Effect of Processing on Crystal Structure[1]

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Abstract

The performance of fats in many of their uses in food products is directly dependent on their crystal structure. Fats exist in several crystal modifications, each of which exhibits physical properties that influence the behavior of the fat differently in various applications. The crystal forms in which fats exist and their rates of transformation from one modification to another are dependent upon their molecular composition and configuration. Processing procedures such as blending, hydrogenation, interesterification, fractionation, etc., markedly alter the molecular composition and configuration. Other processing, such as votating and tempering practices, directly affect the crystal structure of the products. Thus, through judicious choice of processing procedures, the crystal characteristics of products can be governed to obtain the desired performance in specific applications.

Introduction

IT HAS BEEN KNOWN FOR DECADES that some fats perform more satisfactorily in certain applications than do others. For example, liquid oils do not originally by themselves produce an acceptable cake product. After the introduction of hydrogenation to the fat and oil field, it was found that certain partially hydrogenated vegetable oils produced lighter, finer-grained cakes than other kinds of fats. When the rearrangement process was applied to lard, it was found that the interesterified product performed more satisfactorily in many bakery products than did ordinary lard. Fats which produce excellent cakes are not likely to produce acceptable whipped toppings. Fats which are used for confectionery coatings exhibit quite different properties from those used in baking applications.

It is only recently that we have begun to explain the performance of fats and oils in terms of their molecular composition and crystalline structure. There is yet little agreement among the various investigators regarding the interpretation of the polymorphic behavior of fats and oils. The literature contains many papers relating to the polymorphism of individual triglycerides but few which apply this knowledge to interpreting the crystal transformations of fats. In 1960 I spoke at the AOCS Short Course at the University of Illinois on this same subject. In looking over what I said at that time, I must admit that I can add little in the way of new information. The general principles which I discussed then have not been altered by our subsequent work. Essentially all we have done since is to amplify some of the explanations relating to the organization of the molecules in their crystal lattices.

We have known since the early 1930's that triglycerides exist in more than one crystal form. It is true that to this day the various investigators are not agreed on the number of crystal forms in which glycerides may exist or on names by which these forms should be identified. When we consider the polymorphic behavior of fats, we encounter many differences of opinion. The problems are brought about by the complexity of the molecular composition of these materials. We have known for some time that certain fats exist in different crystal forms from others. It is only since the introduction of gas chromatography that we are beginning to be able to correlate these differences in polymorphic behavior with the molecular composition. We now know that certain kinds of glyceride isomers prevent crystal transformations, and consequently certain mixtures of triglycerides cannot be transformed to other crystal forms. Yet other glyceride mixtures transform readily from form to form and exhibit as many as three or four different kinds of crystal modifications.

There is a variety of experimental methods for demonstrating that fats exist in different crystal forms. Each crystal form possesses its own specific physical properties. Thus they differ in melting points, solubility, specific heat, dielectric constants, etc., but, precise as these measurements may be, they do not define the various crystal forms. It is by means of x-ray diffraction that we are able not only to demonstrate that different crystal forms exist but also to measure the dimensions of the molecules and the manner in which they are arranged in the different crystal lattices.

Thus, as fat crystals are transformed from one form to another, we are able to deduce the manner in which the arrangements of the molecules shift with respect to each other in the successive lattices. The crystal lattice which is first formed when the molecules solidify from the molten state is a relatively loose arrangement. As crystallization proceeds, the molecules tend to pack more closely together because of the intermolecular attractive forces which hold them together in the crystal. With the passage of time the molecules in the crystal lattice will pack as closely as their atomic structure permits. Therefore, in the most stable crystal lattice, the molecules will fill the least possible space available.

In thinking about the crystal forms in terms of the arrangements of their molecules in physical space, we have a definite basis for differentiating the various forms. Thus the lowest melting *alpha* form is the most loosely packed arrangement of the molecules. The molecules are as far apart as they can be and still remain in the solid state. As transformation proceeds through the *beta* prime and intermediate forms, the molecules become successively more closely packed. The highest-melting stable *beta* form represents the closest possible arrangement of the molecules.

By visualizing the molecules in space, it will be seen that, if the molecules are all alike, they can readily align themselves with each other. If, on the other hand, the material consists of a mixture of different molecules, perhaps containing fatty acids with different chain-lengths or containing one or more double bonds, the molecules will not all be of the same shape and configuration. Therefore they may not fit together so readily and will not be able to pack so closely as molecules which are alike; transformation to the higher-melting polymorphic forms will be impeded or prevented.

Hence mixtures which consist of homogeneous molecules will tend to transform relatively rapidly through the sequence of crystal forms to the higher-melting modifications. Mixtures which consist of heterogeneous assortments of molecules will tend to become stabilized in the lower-melting crystal form and will therefore exhibit fewer polymorphic modifications.

This interpretation of crystal structure helps us to explain polymorphic phenomena that we have observed empirically for many years. For example, ordinary prime steam lard exhibits a succession of three or four different crystal forms because it consists of a relatively limited assortment of triglycerides in which the palmitic acid components are almost all located on the central carbon atom of the glyceryl group. Rearranged lard, on the other hand, exhibits only two crystal forms because the randomized mixture of molecules of which it consists cannot pack closely together and transformation to higher-melting forms is prevented.

Cocoa butter exhibits at least four different crystal forms because it contains relatively few different types of triglycerides; approximately 57% of this fat consists of triglycerides containing stearic, oleic, and palmitic acids with the oleic acid on the central carbon atom of the glyceryl group.

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Partially hydrogenated cottonseed and soybean oils exhibit only two crystalline forms because of the diversity of triglyceride types which they contain. As hydrogenation proceeds to completion, they exhibit more forms; soybean stearine exhibits the most rapid transformation rate because it consists predominantly of stearic acid.

With this background we are in a position to select processing procedures which will yield products with a crystalline behavior that we desire for specific purposes. Thus, if we need a fat with small *beta* prime crystals for a cake-mix shortening, we will choose a manner of processing which will produce a fat that consists of a heterogeneous assortment of triglycerides which will exist in the desired crystal form and exhibit the desired plastic range. Or if we desire a higher-melting fat in relatively large crystals for making a flaky pie crust, we would choose a process which will yield a fat containing a limited assortment of similar triglycerides with elevated melting-points.

Processing Methods

The various processing methods have for years been achieving the results which we are only now beginning to explain on a molecular basis. Among the methods available for altering the molecular composition and configuration are the following.

Blending

The oldest and still the simplest and most direct way of altering the molecular constituents is by blending various types of fats and oils in order to obtain a mixture which contains a greater variety of components than the individual starting materials. The blending process also includes the addition of emulsifiers to shortenings, which serves not only to diversify the molecular components but also adds other desired performance characteristics.

Hydrogenation

This processing may be used to achieve a variety of results, depending on the operating conditions employed. The addition of hydrogen atoms to double bonds serves to raise the melting point and, at the same time, to diversify the molecular types by producing components which were not in the original mixture. During the early stages of hydrogenation, depending on operating conditions, *trans* isomerization takes place at some of the double bonds. This results in the formation of the elaidic acid isomer of oleic acid, which again yields an elevated melting-point and a greater diversity of molecular types. Also during hydrogenation, again depending on operating conditions, some migration of double bonds occurs, yielding isomers with double bonds in locations different from those in the starting material.

Interesterification

Catalytic interesterification or molecular rearrangement is an obvious means for randomly distributing the fatty acid components among the triglyceride molecules to increase the diversity of components.

Glycerolysis

This process involves the reaction of fat with glycerol. The fatty acid components are distributed among the available glyceryl groups, not only diversifying the triglyceride constituents but yielding new components (mono- and diglycerides) which yield additional performance characteristics.

Fractionation

This again is a relatively old and yet a new processing procedure for altering chemical composition by removing certain components of the mixtures. Refiners have produced salad oils that remain clear and fluid at refrigeration temperatures by a process called "winterization." This simply involves storing the oil in a cold room to allow the higher-melting components to solidify. Subsequent filtration produces an oil which will remain clear at least down to the temperatures at which winterization was effected. Modern commercial crystallization and filtration equipment is now used to separate triglyceride fractions with specific melting ranges from any natural or hydrogenated fat. This process permits the production of high-melting, intermediate-melting, or low-melting fractions of specific desired triglyceride compositions. This recent innovation in commercial processing has resulted in the production of new high-stability cooking oils, confectionery coating fats that exhibit properties similar to cocoa butter, and new fats for imitation dairy products. Besides these processing procedures which alter chemical composition, we have various methods of physical treatment which affect the crystal structure and polymorphic behavior of fats. Among these are solidification, tempering, and storage.

Physical Treatment

Solidification

The manner in which a fat is solidified has a pronounced effect on the character of the crystals that are formed and, at least to some extent, on the rate of crystal transformation. The size of crystals can be regulated by the rate of cooling; smaller crystals are obtained with relatively more rapid chilling conditions and larger crystals are obtained during slow crystallization at relatively higher temperatures. The oldest method for solidifying fats involves pouring the molten fat over a chill roll which, as the name implies, is a cylinder that is cooled by some means of refrigeration. The solidified fat is scraped off the roll and agitated mechanically during the subsequent completion of solidification. By far the most common means of solidification in use today is the scraped-surface heat exchanger, of which the Votator is the unit used most commonly in the United States. This is a continuous unit with a high rate throughout and precise temperature control for producing fat products with the desired crystal characteristics.

Tempering

This is merely the process of maintaining solidified fat products at an elevated temperature for a given period of time. It is not yet understood what actually happens to the crystal structure of fats during this period, but it is known from experience that a period of quiescence is required for the crystal structure to equilibrate with the environment before the fat can be used for most purposes. Under ordinary operating conditions, tempering is usually effected at about 85F for a period of approximately 48 hours although these conditions will vary, depending on the type of product being processed.

Storage

Although this is not actually a processing procedure, it is included because fats must occasionally be held in storage for some period of time before they are used. The conditions under which the fats are stored may have a marked effect on the crystal structure. Since the rate of crystal transformation is dependent on temperature, changes in crystal structure can be retarded by storing the material at relatively low temperatures. On the other hand, undesirable crystal changes may frequently result from storage at elevated temperatures. Consequently some degree of control must be maintained over the storage conditions to insure the desired quality of the finished products.

As our knowledge about the crystal structure of fats increases and as we learn more about the relation of crystal structure to the performance of fats in their many specific applications, we will be able, by judiciously choosing the appropriate starting-material and using the proper combination of processing procedures, deliberately to produce fats with the specific properties needed to achieve the desired performance.

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Classified Advertising

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REFERENCES

1. Bailey, A. E., "Industrial Oil and Fat Products," edited by D. Swern, Third Ed., Interscience Publishers Inc., Division of John Wiley and Sons Inc., New York, 1964.
2. Bailey, A. E., "Melting and Solidification of Fats," Interscience Publishers, Inc., Division of John Wiley and Sons Inc., New York, 1950.
3. Chapman, D., Chem. Rev. *62*, 433 (1962).
4. Hoerr, C. W., and D. Waugh, JAOCS *32*, 37 (1955).
5. Hoerr, C. W., JAOCS *32*, 659 (1955).
6. Hoerr, C. W., and A. A. Kiess, The Baking Characteristics of Rearranged Lard, Proc. 8th Res. Conf. Amer. Meat Inst., 1956.
7. Hoerr, C. W., JAOCS *37*, 539 (1960).
8. Hoerr, C. W., and F. R. Paulicka, "Crystal Structure of Triglycerides," Clark's Encyclopedia of X-rays and Gamma Rays, Reinhold Publishing Corporation, New York, 1963.
9. Hoerr, C. W., JAOCS *41*, 4 (1964).
10. Hoerr, C. W., and J. V. Ziemba, Food Engineering *37*, 90 (1965).
11. Hoerr, C. W., J. Moncrieff, and F. R. Paulicka, Bakers Digest *40*, 38 (1966).
12. Luck, J. V., Manufacturing Confectioner *42*, 29 (1962).
13. Lutton, E. S., J. Soc. Cosmetic Chemists *6*, 26 (1955).
14. Malkin, T., Glyceride Polymorphism, "Progress in the Chemistry of Fats and Other Lipids," Vol. II, Academic Press Inc., New York, 1954.

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• *Industry Items*

Cargill engineers are putting the finishing touches on a new soybean processing plant in Gainesville, Ga. Phillip St. Clair, Cargill manager in Gainesville, said the new facility will process its first soybeans by May 1. Capacity of the plant is 10 million bushels of beans the first year, an amount greater than the total soybean production of the state last year, but less than one third of its annual consumption. Ultimate crushing potential of the new plant is 15 million bushels per year.

DESOTO CHEMICAL COATINGS new 70,000 square foot laboratory is scheduled for completion this month, according to an announcement by company president S. U. Greenberg (1943). The laboratory will engage in its own product research and development, as well as coordinate research being done in the 16 plants comprising DeSoto's five divisions. Under construction concurrently is an addition designed to double the firm's 35,000 square foot administrative headquarters. DeSoto's present administrative center, also located in Des Plaines, Illinois, was opened three years ago.

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aromatic acid and about 0.5 to 3.0 mole equivalents of C_{10} to C_{30} fatty acid per mole equivalent of aromatic acid.

SURFACTANT MIXTURES. G. L. Broussalian (Monsanto Co.). *U.S. 3,303,137.* A detergent mixture is claimed, comprising a mixture of (a) from 40 to 98% by wt. of a vicinal acylamido sulfonate having the formula (I):

$R''—CO—NH—C(R)H—C(SO_3M)H—R'$ where R and R′ are either alkyl radicals or hydrogen, the total number of C atoms in R plus R′ being 8 to 22; M is an alkali metal, alkaline earth metal or ammonium cation; R″ is an alkyl radical containing 1 to 6 C atoms; (b) from 1 to 30% by wt. of a beta-hydroxy sulfonate having the formula: $RCHOH—C(SO_3M)H—R'$ with R, R′ and M having the same meaning as in formula (I); and (c) from 0.5 to 30% by wt. of a beta-ethylenically unsaturated sulfonate having the formula: $RCH{=}CH—C(SO_3M)H—R'$, where M has the same meaning as in formula (I) and R and R′ are either alkyl radicals or hydrogen, the total number of C atoms in R plus R′ being 7 to 21.

TRIETHANOLAMINE STRAIGHT CHAIN SECONDARY ALKYLBENZENE SULFONATE LIQUID DETERGENT COMPOSITIONS CONTAINING DEGELLING AGENTS. W. J. DeWitt and R. C. Taylor (Atlantic Refining Co.). *U.S. 3,303,138.* A non-gelling aqueous solution is described, consisting essentially of 40 to 70% by wt. of triethanolamine straight chain secondary alkylbenzene sulfonates having a straight alkyl side chain length of 9 to 15 C atoms and an organic degelling compound in amounts at least sufficient to prevent the gelling of the sulfonates in aqueous solution. The degelling compounds are selected from the group consisting of glycols, polyglycols, hydroxy diamines, N-alkyl substituted *beta*-amino propionic acids and their salts and derivatives of cycloimidine.

BIODEGRADABLE SURFACTANTS. E. K. Jones (Universal Oil Products Co.). *U.S. 3,303,233.* A process is described for the preparation of an olefinic alkylating agent for use in the production of a biologically soft alkylaryl detergent product. A straight chain paraffin is separated from a paraffinic naphtha boiling in the range 125–250C, where it is contained in admixture with branched isomers. The straight chain paraffin thus separated is then converted to a monoolefin derivative of straight chain structure by a series of steps comprising monohalogenating the paraffin at a temperature from 0 to 400C and dehydrohalogenating the halogenated paraffin at a temperature from 50 to 400C.

CLEANSING COMPOSITION AND METHOD OF MANUFACTURE THEREOF. G. G. Corey (Colgate-Palmolive Co.). *U.S. 3,304,262.* A stable gelated oil-in-water emulsion cleansing composition consists essentially of (by weight of the composition) 20–50% odorless mineral spirits, 40–60% water, 5–15% of a condensate of an aliphatic alcohol with 4–12 mols of ethylene oxide, the aliphatic alcohol containing 12 to 20C atoms, from 0.1 to 10% of a hydrophobic-hydrophilic polyoxyalkylene polyoxypropylene glycol of the formula $HO(C_2H_4O)_m(C_3H_6O)_n(C_2H_4O)_mH$, where n and m are numbers such that the molecular weight of $(C_3H_6O)_n$ is between 1750 and 3500 and that $(C_2H_4O)_m$ equals 20–50% of the total weight of the compound, and about 3 to 14% of higher fatty acid, sufficient to gel the ingredients into a stable oil-in-water emulsion having a pH between 7 and 9.

PHOSPHINE OXIDE DETERGENT COMPOSITION. J. T. Yoke III and R. G. Laughlin (Procter & Gamble Co.). *U.S. 3,304,263.* A detergent composition is claimed, consisting essentially of a tertiary phosphine oxide detergent compound having the formula $RR'R''P \rightarrow O$, where R is an alkyl, alkenyl or monohydroxyalkyl radical with from 10 to 18C atoms and R′ and R″ are each selected from the group consisting of alkyl and monohydroxyalkyl radicals containing from 1 to 3C atoms. In addition to the phosphine oxide detergent compound, the detergent composition contains a material selected from the group consisting of anionic detergents, nonionic detergents, water-soluble inorganic builders, and organic alkaline sequestrant builders, the ratio of the phosphine oxide compound to the other material ranging from about 4:1 to about 1:20.

TERTIARY PHOSPHINE OXIDE COMPOUNDS. J. T. Yoke III and R. G. Laughlin (Procter & Gamble Co.). *U.S. 3,304,330.* Tertiary phosphine oxide compounds having the formula $RR'R''P \rightarrow O$ are claimed, where R is an alkyl or monohydroxyalkyl radical with from 10 to 18C atoms, R′ and R″ are selected from the group consisting of alkyl and monohydroxyalkyl radicals containing from 1 to 3C atoms.

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