic acid; P, palmitic acid; O, oleic acid; L, lauric acid.

These factors influence the macroscopic functionality that is related to physical properties like melting point, SFC, and rheological properties. Out of these, the rheological properties and melting properties of a fat mixture are further dependent on polymorphism and polytypism (the crystalline state of the fat system), packing density, spatial distribution, and size and shape of the microstructure of the resulting network. The rheology of a fat system is determined by its consistency and texture. Consistency depends not only on the solid-to-liquid ratio present at different temperatures but as well on the various structural levels within the shortening network.

Desirable solid-liquid ratio can be achieved by blending and controlling hydrogenation. Oils are chosen for their particular crystal habit. Crystal habit is also affected by the conditions of processing. The polymorphic modification or crystal habit of the fat composition is a very important property. For example, it is important, for example, because *beta*-polymorphs are desirable in chocolate products whereas *beta-prime* polymorphs are desirable in shortenings and spreads (Wiedermann, 1978). *Beta* polymorphs, being large crystal, give a desirable snap in chocolate products, whereas *beta-prime* polymorphs, being small crystals, give smooth mouth feel in table spreads. Types of processing treatment that affect the structure of a fat at the microstructural, crystalline, and molecular levels are hydrogenation, interesterification, fractionation, and blending (Wiedermann, 1978). The degree of cooling rate and shear during processing also greatly affects the microstructure.

10.1. Hydrogenation

Vegetable oils are too soft for margarines or shortenings because of their liquid nature, while on the other hand saturated fats are too hard. Depending on the end use, most shortening fat systems require hardness that is intermediate. Hydrogenation or the hardening process, is a saturation process (Bailey, Feuge, & Smith, 1942). Hydrogen is added to the double bonds of unsaturated

fatty acids, thus transforming them to saturated fatty acids, which in turn converts oil into solid fat. In the case of complete hydrogenation, arachidonic, linolenic, linoleic, and oleic acids present in the original oil will convert entirely into the corresponding saturated acids (Bodman et al., 1951). Hydrogenation can therefore be defined as a process which imparts oxidative stability to oils. Thus, this process maintains the organoleptic characteristics of oils for longer shelf life. Firmness in margarines is increased by the hydrogenation of the base stock due to the formation of saturated and trans fatty acids (TFA; Mensink & Katan, 1993), as shown in Fig. 10. Acids of high molecular weights appear to hydrogenate less readily than low molecular weight acids (Mattil, 1964b). Fully hydrogenated oil is obtained when all the double bonds are saturated; otherwise the oil is referred to as partially hydrogenated oil. Depending on the conditions applied during the process, hydrogenation can be classified into two types: selective and non-selective hydrogenation. Factors that affect the hydrogenation process and consequently the resultant products, are the temperature of the oil mixture, hydrogen gas pressure, catalyst activity, catalyst concentration, agitation of the mixture, and time duration of the process (Bodman et al., 1951; Chrysam, 1985; Coenen, 1976; Mattil, 1964b). Selectivity (Selectivity refers to the hydrogenation of acids containing active methylene groups in preference to acids devoid of such groups) can make a lot of difference in the final composition of TAGs and consequently affects the melting profile of the product obtained as a result of hydrogenation (Bailey 1951; Bailey et al., 1942; Beal & Lancaster, 1954; Chrysam, 1985; Mattil, 1964b). The relationship of the catalyst, temperature, and pressure to the selectivity of the hydrogenation reaction for oil has been studied extensively (Bailey, 1951). It has been reported that selectivity is directly proportional to the temperature applied during hydrogenation (Bodman et al., 1951; Coenen, 1976). Increases in the degree of agitation favors non-selectivity and suppresses the formation of high melting *trans*-isomers (Bailey et al., 1942). Beal and Lancaster (1954) studied the effect of agitation and batch size on the rate of hydrogenation, and on the stability of the fat. They observed that the rate of hydrogenation increased with an increase in the degree of agitation of an oil or mixture of oils. Furthermore, the stability of the fats increased with an increase in the hydrogenation batch size. High temperature of the oil during hydrogenation favors greater selectivity and thus results in more TFA generation (Coenen, 1976; Mattil, 1964b). Mattil (1964b) reported that high hydrogen gas pressure during hydrogenation increased the rate of hydrogenation and caused a decrease in the selectivity of the reaction. Such conditions favor less TFA formation. Furthermore, Mattil also stated that high catalyst concentration favored selectivity with large amounts of TFA formation. High catalyst concentration increases the rate of hydrogenation (Mattil, 1964b).

Normally hydrogenation is done under less selective conditions. In non-selective hydrogenation, lower temperatures and higher hydrogen pressures are applied in the presence of spent nickel as a catalyst (Mattil, 1964b). SFC profiles of selectively hydrogenated oils are much steeper than the oil processed to approximately the same degree of hydrogenation (or same iodine value) under non-selective conditions. An oil with a steeper SFC profile typically has a very narrow plastic range whereas a fat system with a flat SFC profile typically has a wide plastic range (as shown in Fig. 2). The degree of selectivity in hydrogenation also affects the crystal stability of the resulting fat. A study carried out by Yap (1988) showed that selectively hydrogenated canola oil formed a mixture of *beta-prime* and *beta* crystals; whereas non-selective hydrogenation resulted in the *beta* form of crystals. Incorporation of trans fatty acids through selective hydrogenation favors *beta-prime* crystallization (Naguib-Mostafa & deMan, 1985).

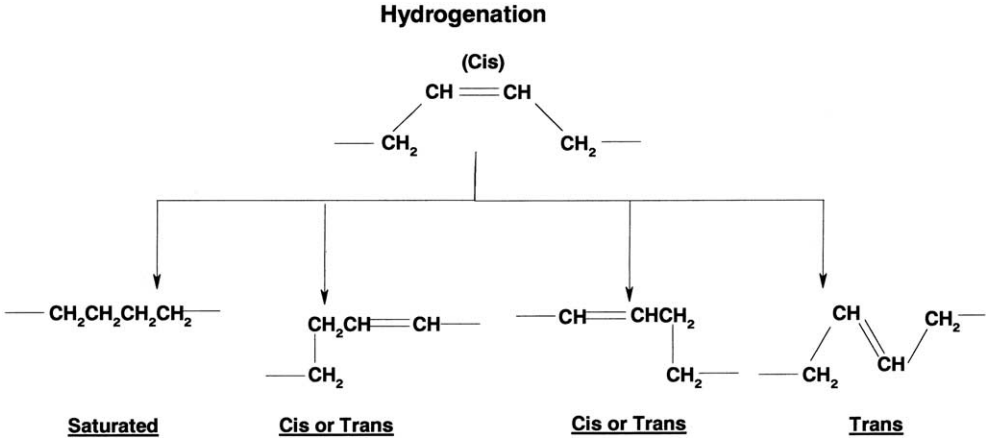


Fig. 10. Hydrogenation.

Therefore it becomes difficult to obtain desirable acceptability in terms of melting profile, low *trans*-acids, and favorable polymorphic behavior (and indirectly rheological behavior) by sticking to only one technique of hydrogenation. Thus, hydrogenation conditions are manipulated to choose the most desirable set of processing parameters. Tables 14 and 15 depict a summary of the effect of process parameters on the selectivity of the hydrogenation process.

Human diet has traditionally contained low levels of TFA. TFAs are formed by bacteria in the rumen of ruminants. Therefore, these TFA are found in the fats and oils obtained from ruminant-derived products such as cow's milk and butter (Hay & Morrison, 1970; Smith, Dunkley, Franke, & Dairiki, 1978). The values of TFAs of such products reported in the literature are one to nine percent of the total fatty acids (Woodrow & deMan, 1968a). In addition to this natural TFA occurrence in food products, partial hydrogenation of oils that are rich in polyunsaturated fatty acids (PUFAs) also generate TFAs (Scholfield, Davison, & Dutton, 1967). In a number of surveys done, it has been reported that margarines contain TFAs in the range of 35–60% (Beare-Rogers, Gray, & Hollywood, 1979) and shortening, frying, and cooking fats contain up to 50% TFAs (Hecker & Melcher, 1978).

All unsaturated fatty acids have at least one carbon–carbon double bond. In the *cis* configuration the two carbon moieties are on the same side of the double bond and in the *trans* configuration they are on opposite sides

Table 14
Summary: hydrogenation

Influence of process conditions		
Increase in	Parameter affected	
	Degree of selectivity	*Trans*-isomer formation
H_2 pressure	Decreases	Decreases
Temperature	Increases	Increases
Agitation	Decreases	Decreases

Table 15
Summary: factors affecting selectivity of a hydrogenation process

Hydrogenation conditions affecting selectivity		
Reaction parameter	Selective hydrogenation	Non-selective hydrogenation
Temperature	High	Low
H_2	Low	High
Agitation	Low	High
Catalyst concentration	High	Low (spent)
Trans-isomer formed	High amount	Low amount
SFC curve shape (Fig. 3)	Steep	Flat
Crystal stability	Beta prime or mixture of beta-prime and beta	Beta only

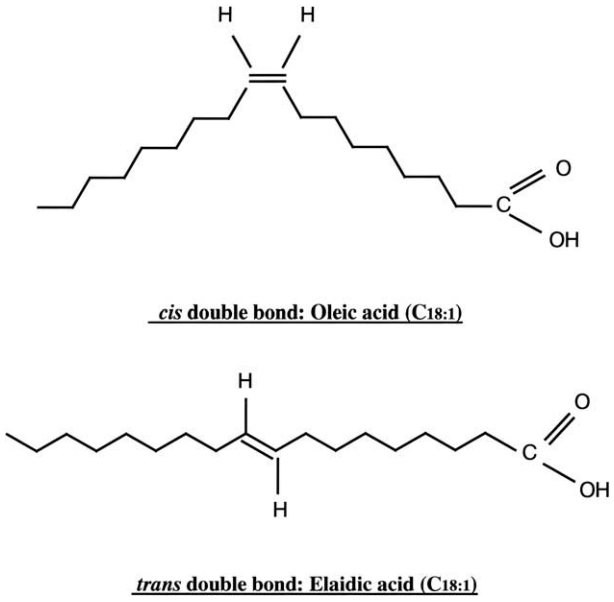


Fig. 11. Molecular structure of *cis* and *trans* isomers of C18:1.

(Fig. 11). The *cis* configuration produces a bend in the molecule, whereas the *trans* configuration resembles more the straight chain of saturated fatty acids.

During partial hydrogenation, some double bonds are isomerized into *trans* fatty acids from their *cis* configuration (Scholfield et al., 1967). *Trans* fatty acids have similar melting points to that of the corresponding saturated fatty acids and are very important contributors to the functional properties of hydrogenated products. This has recently become a controversial health issue. Many studies have been done on the biological effects of *trans*-fatty acids in animal and human subjects (Anderson, Grande, & Keys, 1961; Anderson and Coots, 1967; Beveridge & Connel, 1962; Coots, 1964a, 1964b; Emken, Rohwedder, Dutton, Dejarlais, & Adolf, 1979; Erickson, Coots, Mattson, & Kligman, 1964; Johnston, Johnson, & Kummerow, 1957; Kummerow, Mizuguchi, Arima, Cho, & Hunang, 1978; Mavis & Vegelos, 1972). However, some controversial results were reported regarding their effect on the metabolism and vital organs of the respective subjects under experimental conditions. Kummerow and coworkers (Kummerow et al., 1978) reported the adverse effects of hydrogenated fat on the development of atherosclerotic lesions in swine. In human subjects, it has been found that diet containing trans acids cause an elevation of plasma cholesterols, triacylglycerides and phospholipids (Anderson et al., 1961). These results are supported by Vergrosen (1972) and Houtsmuller (1978). However, Vergrosen (1972) also reported that trans acids are less hypercholesterolemic (increase in plasma cholestrol level) than the shorter-chain saturates, lauric and myristic, but more hypercholesterolemic than either palmitic or oleic. The fact that *trans* fatty acids have a higher

melting point than their corresponding *cis*-isomers suggests that the incorporation of the *trans* fatty acids into cellular membranes may affect the properties of the membrane and its function (Chapman, Owens et al., 1966). High levels of *trans* fatty acids are considered to be a risk factor for cardiovascular diseases (Reddy & Jeyarani, 2001). Industry and regulatory agencies are beginning to work together to ensure that the manufacture of shortenings do not amplify TFA intake. It is expected that USA Food and Drug Administration (FDA) will establish regulations governing the percentage of allowed TFAs in edible oil products in 2002. Specialty oils such as Trisun and Sunola oils (based on sunflower seed oil) do not require hydrogenation for good stability and performance (Mag, 1994). These have potential uses in manufacturing *trans*-free shortenings. Recently, it has been reported that it is possible to prepare TFA-free bakery shortening (puff/cake/biscuit) using Mango and Mahua fats and their fractions (Reddy & Jeyarani, 2001). Reddy and Jeyrani (2001) and Kok and coworkers (Kok, Fehr, Hammond, &, White, 1999), have successfully prepared a shortening without any hydrogenation treatment. They also demonstrated that such a product has functional properties comparable to most of the commercial shortenings.

Further research is required in the following important areas:

1. Improvements in the hydrogenation process for use in the manufacture of *trans*-free shortenings.
2. Effects of *trans* fatty acids on the physiology and biochemistry of vital organs such as the heart.
3. Manipulations of the processing conditions under which shortenings/margarines are produced to deliver comparable functional properties without needing to hydrogenate.

Within our laboratory, our efforts are concentrated around understanding relationships between molecular ensembles, processing conditions, crystalline and microstructural structure of the shortening network, and between all levels of structure of the network and physical functionality of the shortening. In this manner, we hope to build a comprehensive understanding of the ways in which the starting materials and processing conditions affect the functional properties of the final network.

10.2. Manufacturing

There are number of factors that influence the final physical functionality of shortenings and margarines:

1. proportions of solids to liquids;
2. viscosity of the liquid;
3. temperature treatment;
4. mechanical working;
5. super cooling;
6. polymorphism;
7. properties of the crystals: size, number, and composition; and
8. spatial distribution, size, and shape of the microstructure.

Processing, therefore, is as equally important as the design of the oil blend; in the determination of the physical properties and performance of shortenings. For example, whipping of margarines up to fifty percent overrun. (Overrun is defined as incorporation of air into the product that results in decreasing the bulk density, increasing hardness, and in allowing the use of softer (unsaturated) oil blends, (Gorman, Bluff, Christie, & Glenview Kraft, 1960). Formulation of the blend and subsequent processing conditions regulates the type of crystal formation and subsequent network formation. The type of crystals formed has a direct influence on the morphology of the solid structure (microstructure) that traps the liquid phase of the shortening/margarine (Haighton, 1976; Thomas, III 1978; Wiedermann, 1978). Haighton (1959, 1976) reported that the hardness of margarine in terms of yield value has a strong correlation to the solid content. The manufacturing process itself can have significant impact on the solid content of the finished margarine. Margarines are typically manufactured by quick chilling of the fat blend using a swept surface heat exchanger (Unit A, Fig. 12), followed by holding in crystallization tubes before molding or forming. Depending on the rate of cooling, the relative time spent in the heat exchanger and crystallization tubes, whether the fat is 'worked' in the crystallization tubes, and the temperature of the crystallization tube, the solid content, and the crystal type and microstructure of the resulting network is greatly affected. The temperature in the crystallization tube is usually 2 °C higher than the temperature in Unit A, due to the liberation of heat during crystallization (Haighton, 1976). If the rate of crystallization is low, the margarine is typically very soft (Haighton, 1976). The fat continues to crystallize in the holding tubes and usually needs hours to reach complete crystallization. Various arrangements of Unit A and crystallization tubes are applied for different kind of shortening manufacturing, as shown in Fig. 12. For stick margarines, the supercooled fat is allowed to solidify without agitation. This post crystallization, in the absence of agitation, favors the formation of strong networks characterized by sintering between network structures and the product demonstrates a narrow plastic range. When a specific characteristic is desired, the use of an additional working unit, after super cooling in the scraped surface heat exchanger, is required.

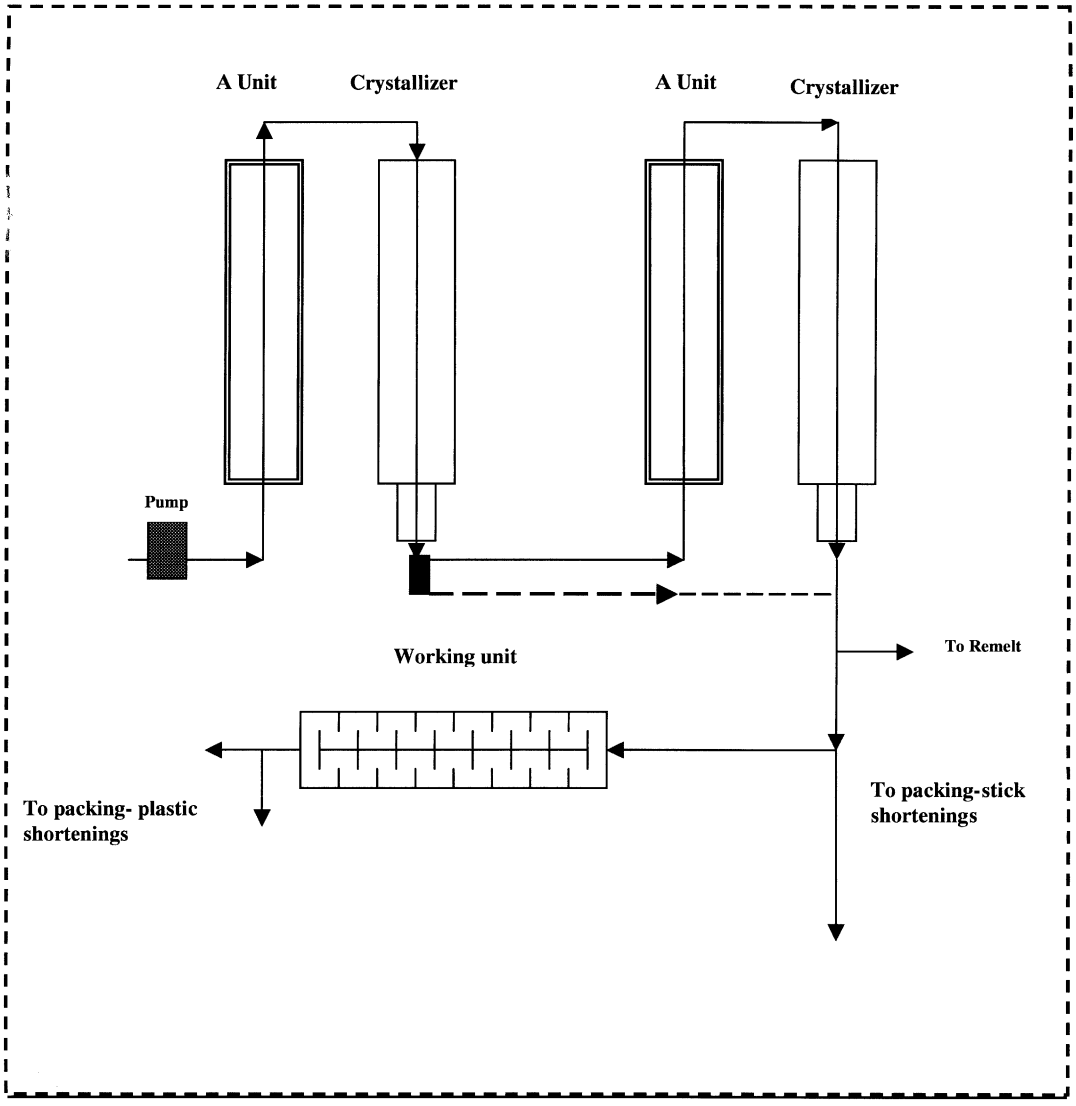


Fig. 12. Production of shortening.

A scraped surface heat exchanger consists of a steel shaft rotating in a stainless steel tube. A suitable coolant (e.g. ammonia) cools the tube externally. The rotating shaft is fitted with scraper blades. At high rotation speeds, these blades scrape the inner surface of the tube due to the applied centrifugal force. High internal pressure and shearing actions induce fast nucleation and crystallization in a very short residence time. The length of required crystallization time varies depending on the fat compositions used in the formulations. Incorporation of a higher melting *beta-prime* tending oil to a base stock can induce the crystallization of the entire fat into a stable *beta-prime* form (Thomas III, 1978). The effects of such formulation practice and processing conditions have been studied extensively by Rivorola and co-workers (Rivarola et al., 1987) for blends of hydrogenated sunflower and cottonseed oil. For strong *beta*-tending sunflower oil, it was found that the tendency to crystallize in the *beta-prime* form increased with the increasing cooling rate. Woodrow and deMan (1968b) investigated the polymorphic behavior of milk fat after slow cooling and rapid cooling. Slow cooling resulted in a mixture of *beta-prime* and *beta* crystals. Rapid cooling of milk fat resulted in the formation of the *alpha* form which eventually transformed into *beta-prime* and *beta* upon holding the sample at 5 °C. It has been known from the literature that TAGs with simple and symmetrical fatty acids tend to exhibit typically *alpha*, *beta-prime*, and *beta* forms; whereas those with asymmetrical mixed fatty acid moieties tend to form *beta-prime* crystals (Hagemann, 1989; Sato, 2001). During processing, the cooling rate and agitation is controlled. Hoerr (1960) reported that rapid crystallization of a fat system induces the formation of small crystals throughout the solidifying mass. The small crystals then transform into large aggregates. Narine and Marangoni (Narine &

Marangoni, 2002b) also observed these effects. This property contributes to the creaming abilities of a shortening (Hoerr, 1960), when small *beta-prime* crystals are preferred due to the increased ability to incorporate air bubbles.

10.3. Tempering and effects of emulsifiers

Tempering is the process whereby fats attain the physical state in which they are normally utilized. Tempering involves a time–temperature relationship where a shortening is held for 1–10 days after initiation of crystallization during processing at temperature which may either be lower or higher than the temperature at which the shortening is packed (Moziar et al., 1989). During tempering, the crystals transform to the preferred polymorphic form. Lack of tempering adversely affects the functional properties of shortening/margarine products. Tempering of shortenings result in significantly better functional properties. For example, higher cake volumes can be obtained by using tempered cake shortening in a cake mix, whereas fresh, untempered shortening gave lower cake volumes (Gillies, 1974). It has also been reported that tempering affects the firmness of the shortening (Nor Aini, 2001). Some shortening may continue to change in structure even after the tempering process. This can lead to among, other detriments, a potential defect in margarine texture called 'graininess' (Vaisey-Genser, Vane et al., 1988). Proper temperature control during subsequent storage of the product reduces such undesirable physical defects (Hoerr, 1960).

Tempering also delays the polymorphic transition from *beta-prime* to *beta* crystal forms (Moziar, de Man, & de Man, 1989). The *beta*-form has a tendency to grow in size upon standing; especially at room temperature. When this happens there is a loss in creaming ability of the shortening (Chrysam, 1985). Tempering of shortening and plastic fats at constant temperatures is an expensive process. Maintaining and rotating inventories of the products in large godowns creates logistic problems.

Emulsifiers in shortening systems may be defined as substances which have the potential to control polymorphism and modify the crystallization properties of fats (Krog, 1977). The effect of emulsifiers on the crystallization and the development of polymorphic forms of fat have been studied by a number of researchers (Nakamura, 1997; Nasir, 2001; Rivarola, Anon, & Calvelo, 1988; Sato, 1999; Yuki, Matsuda, & Nishuimura, 1990). In addition to the aforementioned functions, emulsifiers also primarily impart stability to emulsions, control agglomeration of fat globules, and stabilize aerated systems (Krog, 1977). Nasir (2001) reported that using de-oiled lecithin as an emulsifier delays the crystallization process and inhibits fat bloom in chocolate as well as in other related food products. Yuki and coworkers (Yuki et al., 1990) observed an increase in the rate of fat crystallization when sucrose fatty acid esters (Palmitate and stearate types) are used as emulsifiers. The addition of sorbitan esters stabilizes the intermediate *beta-prime* form during crystallization and prevents the formation of the *beta*-form (Garti et al., 1981, 1982). Sorbitan tristearate is effective as a crystal inhibitor in margarines. It is assumed that the *beta-prime* crystal form of fat crystal networks accommodate sorbitan tristearate. The stearic hindrances prevent the formation of the more densely packed *beta*-crystal form (Krog, 1977). Canola oil in combination with an emulsifier hydrate containing monoglycerides, polysorbate 60, and sodium stearoyl lactylate, was used in a white-layer cake formulation (Vaisey-Genser et al., 1987). It was observed that such an emulsifier system permits a reduction in the fat content of cake formulation from 53% to approximately 11% without loss in the quality. Therefore, the use of emulsifiers has the potential to be very economical for the oil and fat industry. However, no comprehensive theory exists which links emulsifier structure to function in the crystallization process.

10.4. Interesterification

Interesterification (IE) is an acyl rearrangement reaction used to modify triglyceride melting and crystallization properties while maintaining their nutritional quality (although some nutritional quality may be lost by the removal of beneficial fatty acids from the *sn*-2 position of a TAG molecule). Interesterification causes a rearrangement of fatty acids within, and between TAGs on a glycerol backbone (Macrae, 1983). This results in the formation of a new TAG that may not have existed in the original fat. IE reactions can be driven chemically or enzymatically. In chemical IE a chemical catalyst such as sodium metal or sodium alkoxide is used to promote acyl rearrangement around the glyceride molecule (Macrae, 1983). In enzymatic IE, biocatalysts, such as microbial lipases are used for the acyl migration around the glyceride molecule. The acyl exchange can proceed in a controlled manner by replacing the chemical catalysts with biocatalysts (Macrae, 1983; Seriburi & Akoh, 1998). Lipase-catalyzed reactions, unlike chemical IE, do not produce by-products (Seriburi & Akoh, 1998).

Two forms of reactions are recognized; random and directed interesterification (Young, 1980). In directed interesterification, the reaction mixture is cooled, which causes the crystallization of high melting TAGs present in the liquid oil phase. Such conditions disturb the equilibrium of the liquid phase; thereby directing the reaction to form more high melting fractions (Young, 1980). Cottonseed oil containing twenty four percent saturated fatty acids is liquid at room temperature.

Directed interesterification, using sodium methoxide or ethoxide or sodium/potassium alloy as a catalyst, can be used to turn cottonseed oil into solid fat at room temperature (Young, 1980). Wiedermann and co-workers (Wiedermann, Weiss, Jacobson, & Mattil, 1961) worked on the chemical IE of lard, which has a tendency to form *beta* crystals. With chemical IE, modified lard with *beta-prime* crystal form was obtained. Wiedermann and coworkers (Wiedermann et al., 1961) found that final product characteristic depended heavily on the time and temperature relationships used in the treatment.

Cocoa butter TAGs are high in stearic acid, which have a sharp melting profile at 37 °C (Fig. 3). Cocoa butter fat melts in the mouth to give a cooling sensation and a smoother mouth-appeal effect. Palm oil TAGs are high in palmitic acid and have a melting point of 23 °C. Therefore, palm oil is liquid at room temperature. Conversion of some common lauric fats (such as palm oil) into cocoa-butter fat substitute can be achieved by interesterification. A process is reported in which chemical IE is employed to convert lauric fats into confectioners' fats (Brown et al., 1970; Gillies, 1974). The process involves the IE of lauric fats with alkyl fatty acid esters (fatty acids having 12, 14, and 16 carbon atoms) at temperature between 80 °C and 140 °C. The following equation illustrates the process:

$$\text{Lauric fat} + \text{Alkyl ester(s)} \rightarrow \text{New TAG} + \text{New alkyl esters}$$

The IE is carried out using an alkali metal alkoxide as catalyst, such as sodium methylate. Gleason (1960) also reported a process for manufacture of an improved cake shortening utilizing IE of lard with itaconic acid (propylenedicarboxylic acid). Cakes baked using such shortening have a fine uniform texture with an increase in crumb volume.

Many studies have been done on the chemical IE and enzymatic IE of the TAGs that affect the hardness and spreadability of fat systems (Foglia, Petruso, & Feairheller, 1993; Forssell, Kervinen, Lappi, Linko, Suortti, & Poutanen, 1992; Lee & Akoh, 1997; Marangoni & Rousseau, 1998; Moussata & Akoh, 1998; Rousseau, 1996; Rousseau, Forestiere, Hill, & Marangoni, 1996; Rousseau & Marangoni, 1998; Seriburi & Akoh, 1998).

TAGs containing mixtures of short, medium, and long chain fatty acids attached to the glycerol backbone for specific functionality are called structured lipids (SL) (Haumann, 1997). Their first food use has been in the confectionary industry. Enzymatic IE, because of substrate specificity, is widely used for producing SL. Several factors have prompted the increasing interest in structured lipids. SL offer metabolic advantages in chronic health conditions such as impaired gastrointestinal functions, liver disease or congestive heart failure and infants with food allergies and digestive problems. SL has also been used as a valuable component in designing infant formula, beverages, snack bars, confectionary products, and supplements for non-clinical uses, such as for maintaining health or bodybuilding (Haumann, 1997). Softly (Softly, Huang, Finley, Petershein, Yarger, Chrysam et al., 1994) worked on IE of hydrogenated vegetable oils to form Salatrim. Salatrim is a family of structured TAGs containing at least one short chain fatty acid and at least one long chain fatty acid (e.g. stearate) on each glycerol molecule. Because of its chemical design, Salatrim provides five calories per gram, versus the nine calories per gram of typical fats (Haumann, 1997). Salatrim is prepared by IE of hydrogenated vegetable oils, such as soy or canola, with triacetin and/or tripropionin and/or tributyrin. Lee and Akoh (1997) used two immobilized lipases (IM 60 from *Rhizomucor miehei* and SP 435 from *Candida antarctica*) to synthesize a number of SL.

Native lard consists of grainy crystals with large spherulitic aggregates. Chemical IE of native lard results in fine crystals and reduced fat spherulite aggregates (Rousseau, Hill et al., 1996). IE of lard–canola oil (LCO) mixtures leads to reduced spherulite and low-density aggregate formation. This has a direct effect on the hardness index (HI) of these fat blends. It was reported by the Marangoni group (Marangoni & Rousseau, 1998) that the hardness index of lard and LCO increased after IE. Marangoni and Rousseau (1998) reported that the G′ (Elastic modulus) of all LCO blends increased as a result of IE; while G′ of palm oil and soybean oil (POSBO) blends was not affected by IE. A lot of work has been done on the enzymatic IE of palm oil blends (Kurashige, Matsuzaki, & Takahashi, 1993). This results in improvement in the handling properties of the palm oil at low temperatures. Palm oil was blended with either canola or soybean oil and these blended oils were then modified by enzymatic selective IE utilizing an immobilized lipase that had 1, 3- positional specificity (Kurashige et al., 1993). They reported that enzymatic IE lowered the SFC of the treated blend. No such effect was reported when a similar blend was subjected to chemical IE. Therefore, it was concluded that enzymatic IE is a useful treatment to improve the fluidity of blends of palm and canola oil.

By employing IE, the manufacturing industry may be able to achieve freedom from hydrogenation odor and trans-fatty acids in the final product. Lard and high oleic sunflower oil (Trisun) were interesterified at 55 °C for 24 h with SP 435 lipase (obtained from *Candida antartica*) to produce plastic fats (Seriburi & Akoh, 1998). Seriburi and Akoh (1998) reported that 60:40 (w/w) ratio of lard to Trisun had the widest plastic range (from 3 to 26 °C). Their study demonstrated that enzymatic interesterification of saturated fat (lard) with an unsaturated vegetable oil (Trisun) can be used as an

alternative to partial hydrogenation for commercial applications. The proportions of lard and Trisun can be varied to produce various plastic fats with different solid fat contents. Moreover, IE can increase the stability of unsaturated TAGs. Moussata and Akoh (1998) worked on the lipase-catalyzed IE of melon seed oil. The stability of melon seed oil is low because of its high content of linoleic acid ($C_{18:2}$). In the experiment, melon seed oil was interesterified with high oleic sunflower oil. After interesterification, palmitic acid ($C_{16:0}$), stearic acid ($C_{18:0}$), and oleic acid ($C_{18:1}$) contents increased at the *sn*-2 position of TAG. Due to such rearrangement of fatty acids among TAGs, stability of the melon seed oil was increased.

Weiss (1983) used IE to form an acetoglyceride. IE of TAGs with triacetin (glycerin triacetate) yields acetoglyceride (Weiss, 1983). These are waxy solids which are stable in the alpha crystalline form. They have emulsifying properties (Gehrke, Marmor, Henry, & Greenberg, 1959) and can be used as coating fats (Luce, 1967) and as whipped toppings (Anonymous, 1968).

11. Conclusions

Although a lot of research has been done on shortening systems, not much comprehensive understanding has been established regarding the relationships between the starting ensemble of molecules (TAGs, fatty acids, emulsifiers, etc.), processing conditions, crystalline and microstructural levels of structure, and final physical functionality (solid content, melting behavior, texture and hardness, density). There exists a wealth of knowledge in the field; as is evidenced by the large amount of publications cited herein and elsewhere. However, this data has not been, in general, accumulated in a directed, concerted, and logical manner designed to answer fundamental questions of the underlying concepts governing the relationships that are mentioned above. Conclusions can nevertheless be drawn, in part, on the efficacy of the contributing properties of various molecular species to final shortening functionality, on the required processing conditions to produce particular functionality from specific blends of TAGs and emulsifiers, and on the efficacy of modification methods such as hydrogenation and interesterification. These partial answers have been highlighted in this review.

Additionally, a tremendous amount of theoretical work has been performed on the theory of fat crystallization (led by groups such as the Hartel group in the United States, the Sato group in Japan, the Ollivon group in France, the Toro-Vazquez group in Mexico, Phillipe Rousset in Switzerland, Nissim Garti in Israel, and many notable others), the quantification of microstructure (primarily from the Marangoni group at the University of Guelph in Canada), the relationship of microstructure to rheology (Marangoni group in Canada, Toro-Vazquez group in Mexico, Hartel group in the USA, etc.), the preparation of structured lipids via interesterification (the Marangoni group in Canada, Akoh group in the United States, etc.), and the elucidation of the crystallization structure of the established polymorphic forms (the Sato group in Japan). The vast amount of scientific literature from these groups and others must not be discounted. This review has attempted to group the literature relevant to shortenings in an easy to understand description of the state of the understanding of the field, but it is impossible in one review to also take into consideration the many discrete pieces of advancements that have been made in the areas mentioned earlier. Certainly even with the volume of work out there, we are still very far from a predictive conceptual understanding of the relationships mentioned at the beginning of this section of the report. It is the objective of our research group at the University of Alberta to collate the knowledge offered on the various areas, to identify the gaps as that knowledge pertains to an understanding of shortenings and margarines, and to do targeted experimental and theoretical development in the shortenings and margarines field. Much of this effort can borrow from the excellent work done on the general area of fat crystal networks already in the literature.

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