Part IV

Fats in Food
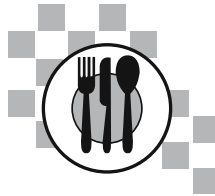
Fat and Oil Products

Introduction

Fat is a principal component of the diet. It is enjoyed in the diet due to such characteristics as its *flavor/mouthfeel*, *palatability*, *texture*, and *aroma*. Fats also carry *the fat-soluble vitamins* A, D, E, and K. Sources of fats and oils may be animal, vegetable, or marine that may be manufactured in some combination in industrial processing. *Fats* appear solid at room temperature, whereas *oils* are liquid at room temperature.

Several fats are essential, such as linolenic and linoleic fatty acids, indicating that the body *can either not* make them or make *enough*. Fats and oils are *insoluble* in water and have a greasy feel that the consumer may feel or see evidence of on a napkin or dinner plate. Fats may be *processed* into monoglycerides and diglycerides—glycerol units that have one or two fatty acid chains, respectively—and they may be *added* to many food products functioning as emulsifiers and more.

> Some of the functions of fat in food preparation are as follows:
> - Add or modify flavor, texture
> - Aerate (leaven) batters and doughs
> - Contribute flakiness
> - Contribute tenderness
> - Emulsify (see Chap. 13)
> - Transfer heat, such as in frying
> - Prevent sticking
> - Provide satiety

Edible oils are used in margarines, spreads, and dressings, as retail bottled oils, as frying oils, and more. Soybean oil is currently the highest volume vegetable oil used in the United States. It is incorporated into a variety of products.

Various fat replacements attempt to mimic fat in mouthfeel and perception so that it is good tasting and low-fat. With the use of fat replacements, the caloric and cholesterol level may be made significantly less than a fat. Fats and oils are in many food groups, yet, they are not part of the composition of fruits and many vegetables.
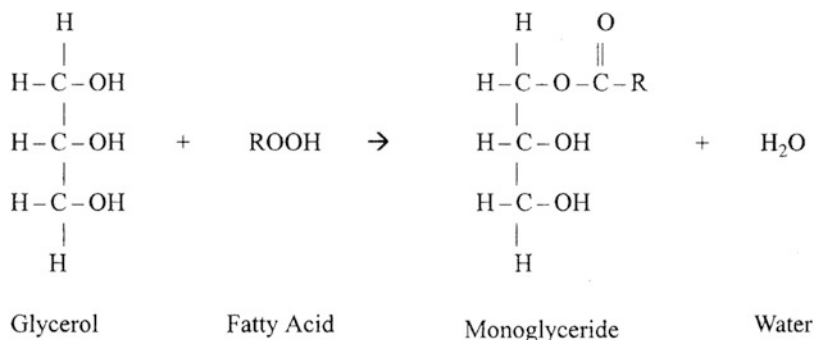
Most current health recommendations state that, as a group, fats and oils should be used sparingly in the diet. Fats and oils are triglycerides, the major constituent of lipids. Overall, lipid is the umbrella term that includes the triglycerides, phospholipids, and sterols.

Structure and Composition of Fats

Glycerides

Glycerides include *mono*glycerides (Fig. 12.1), *di*glycerides, and *tri*glycerides. The first two act

Fig. 12.1 Formation of a monoglyceride

$$
\begin{array}{c}
\mathrm{H} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{H}
\end{array}
\quad + \quad \mathrm{ROOH} \quad \rightarrow \quad
\begin{array}{c}
\mathrm{H} \qquad \mathrm{O} \\
| \qquad \parallel \\
\mathrm{H-C-O-C-R} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{H-C-OH} \\
| \\
\mathrm{H}
\end{array}
\quad + \quad \mathrm{H_2O}
$$

Glycerol   Fatty Acid   Monoglyceride   Water

as emulsifiers in foods, while the most abundant fatty substance in food—more than 95 %—is the latter, triglycerides. Triglycerides are insoluble in water and may be either liquid or solid at room temperature, with liquid forms generally referred to as oils and solid forms as fats.

If two fatty acids are esterified to glycerol, a diglyceride is formed, and three fatty acids undergoing the same reaction make a triglyceride. If a triglyceride contains three identical fatty acids, it is called a *simple* triglyceride; if it contains two or three different fatty acids, it is called a *mixed* triglyceride. Spatially, there is no room for all three fatty acids to exist on the same side of the glycerol molecule; thus, triglycerides are thought to exist in either a stair-step (chair) or a tuning-fork arrangement (Fig. 12.2). The arrangement and specific type of fatty acids on the glycerol determine the chemical and physical properties of a fat.

Minor Components of Fats and Oils

In addition to glycerides and free fatty acids, a lipid may contain small amounts of phospholipids, sterols, tocopherols, fat-soluble vitamins, and some pigments. Each is discussed, if only briefly, in this section of the text.

Phospholipids are similar to triglycerides but contain only *two* fatty acids esterified to glycerol. In place of the third fatty acid, there is a polar group containing phosphoric acid and a nitrogen-containing group; the most common phospholipid is *lecithin* (Fig. 12.3, and for more, see the chart at the closing of the chapter). Lecithin is

found in nearly every living cell. The word is derived from the Greek *lekithos* that means "yolk of an egg," and lecithin is in egg yolk. However, the primary *commercial* source of lecithin is the soybean (Central Soya Company, Inc., Ft. Wayne, IN). Sunflower lecithin is also commercially available.

The two fatty acids of a phospholipid are attracted to fat, whereas the phosphorus and nitrogen portions are attracted to water. Therefore, a phospholipid forms a bridge between fat and water, two ordinarily *immiscible* substances, and thus, *emulsification* is observed (see section "Emulsification," Chap. 13). "Refined" lecithins are modified to provide important surface-active properties to a variety of foods such as instant drink mixes, infant formulas, meat sauces and gravies, dispersible oleoresins, pan releases, chewing gum, and fat-replacer systems (Central Soya Company, Inc., Ft. Wayne, IN).

Lecithins are significant in the food industry, and they are available in numerous forms—the standard fluid, a modified chemical lecithin, a modified enzymatic lecithin, and a deoiled or powdered form. There exist two lecithin properties of significance—acetone insolubles (AI) and hydrophilic/lipophilic balance (HLB). The AI for a standard fluid lecithin is 62–64 %; deoiled lecithin has a minimum of 97 % AI. The HLB value for a standard fluid lecithin is 2–4; deoiled lecithin has a 7–10 HLB. HLB values are indicative of the size and strength of the groups on the lecithin emulsifier. See Table 12.1.

The presence of lecithin promotes a more stable formation of oil-in-water and water-in-oil emulsions (see more in Seabolt 2013).

Fig. 12.2 Fatty acid
tuning-fork (*left*) and stair-
step or chair arrangements
(*right*)
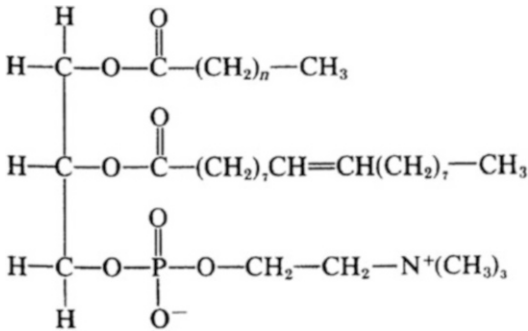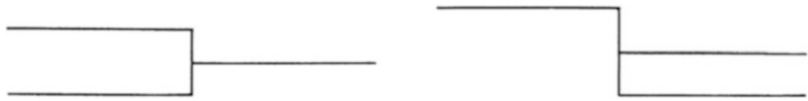
Fig. 12.3 Lecithin (phosphatidylcholine)

Sterols contain a common steroid nucleus, an
8–10 carbon side chain and an alcohol group. The
chemists' view of sterols is *unlike* triglycerides or
phospholipids—sterols are round in shape. Cho-
lesterol is the primary *animal sterol* (Fig. 12.4)
although *plant sterols* or stanols also exist; the
most common ones are sitosterol and stigmas-
terol. Other plant sterols are found in "marga-
rine"-type products, including those marketed
under the trade name Benecol®.

Tocopherols are important minor constituents
of most *vegetable oils*; *animal fats* contain *little
or no* tocopherols. Tocopherols are antioxidants,
helping to prevent oxidative rancidity, and are
also sources of vitamin E. They are *partially
removed* by the heat of processing and may be
added after processing to improve oxidative sta-
bility of oils. If vitamin E is added to oil, for
example, the oil is frequently marketed as a
source of vitamin E, or as an antioxidant-
containing oil.

Vitamins soluble in fat can be carried by fat.
The fat-soluble vitamins A, D, E, and K, and if
not in a food naturally, or at significant levels,
may be added to foods—such as margarine and
milk or a wide variety of other foods—in order to
increase nutritive value. Fats in the diet promote
the absorption of these fat-soluble vitamins.

Pigments such as carotenoids and chlorophylls
may be present in fats, and these may impart a
distinct color to a fat. Such colors may be removed
by bleaching during processing (e.g., milk).

Structure of Fatty Acids

Fatty acids are long hydrocarbon chains, with a
methyl group (CH_3) at one end of the chain and a
carboxylic acid group (COOH) at the other. Most
natural fatty acids contain from 4 to 24 carbon
atoms, and most contain an *even* number of carbon
atoms in the chain. For example, butyric acid is
the smallest fatty acid, having four carbon atoms,
and it is found in butter; lard and tallow contain
fatty acids with longer hydrocarbon chains.

Fatty acids may be *saturated*, in which case
they contain single carbon-to-carbon bonds and
have the general formula $CH_3(CH_2)_nCOOH$.
They have a linear shape, as shown in Fig. 12.5,
and appear solid at room temperature with a high
melting point. Fatty acids may be *unsaturated*,
containing one or more carbon-to-carbon double
bonds. *Monounsaturated* fatty acids, such as oleic
acid, contain only one double bond, whereas
polyunsaturated fatty acids (PUFAs), such as
linoleic and linolenic acids, contain two or more
double bonds. Generally, *unsaturated* fats are
*liquid* at room temperature and have low melting
points.

The double bonds in fatty acids occur in either
the *cis* or the *trans* configuration (Fig. 12.6),
representing different isomeric structures. In the
cis form, the hydrogen atoms attached to the
carbon atoms of the double bond are located on
the *same* side of the double bond. In the ***trans***
configuration of the isomer, the hydrogen atoms
are located on *opposite* sides of the double bond,
across from one another.

This *configuration* of the double bonds affects
both melting point and shape of a fatty acid
molecule. The *trans* double bonds have a *higher*
melting point than the *cis* configurations, and
trans configurations do *not* significantly change

Table 12.1 Lecithin

Lecithin properties
Emulsification; capacity to prevent sticking; improve wettability and dispersibility of powders; in every cell, not strictly plants
Benefits
Provides a "clean" label; dough improvements; anti-staling
Composition—amounts and ratios vary with the plant
Phospholipids—acetone insoluble, glycolipids, neutral lipids, and sugar

PC phosphatidylcholine, *PE* phosphatidylethanolamine, *PI* phosphatidylinositol, *PA* phosphatidic acid
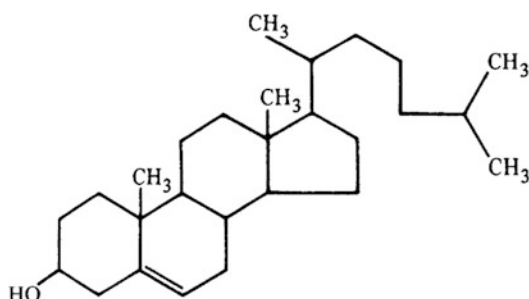
Fig. 12.4 Cholesterol, phytosterols

the linear shape of the molecule. However, a *cis* double bond causes a *kink* in the chain. (A *cis* double bond introduces a bend of about 42° into the linear hydrocarbon chain.) Such kinks affect some of the properties of fatty acids, including their melting points as was mentioned.

Almost all naturally occurring fats and oils that are used in food exist in the *cis* configuration. (Vaccenic acid [11-octadecenoic acid] is a naturally occurring *trans*-fatty acid found in small amounts in the fat of ruminants and in dairy products such as milk, butter, and yogurt. In fact, the name is derived from the word vacca, which is the Latin word for cow. Vaccenic acid comprises about 2.7 % of the fatty acids of milk (MacGibbon and Taylor 2006). *Trans* isomers of conjugated linoleic acid may also occur in trace amounts in these sources; they are synthesized from vaccenic acid by bacteria in the gut.)

In the process of *hydrogenation* of oils, a conversion of some double bonds to the *trans* configuration may be the result in foods (see *trans* fat). The National Cholesterol Education Program (NCEP) has stated that "*trans* fatty acids are another LDL-raising fat that should be kept to a

low intake." Specific labeling that includes *trans*-fatty acid content had been desired by some nutrition activists (Huffman 2001, Federation of American Societies for Experimental Biology (FASEB), Bethesda, MD). Effective January 2006, it became law that Nutrition Facts food labels and advertisements must *include* data on *trans*-fatty acids in foods.

As a result of this legislation, some food manufacturing companies made an early decision to simply not use *trans* fats in their products. Food manufacturers may only be required to list *trans* fats if they total more than 0.49 g per serving. Thus, some food content modification may have been necessary for better labeling. The last 15 years have seen a lot of developments in the industry in terms of *trans*-fat-free oils and fats for multiple uses: frying, fillings, and so forth.

Isomerism

Fatty acids may have geometric or positional *isomers*, which may be *similar* in number of C, H, and O, but which form *different* arrangements, thus offering different chemical and physical properties. Oleic and elaidic acids are examples of *geometric* isomers, existing in the *cis* and *trans* forms, respectively. *Positional* isomers have the same chemical formula; however, the *position* of the double bonds varies. Examples include alpha-linolenic acid, which has double bonds at carbons 9, 12, and 15, counting from the acid end of the chain, and the rare isomer gamma-linolenic acid, which has double bonds at positions 6, 9, and 12.

Fig. 12.5 Example of a fatty acid
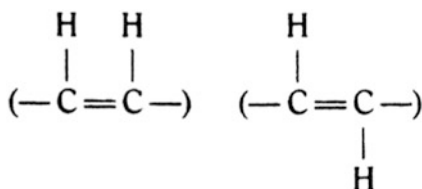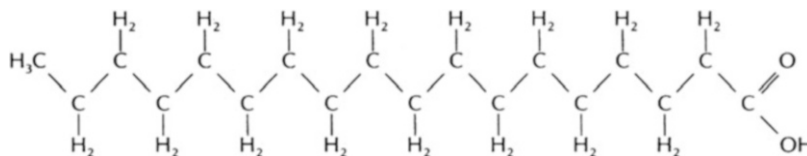
Fig. 12.6 *Cis* (*left*) and *trans* (*right*) configurations representing isomeric structures of fatty acids

Commercial *modification* of fats may produce *either* geometric or positional isomers. Geometric isomers tend to be produced during hydrogenation of fats, and positional isomers may be formed during interesterification or rearrangement of fats.

Nomenclature of Fatty Acids

Fatty acids are named in three ways: (1) each has a *common* or *trivial* name, which has been used for many years, and they also have (2) a *systematic* or *Geneva* name, which is more recent and has the advantage of describing the structure of the fatty acid to which it belongs. In addition, there is (3) the *omega* system, which classifies fatty acids according to the position of the first double bond, counting from the methyl end of the molecule. This system was developed to classify families of fatty acids that can be synthesized from each other in the body. Examples of all three names for some of the most common fatty acids are given in Table 12.2.

Fatty acids are also denoted by two numbers, the first signifying the number of carbon atoms in the chain and the second indicating the number of double bonds present. For example, oleic acid, which contains 18 carbon atoms and one double bond, could be written as 18:1 (Table 12.2).

Geneva or Systematic Nomenclature

The Geneva naming system is a systematic method of naming the fatty acids, and each name completely describes the structure of the fatty acid to which it belongs. Each unsaturated fatty acid is named according to the number of carbon atoms in the chain, as shown in Table 12.1. For example, stearic acid, which has 18 carbon atoms in its chain, has the name octadecanoic acid; **octadec** means 18. The *oic* ending signifies that there is an acid group (COOH) present, and **anoic** signifies that there are no double bonds in the chain. Palmitic acid, which contains 16 carbon atoms, is named hexadecanoic acid. **Hexadec** means 16, and the **anoic** ending again shows that there are no double bonds in this fatty acid chain (the **oic** equals presence of an acid group).

Fatty acids that contain double bonds are also named according to the number of carbon atoms they contain. Therefore, oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3) all have **octadec** as part of their name, signifying that they each contain 18 carbon atoms. The rest of the name differs, however, because they contain one, two, or three double bonds, respectively. The number of double bonds and their position in the fatty acid chain are both specified in the name.

It is important to note that the position of each double bond is specified counting from the functional group or **acid end** of the molecule, *not* from the methyl end. Thus, oleic acid has the name 9-octadecenoic acid. The number 9 refers to the position of the double bond between carbon-9 and carbon-10, counting from the acid end. Note that the name ends with **enoic** acid, the **en** signifying that there is a double bond present.

Linoleic acid is named 9,12-*octadecadienoic* acid. Again, the position of double bonds is specified, counting from the acid end. **Octadeca** means that there are 18 carbon atoms in the

Table 12.2 Nomenclature of some common fatty acids

Systematic name	Common name	Carbons: double bonds	Melting point °F (°C)
Ethanoic	Acetic	2	
Butanoic	Butyric	4	18 (−7.9)
Hexanoic	Caproic	6	26 (−3.4)
Octanoic	Caprylic	8	62 (16.7)
Decanoic	Capric	10	89 (31.6)
Dodecanoic	Lauric	12	112 (44.2)
Tetradecanoic	Myristic	14	130 (54.4)
Hexadecanoic	Palmitic	16	145 (62.9)
Octadecanoic	Stearic	18	157 (69.6)
Eicosanoic	Arachidic	20	168 (75.4)
Docosanoic	Behenic	22	176 (80.0)
9-Octadecenoic	Oleic	18:1	61 (16.3)
9-Octadecenoic[a]	Elaidic	18:1	110.7 (43.7)
11-Octadecenoic[a]	Vaccenic	18:1	111.2 (44)
9,12-Octadecadienoic	Linoleic/omega-6	18:2	20 (−6.5)
9,12,15-Octadecatrienoic	Linolenic/omega-3	18:3	9 (−12.8)

Source: Adapted from Institute of Shortening and Edible Oils (Decker 2012)
[a]All double bonds are in the *cis* configuration except for elaidic acid and vaccenic acid, which are in the *trans* configuration. Vaccenic occurs naturally; elaidic is produced by hydrogenation

chain, and **dien** signifies that there are two double bonds in the chain. Similarly, linolenic acid, which contains three double bonds, is named 9,12,15-*octadecatrienoic* acid. The letters **trien** indicate that there are three double bonds in the chain, and again their positions are specified counting from the acid end of the molecule.

The configuration of the double bonds may also be specified in the name. For example, oleic acid and elaidic acid are geometric isomers, because the double bond in oleic acid exists in the *cis* configuration, whereas elaidic acid contains a double bond in the *trans* configuration. The complete name for oleic acid is ***cis*, 9-octadecenoic acid**, and elaidic acid is named ***trans*, 9-octadecenoic acid**.

By looking at a systematic name for a fatty acid, it is possible to tell how many carbon atoms it contains, and how many double bonds and where they are located. Each name gives important information about the fatty acid that is not available just by looking at the trivial or omega name of the acid.

The Omega Naming System

The omega naming system is used for unsaturated fatty acids and denotes the position of the first double bond in the molecule, counting from the **methyl** (CH_3) end, not the acid (as in the Geneva system). This is because the body lengthens fatty acid chains by adding carbons at the acid end of the chain. Using the omega system, a family of fatty acids can be developed which can be made from each other in the body. For example, an omega-6 fatty acid contains its first double bond between carbon-6 and carbon-7, counting from the methyl end. Linoleic acid is an example of an omega-6 fatty acid, and it is the primary member of the omega-6 family. Given linoleic acid, the body can add two carbon atoms to make arachidonic acid (20:4), which is also an omega-6 fatty acid.

The primary omega-3 fatty acid is linolenic acid, which contains three double bonds. The first double bond is located on carbon-3, counting from the methyl end. The body can synthesize

both eicosapentaenoic acid (EPA: 20:5) and docosahexaenoic acid (DHA: 22:6) from linolenic acid. Both EPA and DHA are omega-3 fatty acids, because their first double bond is located at carbon-3 (again, counting from the methyl end of the molecule).

Properties of Fats and Oils

Crystal formation: When liquid fat is cooled, the molecular movement slows down as energy is removed, and the molecules are attracted to each other by van der Waals forces. These forces are weak and of minor significance in small molecules. However, their effect is cumulative, and in large or long-chain molecules, the total attractive force is appreciable. Consequently, fat molecules can align and bond to form crystals.

Symmetrical molecules and molecules with fatty acids that are similar in chain length align most easily to form crystals. Fats containing *asymmetrical* molecules and molecules containing kinks due to double bonds align less easily, because they cannot pack together closely in space. Molecules that align easily need less energy to be removed before they will crystallize, and so they have high melting points. They also tend to form *large* crystals. Molecules that do not align easily have low melting points, because more energy must be removed before they crystallize and they tend to form *small* crystals.

Polymorphism

Fats can exist in different crystalline forms, and this phenomenon is known as ***polymorphism***. A fat may crystallize in one of four different crystal forms, depending on the conditions during crystallization and on the composition of the fat. The smallest and least stable crystals are called **alpha** (α) **crystals**. These are formed if fats are chilled rapidly. The alpha crystals of most fats are unstable and change readily to **beta prime** (β′) **crystals**. These are small needlelike crystals, approximately 1 μm long. Fats that can form

stable β-crystals are good for use as shortenings, as they can be creamed easily, and give a smooth texture. Unstable β′-crystals change to the **intermediate crystal** form, about 3–5 μm in size, and finally convert to **coarse beta** (β) **crystals**, which can range from 25 to 100 μm in length. Beta crystals have the highest melting point.

Formation of small crystals is favored by rapid cooling with agitation. This allows formation of many small crystals, instead of slow growth of fewer large crystals. (Smaller crystals are desirable if a fat contributes aeration to a food.) Growth of large crystals occurs if cooling is slow. (The reader may want to read more about fat polymorphism and its effects on chocolate bloom.)

The more heterogeneous the fat, the more likely that the molecules form small stable crystals. Homogeneous fats readily form large crystals. Lard is an example of a homogeneous fat; more than 25 % of the molecules contain stearic acid, palmitic acid, and one unsaturated fatty acid molecule (usually oleic acid). Therefore, lard exists in the coarse *beta* crystalline form. However, lard can be modified by interesterification, which causes the fatty acids to migrate and recombine with glycerol in a more random manner.

Rearranged lard forms stable β′-crystals, because it is more heterogeneous. Acetoglycerides are able to form stable α-crystals, because they contain acetic acid esterified to glycerol, in place of one or two fatty acids. This increases the heterogeneity of the fatty acid composition of each individual triglyceride, which hinders the formation of large crystals.

All other things being equal, a fat with small crystals contains many more crystals and a much greater total crystal surface area than does a fat containing large crystals. Fats with small crystals are harder fats, have a smooth, fine texture, and appear to be less oily because the oil is present as a fine film surrounding the crystals, whereas the reverse is true of fats with large crystals.

The food industry uses controlled polymorphism to obtain fats with crystal sizes that improve their functional properties in foods.

For example, fats used for creaming must contain small, stable crystals in the β′ form; thus, crystallization is controlled during the manufacturing process.

Melting Points

The melting point of a fat or oil is an index of the force of attraction between molecules. The greater the attractive forces between molecules, the more easily they will associate to form a solid, and the harder it is to separate them when they are in the crystalline form and convert them to a liquid. A lot of energy in the form of heat must be put in to convert a solid to a liquid; thus, the melting point will be high. In other words, a high melting point indicates a strong attractive force between molecules. A strong attractive force indicates a good degree of fit between the molecules. Molecules that do not fit together well do not have strong attractive forces holding them together, and so they have lower melting points.

A fat or oil, which is a mixture of several triglycerides, has a lower melting point and a broader melting range than would be expected based on the melting points of the individual components. However, the *melting range* is dependent on the fatty acids of the component triglycerides. Fats may also be plastic at room temperature, containing some triglycerides that are liquid and some that are solid.

Generally speaking, oils, which are liquid at room temperature, tend to be more unsaturated, have shorter chains, and have lower melting points than fats, which are plastic or solid, with long chains and high melting points at room temperature. (See Table 12.1 for melting points of several fatty acids.) However, this is not the case always, as illustrated by coconut oil (see Tropical Oils), which has a high level of saturates (90 %), with a low *melting range* [75–80 °F (24–27 °C)]. It is liquid at room temperature because it contains an appreciable number of relatively short-chain (12 carbons) fatty acids, as is the case with palm and palm kernel oils. Lard, on the other hand, contains only about 37 % saturates, with mostly long-chain fatty acids, and so it is semisolid at 80 °F (27 °C).

As mentioned, the melting point of a fat or oil is actually a range, not a sharply defined temperature. The melting range depends on the composition of the fat. Each fat or oil contains triglycerides that melt at different temperatures, depending on their component fatty acids. Some fats have a wide melting range, whereas others, such as butter or chocolate, have a narrow melting range. Chocolate has a narrow melting range that is close to body temperature, and this accounts for its characteristic melt-in-your-mouth property.

The melting points of individual fatty acids depend on such factors as *chain length*, *number of double bonds* (degree of saturation), and *isomeric configuration*, because all these factors affect the degree of fit and the force of attraction between fatty acid molecules.

Chain length: *Long-chain* fatty acids have a higher melting point than *short-chain* fatty acids, because there is more potential for attraction between long chains than there is between short chains. The attractive forces are cumulative and can be appreciable if the chain is long enough. (In other words, you can think of them as having a zipper effect. A long zipper is much stronger than a short one, because more teeth are intersecting with each other.) For example, butyric acid (4:0) has a melting point of 18 °F (−7.9 °C), whereas stearic acid (18:0) has a higher melting point of 157 °F (69.6 °C). Stearic acid is a crystalline solid at room temperature, whereas butyric acid is a liquid unless the temperature drops below the freezing point of water.

Number of double bonds: A second factor that determines melting point is the *number of double bonds*. As the number of double bonds *increases*, the melting point *decreases*. Double bonds introduce kinks into the chain, and it is harder for molecules to fit together to form crystals; thus, the attractive forces between the molecules are weaker. This is demonstrated by comparing the melting points of stearic, oleic, linoleic, and linolenic acids, as shown in Table 12.1.

Isomeric configuration: A third influence on melting point is *isomeric configuration*. Geometric isomers have different melting points, because the *cis* double bond configuration introduces a much bigger kink into the molecule than does the *trans* configuration. Consequently, the *cis* isomer

has a lower melting point than the *trans* isomer, because molecules in the *cis* configuration do not fit together as well as molecules in the *trans* configuration. This can be seen by comparing the melting points of oleic and elaidic acids. Oleic acid (*cis*) has a lower melting point than elaidic acid (*trans*—*see* Table 12.1). Low-*trans* liquid shortening such as the high oleic, mono-unsaturated sunflower oil requires no *trans* or "hydrogenated" reporting on labels, because it has a level of less than 2 % *trans*-fatty acids. A standard shortening may contain more than 30 % *trans*-fat levels.

The melting point of a triglyceride depends on the melting point of the component *fatty acids* as discussed above. *Simple* triglycerides can fit together easily, because the three fatty acid chains are identical and therefore allow for close packing of the molecules and high melting points. In general, the more *heterogeneous* triglycerides will not fit together as well, and so will have lower melting points. The melting point of a fat increases with each shift in polymorphic form, from alpha to coarse beta crystals.

Plastic Fats

Fats may be either liquid, solid, or plastic at room temperature. A **plastic fat** is moldable because it contains both *liquid* oil and *solid* crystals of triglycerides. Its consistency depends on the *ratio* of solid to liquid triglycerides: the more *liquid* the triglycerides, the *softer* the fat will be, and the more *solid* the triglycerides, the *harder* it will be. A plastic fat is a two-phase system, containing solid fat crystals surrounded by liquid oil. The liquid phase acts as a lubricant, enabling the solid crystals to slide past one another, and thus conferring moldability to the fat. A fat that contains only solid triglycerides is hard and brittle and cannot be molded, because the crystals cannot move past each other.

CULINARY ALERT! Fats that are "creamed" as per a recipe set of instructions (for some cookies or shortened cakes) must be plastic, so that they are easily workable and incorporate air into a mixture without breaking.

Ideally, plastic fats should be semisolid or plastic over a *wide* temperature range, so that creaming can be carried out at different (high or low) temperatures. Fats with a wide plastic range contain some triglycerides that are *solid* at high temperatures and some triglycerides that are *liquid* at low temperatures.

Fats with a *wide* plastic range are obtained by commercial modification, including the processes of hydrogenation and interesterification. Examples of such fats include *partially hydrogenated* soybean oil (found in margarine) and *interesterified lard*. Shortenings that are to be creamed must also contain small crystals, preferably in the β′ form. Rearranged lard forms stable β′-crystals, and so has a fine-grained texture that is suitable for creamed fats.

Butter has a *narrow* plastic range and is, therefore, *not* a good choice for a fat that needs to be creamed. It cannot be creamed if taken straight out of the refrigerator, because it is too hard; neither can it be creamed if it sits on the counter on a warm day, because it will be too liquid.

Composition of Dietary Fats and Oils

A table showing fatty acid composition of various fats and oils frequently used by the consumer in food preparation is shown in Fig. 12.7. Time has shown variability as to which oil is best! The pendulum has swung from one product to another!

Polyunsaturated fats are liquid at room temperature and found primarily in *plants*. Safflower oil is 76 % polyunsaturated, sunflower oil is 71 %, soybean oil 54 %, and corn oil 57 % ("partially hydrogenated" oils are hydrogenated to have a *greater* degree of saturation).

Monounsaturated fats are liquid at room temperature and found chiefly in *plants*. Olive oil is 75 % monounsaturated, and canola (rapeseed oil) is 61 % monounsaturated. These fats are associated with a *decrease* in serum cholesterol and a decreased risk of coronary heart disease (CHD). There is not uniformity among researchers in suggesting that one of these fats is the best of all fats/oils to consume.

DIETARY FAT	Fatty acid content normalized to 100%			
	Saturated Fat	**Polyunsaturated**	**Alpha Linolenic**	**Monounsaturated Fat**
Canola oil	7%	21%	11%	61%
Safflower oil	10%	76%	Trace	14%
Sunflower oil	12%	71%	1%	16%
Corn oil	13%	57%	1%	29%
Olive oil	15%	9%	1%	75%
Soybean oil	15%	54%	8%	23%
Peanut oil	19%	33%	Trace	48%
Cottonseed oil	27%	54%	Trace	19%
Lard[*]	43%	9%	1%	47%
Beef tallow[*]	48%	2%	1%	49%
Palm oil	51%	10%	Trace	39%
Butterfat[*]	68%	3%	1%	28%
Coconut oil	91%	--	2%	7%

*Cholesterol content (mg/Tbsp): Lard 12; beef tallow 14; butterfat 33.
(No cholesterol in any vegetable-based oil.)

Alpha-Linolenic Acid (an Omega-3 Fatty Acid)

Source: POS Pilot Plant Corporation, Saskatoon, Saskatchewan, Canada June 1994

Canola Council of Canada, 400·167 Lombard Avenue, Winnipeg Manitoba Canada R3B OT6

Fig. 12.7 Comparison of composition of dietary fat (*Source*: Canola Council of Canada)

Saturated fats are solid at room temperature and found primarily in *animals*, although they are found in some tropical oils (see the listing below). These saturated fats are implicated in a *greater* rise in serum cholesterol than that produced by intake of dietary cholesterol!

Animal Fats
Animal fats typically have 18 carbons in the fatty acid chain. These long chains are made of various fatty acids and are chiefly *saturated*. Such fats may be *rendered* for use in baking and cooking applications (see section "Rendered Fat"). Animal fats derived from hogs and cattle include the following:

- **Lard**. Rendered from hogs, 43 % saturated fatty acids
- **Tallow** (**suet**). Rendered from cattle, 48 % saturated fatty acids

Tropical Oils
Oils derived from plants grown in tropical areas of the world are referred to as *tropical oil*. Unlike most plants, these in particular are high in saturated fat content and contain an appreciable amount of short-chain fatty acids. Examples of tropical oils include the following:

- **Cocoa butter**. Extracted from cocoa beans, typically used in candies and chocolate confections
- **Coconut oil**. Highest saturated fat vegetable oil—over 90 % saturated; very stable against oxidation and, to a lesser degree, stable against hydrolysis
- **Palm oil**. 50 % saturated fatty acids; stable against oxidation
- **Palm kernel oil**. 84 % saturated fatty acids; derived from the kernel of the palm tree; stable against oxidation

CULINARY ALERT! In part due to the fact that animal fats contain cholesterol, saturated fat, and a pronounced flavor, the use of animal fat such as lard and tallow in foods has declined in favor of vegetable oils.

Production and Processing Methods

Crops are bred to increase the grower's yield while offering health benefits to *consumers* who want desirable health features in fats and oils. Both groups—growers and consumers—desire shelf stability. A brief discussion of the *conventional* as well as *nonconventional* approaches to breeding appears in the following text. Techniques are provided by the molecular geneticist and are available to growers and oilseed processors so that suppliers of edible oils can make both shelf stability *and* consumer health their priorities.

For example, *ordinary* soybean oil is *not* shelf stable because it contains 7.6 % linolenic acid, an unstable, 18-3, PUFA. To improve on this, *conventional* cross-breeding and selection has developed a low-linolenic soybean oil (LLSO), containing 2.5–3 % linolenic content This lower-linolenic soybean oil, derived from selected soybeans, is more stable than ordinary soybean oil and does not require hydrogenation for protection against rancidity. Consumers who want *less* saturated fat may make this oil their choice.

Unconventional approaches to breeding include gene modification, which produces a more stable oil that does not require hydrogenation. Then, stability as well as lower saturated fat may be achieved in a product. So, either conventional cross-breeding or unconventional genetic modification offers increased shelf stability without loss of health benefits, and this may be desirable.

Deodorized Oils

Deodorized oils are those that have undergone the process of removing odors by heat and vacuum or by adsorption onto charcoal. For example, olive oil may be deodorized to provide broader use in *baking* applications, without imparting its characteristic odor and flavor to food.

Rendered Fat

Rendered fat is the solid, usable fat derived from animal fat after it is heated and freed from connective tissue and then cooled. Food manufacturers render *hog* fat and process it to become *lard*, or *cattle* fat to become *tallow*. On a small scale, the consumer renders fat by (1) cutting animal fat into small pieces and gently boiling the pieces to extract liquid fat and then (2) cooling, until it becomes solid. The leftover rind, devoid of usable fat, has uses outside the scope of this discussion of fats.

In structure, the large crystalline structure of lard is composed of many similar triglycerides that are used to produce a highly desirable, flaky piecrust. Today, lard may be processed to contain smaller crystals, and then it functions more like a hydrogenated shortening. The addition of antioxidants such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) protects it against rancidity.

As previously mentioned, lard and tallow are not as commonly used in cooking as they were in the past, partially because of the pronounced flavor, saturated fat, and cholesterol content. As well, animals are now bred to be leaner, so lard is less available. Today, there are many convenient, commercially prepared shortenings on the market that replace lard in cooking.

Modification of Fats

Hydrogenation

Hydrogenation is the process of adding hydrogen to *un*saturated fatty acids to reduce the number of double bonds. The purpose of hydrogenation is twofold:

- To convert liquid oils to semisolid or plastic fats
- To increase the thermal and oxidative stability of the fat, and thus the shelf life

Hydrogenation of unsaturated fatty acid occurs when *hydrogen gas* is reacted with *oil* under controlled conditions of *temperature* and *pressure* and in the presence of a nickel, copper, or other *catalyst*. The reaction is carefully controlled and stopped when the desired extent of hydrogenation has been reached. As the reaction progresses, there is a gradual production of *trans*-fatty acids which increases the melting point of the fat or oil and creates a more solid product. *Solid* shortening is created out of a hydrogenated *oil*.

The extent of the hydrogenation process is carefully controlled to achieve stability and/or the physical properties required in the finished food product. If the reaction is taken to completion, a *saturated* fat is obtained, and the product is hard and brittle at room temperature. However, this is not usually the aim of hydrogenation, as *partial* hydrogenation is normally desired for foods, providing an *intermediate* degree of solidification, reducing the number, yet, while not eliminating all double bonds. In fact, approximately 50 % of the total fatty acids present in *partially hydrogenated vegetable shortening* products are *mono*unsaturated and about 25 % are *poly*unsaturated.

Polyunsaturated fats are subject to oxidative rancidity. Thus, reducing the number of double bonds by hydrogenation serves to increase their stability. Once saturated though, consumption of the fat contributes more toward the elevation of serum cholesterol than does dietary cholesterol intake. The process of hydrogenation causes conversion of some *cis* double bonds to the *trans* configuration. Most of the *trans*-fatty acids formed are monounsaturated. Tub margarines, for examples, typically contain *trans*-fatty acid at levels of 13–20 %.

A previous *Federation of American Societies for Experimental Biology* (*FASEB*) report

published in 1985 (Huffman 2001) concluded that there was little cause for concern with the safety of dietary *trans*-fatty acids, both at present and expected levels of consumption. However, this was challenged by later research.

"A small amount of *trans* fat is found naturally, primarily in dairy products, some meat, and other animal-based foods" (FDA). The majority is formed when manufacturers add hydrogen to turn liquid oils into partially/hydrogenated oils. Thus, *trans* fat *can* be found in hydrogenated vegetable shortenings, some margarines (not butter), crackers, snack items, and convenience fast food. The advice is to read labels.

Plastic fats have useful functional properties for use in margarines or shortenings that are to be creamed. Hydrogenated fats are frequently specified in batter and dough recipes that depend on the creaming ability of solid fats for aeration (Chap. 14). Creaming increases volume by incorporating air and results in numerous air cells. As a result, the grain of the crumb in baked products is small and even.

Interesterification

Interesterification, or **rearrangement**, causes the fatty acids to migrate and recombine with glycerol in a more random manner. This causes new glycerides to form and *increases* the *heterogeneity* of the fat. However, it does *not* change the degree of unsaturation or the isomeric state of the fatty acids.

Lard is an example of a fat that is modified in this way to improve its functional properties. In its natural state, lard is a relatively *homogeneous* fat, as has already been mentioned. Therefore, it has a *narrow* plastic range and is *too firm* to be used straight from the refrigerator and *too soft* at temperatures above normal room temperature. Lard also contains coarse β-crystals. Rearrangement increases the *heterogeneity* of lard, enabling it to form stable β′-crystals and *increasing* the temperature range over which it is plastic or workable. This significantly enhances its use as a shortening product.

Hydrogenation may be used in conjunction with interesterification and may either precede or follow it. This gives a shortening manufacturer the ability to produce fats with a *wide* range of properties.

Acetylation

Acetoglycerides or ***acetin fats*** are formed when one or two fatty acids in a triglyceride are replaced by acetic acid (CH_3COOH). Acetin fats may be liquid or plastic at room temperature depending on the component fatty acids. However, the presence of acetic acid lowers the melting point of the fat, because the molecules do not pack together as readily. It also enables the fat to form stable α-crystals.

Acetin fats are used as edible lubricants; they also form flexible films and are used as coating agents for selected foods such as dried raisins and produce to prevent moisture loss.

Winterization

Winterized oil is oil that has been *pretreated* to control undesirable cloudiness. The large, high-melting-point triglyceride crystals in oil are subject to crystallization (forming solids) at refrigeration temperatures. Therefore, in the process of winterization, oil is refrigerated and subsequently filtered to remove those large, undesirable crystals, which could readily disrupt a salad dressing emulsion. The treated oil is called *salad oil*, which is specially used in salad dressing.

CULINARY ALERT! *Salad oils* are clear and are bleached, deodorized, and refined, in addition to undergoing winterization. Salad oils differ from *cooking oils*, the latter of which do not undergo winterization.

Deterioration of Fats

Fats deteriorate either by absorbing odors or by becoming *rancid*. Both of these are described below. For example, deterioration by *absorbing odors* becomes evident when *chocolate fat* absorbs the odor of (1) smoke in a candy store environment or (2) soap packaged in the same grocery bag at the supermarket. Butter may also deteriorate by readily absorbing *refrigerator* odors. When *rancidity* causes deterioration, it produces a disagreeable odor and flavor in fatty substances.

CULINARY ALERT! Processing does not remove *all* chance of fat and oil deterioration and rancidity, but it prolongs the life of a fat or oil.

Deterioration by rancidity may occur in two ways (details below) making fats undesirable for use in foods. One way is ***hydrolytic rancidity*** which involves reaction of fats with water and liberation of free fatty acids. The other, ***oxidative rancidity***, is a more complex and potentially more damaging reaction. In this second case, the fat is oxidized and decomposes into compounds with shorter carbon chains such as fatty acids, aldehydes, and ketones all of which are volatile and contribute to the unpleasant odor of rancid fats.

Hydrolytic Rancidity

Fats may become rancid by hydrolytic rancidity when the triglycerides react with water and free their fatty acids from glycerol. The reaction is shown in Fig. 12.8. If one molecule of water reacts with a triglyceride, *one* fatty acid is liberated and a *di*glyceride remains. To liberate glycerol, *all three* fatty acids must be removed from the molecule. The reaction is catalyzed by heat and by enzymes known as lipases. Butter contains lipase, and if left on the kitchen counter on a warm day, a characteristic rancid smell frequently develops due to liberation of the short-chain butyric acid. (Unlike long-chain fatty acids, these short-chain fatty acids may form an unpleasant odor and flavor.)

Hydrolytic rancidity is also a problem with deep-fat frying, where the temperature is high

$$CH_2 - OOC - R \qquad\qquad CH_2 - OH$$
$$\begin{array}{ccc} | & & | \\ CH - OOC - R + 3H_2O & \longrightarrow & CH - OH + 3RCOOH \\ | & & | \\ CH_2 - OOC - R & & CH_2 - OH \end{array}$$

Fig. 12.8 Hydrolytic rancidity

and wet foods are often introduced into the hot fat. The continued use of rancid oil results in additional breakdown of the oil. To avoid this type of rancidity, fats should be stored in a cool place and, if possible, lipases should be inactivated.

CULINARY ALERT! Fats should be kept away from water, and foods to be fried should be as dry as possible before they are added to hot fat. The kind of fat used for frying should be selected based on stability.

Oxidative Rancidity or Autoxidation

Oxidative rancidity is the *predominant* type of rancidity. In this process, the unsaturated fatty acids are subjected to oxidative rancidity or autoxidation, and the *more* double bonds there are, the *greater* the opportunity for addition of oxygen to double bonds, increasing risk that the fat or oil will become rancid. *Autoxidation* is complex and is promoted by heat, light, certain metals (iron and copper), and enzymes known as lipoxygenases. The reaction can be separated into three stages: initiation, propagation, and termination.

The **initiation stage** of the reaction involves formation of a free radical. A hydrogen on a carbon atom adjacent to one carrying a double bond is displaced to give a free radical, as shown in Fig. 12.9. There is chemical activity around and in the double bonds. (The bold type indicates the atoms or groups of atoms involved in the reactions.) As previously mentioned, this reaction is catalyzed by heat, light, certain metals such as copper and iron, and lipoxygenases. The free radicals that form are unstable and very reactive.

The **propagation stage** follows the initiation stage and involves oxidation of the free radical to yield activated peroxide. This, in turn, displaces hydrogen from another unsaturated fatty acid,

forming another free radical. The liberated hydrogen unites with the peroxide to form a hydroperoxide, and the free radical can be oxidized as just described. Thus, the reaction repeats, or propagates, itself. Formation of one free radical, therefore, leads to the oxidation of many unsaturated fatty acids.

Hydroperoxides are very unstable and decompose into compounds with shorter carbon chains, such as volatile fatty acids, aldehydes, and ketones. These are responsible for the characteristic odor of rancid fats and oils. The two reactions of the propagation stage of autoxidation are shown in Fig. 12.10.

The **termination stage** of the reaction involves the reaction of free radicals to form nonradical products. Elimination of all free radicals is the only way to halt the oxidation reaction.
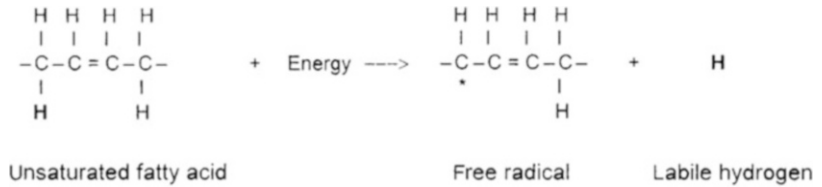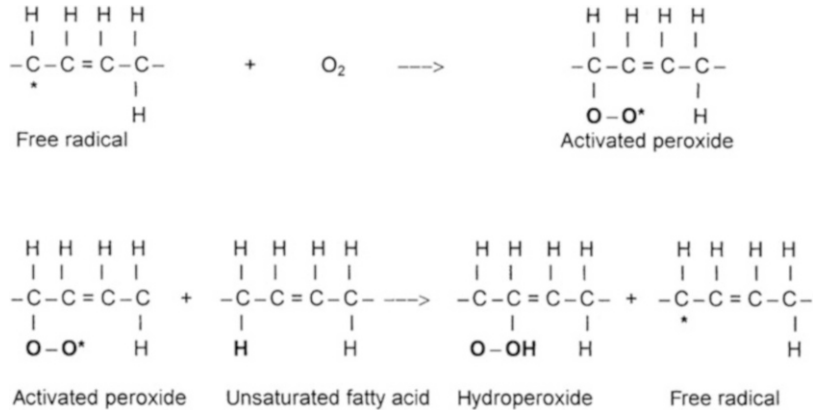
Prevention of Autoxidation

Oxidation can be prevented or delayed by *avoiding* situations that would serve as catalysts for the reaction. For example, fats and oils *must be stored* in a cool dark environment (offering temperature and light change controls) and in a closed container (to minimize oxygen availability). *Vacuum packaging* of fat-containing products controls oxygen exposure, and *colored glass* or wraps control fluctuations in light intensity. Fats must also be stored *away from metals* that could catalyze the reaction, and any cooking utensils used must be free of copper or iron. Lipoxygenases should be inactivated.

CULINARY ALERT! Store fats and oils in a cool dark environment and in a closed container. Colored glass jars or wraps control rancidity.

In addition, *sequestering agents* and *antioxidants* can be added to fats to prevent autoxidation, increasing keeping quality and shelf life of fats.

Sequestering agents bind metals, thus preventing them from catalyzing autoxidation. Examples of sequestering agents include EDTA (ethylenediaminetetraacetic acid) and citric acid.

Fig. 12.9 The initiation stage of autoxidation

Unsaturated fatty acid   Free radical   Labile hydrogen

Fig. 12.10 The two reactions of the propagation stage of autoxidation

Free radical   Activated peroxide

Activated peroxide   Unsaturated fatty acid   Hydroperoxide   Free radical

Antioxidants help prevent autoxidation with its formation of fatty acid free radicals. Antioxidants prevent rancidity by donating a hydrogen atom to the double bond in a fatty acid and preventing the oxidation of any unsaturated bond. They halt the chain reaction along the fatty acid, which leads to rancidity.

Most antioxidants are phenolic compounds. Those approved for use in foods include *BHA*, *BHT*, *TBHQ* (tertiary butylhydroquinone), and propyl gallate. These are *all synthetic* antioxidants. The effectiveness of antioxidants may be increased if they are used together. For example, propyl gallate and BHA are more effective when *combined* than if used separately.

BHA is a waxy white solid that survives processing to create a stable product. It is effective in preventing oxidation of *animal* fats yet *not vegetable* oils. BHT is a white crystalline solid that may be combined with BHA. It is effective in preventing oxidation of animal fats. TBHQ is a white-to-tan-colored powder that functions best in frying processes rather than baking applications.

Tocopherols are naturally occurring antioxidants that are present in vegetable oils. They can be added to both animal and vegetable oils to prevent oxidation. The tocopherols are also sources of essential nutrient vitamin E.

Use of antioxidants in foods containing fat increases their keeping quality and shelf life. Examination of food labels reveals that antioxidants are widely used in many food products, from potato chips to cereals. Without them, the quality of fat-containing foods would not be as good, and off-flavors and odors due to oxidative rancidity would be commonplace.

Shortening and Shortening Power of Various Fats and Oils

Plant, animal, or numerous plant–animal blends of fats and oils may be used for shortening, and, typically, the blend is creamy. The shortening potential of a fat or oil is influenced by its fatty acid composition (see Fig. 12.5), and various fats and oils may function as shortenings. "Shortenings" may include many types, from *pourable liquids to stiff solids*, with the latter being most commonly considered shortening. A shortening is hydrogenated oil and it functions to physically shorten platelets of protein–starch

structure developed in manipulated wheat flour mixtures.

Shortening power of some fats and oils appears below.

Lard has a large fatty acid crystal structure, unless it is interesterified. It forms a desirable flaky product. This solid fat when cut into pea-sized chunks or smaller melts within the gluten structure of flour, creating many layers or *flakes* in baked piecrusts or biscuits (more later).

Butter and margarine contain water and milk (20 %) in addition to a variety of fat or oils (80 %). One stick is derived from 2.5 quarts of milk. Due to this water, butter and margarine have less shortening potential than lard, hydrogenated shortening, or oil that contains 100 % fat. When butter or margarine is incorporated into flour-based formulations, they toughen the mixture, as its water component hydrates the starch.

CULINARY ALERT! A recipe substituting butter or margarine for lard or hydrogenated shortening adds water; thus, the recipe requires less additional water and yields a *less flaky* piecrust.

A replacement for butter originated in 1869 when margarine was formulated by a French pharmacist. Today, margarine may contain part cultured skim milk or whey, optional fat ingredient(s), emulsifier, and color (annatto or carotene) and may include added salt, flavoring, and vitamins A and D. The margarine is likely to be high in PUFAs, if oil is listed as the first ingredient on a margarine label. If *partially hydrogenated oil* is listed on a label as the first ingredient, there is less PUFA. A product must be labeled "spread" if it does not meet the Standard of Identity for margarine. Also, today, margarine *substitutes* may be milk-free, sodium-free, or even fat-free.

Hydrogenated fats are saturated and easily workable. When creamed, they incorporate air into a mixture. They are processed to be *without* a pronounced flavor and have a *wide* plastic range. Hydrogenated fats contain 100 % fat and have greater shortening power than butter or margarine. Finished food products may be *flaky*, however not as flaky as if lard is used.

Oils contain a *high* liquid-to-fat crystal ratio and are *un*saturated. They shorten strands of protein *mechanically* by coating the platelets. Oil controls gluten development and subsequent toughness because *less* water contacts the gluten proteins. Oil helps produce a *tender* product, but in pastries, *flakiness* may be sacrificed. Flakes are *not* readily obtained because there are no large chunks of fat to melt between layers of dough.

Tenderization Versus Flakiness Provided by Fats and Oils

Lipids provide either ***tenderization*** or ***flakiness***, as discussed, and impart distinct characteristics of a food product. The differences are especially evident in finished piecrusts and can also be observed in biscuits. *Tender* products are easily crushed or chewed; they are soft and fragile—i.e., oil piecrusts. *Flaky* products contain many thin pieces or layers of cooked dough, i.e., puff pastry and lard piecrusts.

Some factors that affect these two distinct attributes are presented in Table 12.3. The *type of fat or oil* chosen to be incorporated into food, its *concentration*, *degree of manipulation*, and *temperature* each affect the flakiness and tenderness of a product. Fats and oils should be selected and used with knowledge of these factors. Yet, health attributes of a fat or oil may supersede other quality attributes creating products that do not meet traditional product standards. For example, for health reasons, a piecrust may not incorporate solid fat but may be prepared using oil. If that is the case, the finished piecrust will sacrifice flakiness but will be tender and crumbly.

CULINARY ALERT! In order to control formation of an undesirable crumbly food product, some gluten formation may be needed *prior* to the addition of the fat or oil. This may be achieved by adding fat to a recipe, *after* some hydration and manipulation has formed gluten.

Table 12.3 Factors affecting the tenderness and flakiness of a product

The type of fat or oil—Chunks of *solid fat* create layers or flakes in the gluten starch mixture as they melt, whereas *oil* coats flour particles more thoroughly, *creating less layers* and a mealy product. Substituting one fat or oil for another may not produce acceptable or expected results

Fat concentration—Fat may be reduced or omitted in a formulation, or the fat that *is* used may not be 100 % fat; it may be a butter, margarine, or "spread." Adequate levels of fat or oil must be present in foods if they are to meet acceptable standards. For example, sufficient fat in flour-based mixtures is needed to control gluten development and generate a tender crumb. Imitation "butters" or "spreads" have a high water content and may not have the high percentage of fat needed to perform satisfactorily in all baking, sautéing, or "buttering" processes

Degree of manipulation—An insufficient degree of manipulation may result in poor distribution of fat throughout the food mixture. Inversely, excess manipulation may cause the fat to spread or be softened, thus minimizing the possibility of flakes. For example, a flaky piecrust is produced when solid fat is incorporated in the formulation as pea-sized chunks

Temperature—Depending on the type of fat, *cold* shortenings (solid or liquid) provide less covering potential than *room temperature* shortenings and produce more flaky biscuits and piecrusts. Food items prepared with cold shortenings also remain slightly more solid in the hot oven while the item bakes. When a shortening is *melted*, it displays a greater shortening potential than an *unmelted* solid shortening; it coats better than the same amount of unmelted solid fat. Melted shortening produces a more tender, less flaky product

Emulsification (See Chap. 13)

Fats and oils are *not* emulsifiers; however, in addition to providing flavor, aerating batters and doughs, and shortening, fats and oils are important *constituents* of emulsions. An emulsion consists of a three-phase system composed of (1) a **continuous phase**, the phase or medium in which the dispersed phase is suspended; (2) a **dispersed phase**, the phase which is disrupted or finely divided within the emulsion; and (3) an **emulsifier**, **which** is present at the interface between the dispersed phase and the continuous phase and keeps them apart. An emulsifier acts in the following ways:

- It adsorbs at the interface between two immiscible liquids such as oil and water.
- It reduces the interfacial tension between two liquids, enabling one liquid to spread more easily around the other.
- It forms a stable, coherent, viscoelastic interfacial film, which prevents or delays coalescence of the dispersed emulsion droplets.

Molecules that can act as emulsifiers contain both a polar, **hydrophilic** (water-loving) section, which is attracted to water, and a **hydrophobic** (or water-hating) section, which is attracted to hydrophobic solvents such as oil. In order for the hydrophilic section to be dispersed in the water phase and for the hydrophobic section to be dispersed in the oil phase, the molecule must adsorb at the *interface* between the two phases, instead of being dispersed in either bulk phase.

Good emulsifiers are able to interact at the interface to form a *coherent* film that does not break easily. Therefore, when two droplets collide, the emulsifier film remains intact, and the droplets do *not* coalesce to form one big droplet. Instead, they drift away from each other.

The *best* emulsifiers are proteins, such as egg yolk (lipoproteins) or milk proteins, because they are able to interact at the interface to form stable films and hence to form stable emulsions. However, many *other* types of molecules are used as emulsifiers.

Mono- and diglycerides are examples of emulsifiers that are added to products in order to provide ease of mixing. They adsorb at the interface, reducing **interfacial tension** and increasing the spreadability of the continuous phase or the wettability of the dispersed phase.

In some cases, finely divided *powders* such as dry mustard or spices are used to act as emulsifiers in oil-in-water mixture. The mustard

and spices adsorb at the interface and reduce interfacial tension. However, they *cannot* form a stable film around oil droplets, and so they are *unable* to form a stable emulsion. Therefore, they should *not* really be considered as emulsifiers.

Emulsions may be temporary or permanent. A *temporary emulsion* separates upon standing. The emulsion is not permanent because the hydrophobic oil and hydrophilic water components separate upon standing. This is because the emulsifiers used are unable to form a stable interfacial film to prevent coalescence of the droplets of the dispersed phase. As coalescence occurs, the droplets combine to form bigger ones, and eventually the two phases separate out completely. An example of a temporary emulsion would be French dressing, which separates out a few seconds after it has been shaken.

A *permanent emulsion* is formed when two ordinarily nonmiscible phases, such as water and oil, are combined with an emulsifier. One phase (usually the oil phase) is dispersed within the other as small droplets. These remain dispersed in the continuous phase (usually water), because they are surrounded by a stable film of emulsifier that resists coalescence, and so prevents separation of the two phases.

Thus, the time of separation of oil and water is dependent upon the effectiveness of an emulsifier and the degree of agitation. As mentioned, more detail on emulsification is provided in Chap. 13.

Various examples of emulsified mixes are cake mixes, mayonnaise, and salad dressings, discussed below.

Cake mixes contain an emulsifier that aids in incorporation of air upon stirring or beating. The emulsifiers are usually monoglycerides and diglycerides, which act by dispersing shortening in smaller particles. This creates a maximum number of air cells that *increase* cake volume and creates a more even grain in the baked product (Chap. 14).

Mayonnaise is an emulsified product. A real mayonnaise as opposed to salad dressing (mayo type) is described in the 1952 Standard of Identity. Mayonnaise is an emulsified semisolid, with not less than 65 % by weight, edible vegetable oil.

Salad dressings are typically emulsified, containing oil, vinegar, water, salts, and so forth. Oil coats the salad contents and disperses herbs, spices, and other substances. Early application may *wilt* the salad due to salt in the dressing. Winterized oils are used. Some dressings are available in no-fat formulations. Except for bacon dressing, which uses bacon fat, *solid* fats are generally *not* acceptable for use in a dressing.

Hydrocolloids (see section "Fat Replacements" and Chap. 5) such as gelatin, gums, pectin, and starch pastes may be added in the preparation of salad dressings, but they contain only a hydrophilic section and are *not* considered *emulsifiers*. Rather, they act as stabilizers in emulsions, and help to prevent or lessen coalescence, because they increase the viscosity of the continuous phase.

Frying

Frying with melted fat or oil is a common cooking technique because frying is a *rapid* heat transfer method that achieves a *higher* temperature than boiling or dry heat temperature. The characteristics of fats for frying include that the fat must be colorless, odorless, and bland and have a high smoke point.

Smoke Point

The **smoke point** is the temperature at which fat may be heated before continuous puffs of blue smoke come from the surface of the fat under controlled conditions. The presence of smoke indicates that free glycerol has been further hydrolyzed to yield *acrolein*, a mucous membrane irritant. Monoglycerides, in hydrogenated shortenings, and diglycerides are hydrolyzed more easily than triglycerides and they tend to have a low smoke point. Therefore, they are not recommended in frying oils.

When fat *exceeds* the smoke point, it may reach *flash point*, when small flames of fire begin in the oil. Subsequently, it reaches the *fire point* where a fire is sustained in the oil. Oils such as cottonseed or peanut oil have a high smoke

point of 444 or 446 °F (229 or 230 °C), respectively. Other oils with a lower smoking point may not perform satisfactorily when exposed, for example, to the high heat of a wok.

CULINARY ALERT! Lard, butter, margarine, and animal fats have a low smoke point and less tolerance of heat when compared to hydrogenated fat and oils.

Changes During Frying

Frying exposes the food product to high temperatures, removes internal water, and allows a level of oil absorption. The duration of frying, composition of the food, surface treatment, and other factors determine levels of oil uptake.

The subsequent thermal decomposition of oil occurs in fat as air, water, and prolonged high temperature lead to fat oxidation and hydrolysis. Oil may become an unwanted orange or brown color or it may become more viscous and foam. The smoke point decreases as oil is repeatedly used for frying. And the quality is reduced.

Numerous factors are reported to affect oil uptake during frying, and a better understanding of how oil is absorbed during frying can lead to improved food quality of fried foods. For example, porosity requires more study in order to determine its effect on oil uptake. Some of these factors that affect oil uptake during frying are addressed in Table 12.4.

Low-Fat and No-Fat Foods

Consumer interest in eating reduced-fat or fat-free foods has increased, as is evidenced by the trend for more healthy foods. Yet, the per capita consumption of fats and oils has *not* decreased to meet the Surgeon General's recommendation (<30 % of a day's calories from fat) in the Report on Nutrition and Health. This may be in part due to the fact that the function, flavor, and mouthfeel of fat have *not* been duplicated by any nonfat component in the diet.

Overcoming flavor challenges in low-fat frozen desserts may involve the removal of fat in ice cream products that affects flavor and aroma, texture, and mouthfeel. Overcoming flavors is challenging.

The USDA reports one attempt at meeting flavor challenges. Utilizing a starch–lipid ratio varying from 10:1 to 2:1, oil droplets are suspended in cooked starch dispersions and then added as an ingredient to embellish flavor, texture, and mouthfeel (USDA).

> The fats and oils in dressings and sauces play several roles and provide a number of attributes" "When you consider a full-fat salad dressing may contain as much as 30 % to 50 % oil, and mayonnaise or sauces from it, fully 80 %—you gain a better understanding of why the low-fat, fat-reduced, "lite", or fat-free versions fall so short of expectations. (Decker 2013)

Fat Replacements

Fat replacements in a formulation may be protein-, carbohydrate-, or fat-based. Of course, the noncaloric water and air may be added if it works! Replacements are "useful when they help with calorie control and when their use encourages the consumption of foods delivering important nutrients" (The Academy of Nutrition and Dietetics, Eatright.org).

The use of a particular fat replacement may be determined by answering the question: What properties of fat are fat replacers attempting to simulate?

Today, there are many materials designed to replace fat; they are derived from several different categories of substances. Some replacers that attempt to simulate fat include protein-, carbohydrate-, and fat-derived fat replacements described below.

Using "the systems approach" in problem-solving, the Calorie Control Council reports that "...a variety of synergistic components are used to achieve the functional and sensory characteristics of the full-fat product. Combinations of ingredients are used to compensate for specific functions of the fat being replaced. These combinations may

Table 12.4 Selected factors that affect oil uptake during deep-fat frying

Frying temperature, ***duration***, **and product shape**—Increases in temperature decrease oil uptake due to short frying duration
Pressure frying decreases duration and oil uptake
A high surface-to-mass ratio or surface roughness increases oil absorption
Composition—The addition of soy protein, egg protein, or powdered cellulose decreases oil uptake. High sugar, soft flour, or developed gluten increase oil uptake
Prefrying treatments—Blanching, prewashing with oil containing emulsifiers, freezing, and steam pretreatment have been shown to decrease oil uptake
Surface treatment—Hydrocolloids (see section "Fat Replacements") and amylose coatings may function as barriers to fat uptake

include proteins, starches, dextrins, maltodextrins, fiber, emulsifiers and flavoring agents. Some fat replacers are now available that are themselves a combination or blend of ingredients (for example, one ingredient currently in use is a combination of whey, emulsifiers, modified food starch, fiber and gum)" (Calorie Control Council, CalorieControl. org).

The Academy of Nutrition and Dietetics (formerly the American Dietetic Association [ADA]) states "Fat replacements provide an opportunity for individuals to reduce intake of high-fat foods and enjoy reduced-fat formulations of familiar foods while preserving basic food selection patterns." It is the position of the ADA that "the majority of fat replacers, when used in moderation by adults, can be safe and useful adjuncts to lowering the fat content of foods and may play a role in decreasing total dietary energy and fat intake. Moderate use of low-calorie, reduced-fat foods, combined with low total energy intake, could potentially promote dietary intake consistent with the objectives of *Healthy People 2010* and the 2005 *Dietary Guidelines for Americans*" (The Academy of Nutrition and Dietetics, Eatright.org).

Reported by the Institute of Food Technologists is that nutrition, a healthy lifestyle, regular exercise, and a reduction of total dietary fat are significant in lifestyles that incorporate fat.

http://www.caloriecontrol.org

Featured in the following text are a discussion, examples, and label designation for each group of derived fat replacers.

Carbohydrate-Derived Fat Replacements

Fat replacements may be derived from carbohydrates with 0–4 kcal/g instead of 9 kcal/g. *Starches* work well as fat replacements in high moisture systems to absorb water and form gels that mimic fat. They have been utilized in the bakery industry for many years.

Fruit purees or dried puree powder is also used to replace fats, as are *cellulose*, *gums*, *fiber*, *dextrins*, *maltodextrins*, *modified food starch*, *modified dietary fibers*, *and polydextrose*. Starch hydrolysis derivatives known as ***maltodextrins*** (classified as hydrocolloids) are bland in flavor and have a smooth mouthfeel. They are fat-replacing ingredients of commercial cakes and also assist in maintaining product moisture. Gelling, thickening, and stabilizing are desirable functional properties.

The plant root, tapioca, and the tuber, potato, as well as the cereal starches corn and rice, are also used as fat replacers. An oat-based fat replacement is made by partial hydrolysis of oat starch using a food-grade enzyme, and barley is being investigated for use as a possible fat substitute.

Fat replacers may be basically hydrocolloid materials or contain hydrocolloids as an important part of their ingredient composition (see below).

Hydrocolloids are long-chain polymers, principally carbohydrate, that thicken or gel in aqueous systems, creating the creamy viscosity that mimics fat. Some are listed below. They include

the starch derivatives, hemicelluloses, β-glucans, soluble bulking agents, microparticulates, composite materials [i.e., carboxymethyl cellulose (CMC) and microcrystalline cellulose or xanthan gum and whey], and functional blends (gums, modified starches, nonfat milk solids, and vegetable protein).

Polydextrose may be used as a 1 kcal/g substitute for either fat or sucrose. Polydextrose is a bulking agent created by the random polymerization of glucose, sorbitol, and citric acid, 89:10:1. It may be used in a variety of products such as baked goods, chewing gum, salad dressings, and gelatins, puddings, or frozen desserts.

Several dried-fruit-based substances are available for replacement of fat in recipes. Raisin, plum, and other fruit mixtures are available for consumer use at this time. Applesauce is also used to partially replace fat in formulations. Many additional fat replacers are being explored, including the use of encapsulated technologies (USDA).

Examples of <u>carbohydrate-derived</u> Food and Drug Administration (FDA)-approved *or* currently researched fat replacers:

Examples of Carbohydrate-Based Fat Replacers

Cellulose (Avicel® cellulose gel, Methocel™, Solka-Floc®)

Various forms are used. One is a non-caloric purified form of cellulose ground to microparticles which, when dispersed, form a network of particles with mouthfeel and flow properties similar to fat. Cellulose can replace some or all of the fat in dairy-type products, sauces, frozen desserts and salad dressings.

Dextrins (Amylum, N-Oil®)

Four calories per gram fat replacers which can replace all or some of the fat in a variety of products. Food sources for dextrins include tapioca. Applications include salad dressings, puddings, spreads, dairy-type products and frozen desserts.

Fiber (Opta™, Oat Fiber, Snowite, Ultracel™, Z-Trim)

Fiber can provide structural integrity, volume, moisture holding capacity, adhesiveness and shelf stability in reduced-fat products. Applications include baked goods, meats, spreads and extruded products.

Gums (KELCOGEL®, KELTROL®, Slendid™)

Also called hydrophilic colloids or hydrocolloids. Examples include guar gum, gum arabic, locust bean gum, xanthan gum, carrageenan and pectin. Virtually non-caloric; provide thickening, sometimes gelling effect; can promote creamy texture. Used in reduced-calorie, fat-free salad dressings and to reduce fat content in other formulated foods, including desserts and processed meats.

Inulin (Raftiline®, Fruitafit®, Fibruline®)

Reduced-calorie (1–1.2 calories/g) fat and sugar replacer, fiber and bulking agent extracted from chicory root. Used in yogurt, cheese, frozen desserts, baked goods, icings, fillings, whipped cream, dairy products, fiber supplements and processed meats.

Maltodextrins (CrystaLean®, Lorelite, Lycadex®, MALTRIN®, Paselli®D-LITE, Paselli®EXCEL, Paselli®SA2, STAR-DRI®)

Four calorie per gram gel or powder derived from carbohydrate sources such as corn, potato, wheat and tapioca. Used as fat replacer, texture modifier or bulking agent. Applications include baked goods, dairy products, salad dressings, spreads, sauces, frostings, fillings, processed meat, frozen desserts, extruded products and beverages.

Nu-Trim

A beta-glucan rich fat replacer made from oat and barley using an extraction process that removes coarse fiber components. The resulting product can be used in foods and beverages such as baked goods, milk, cheese and ice cream, yielding products that are both reduced fat and high in beta-glucan. (The soluble fiber beta-glucan has been cited as the primary component in oats and barley responsible for beneficial reduction in cardiovascular risk factors.)

Oatrim [Hydrolyzed oat flour] (Beta-Trim™, TrimChoice)

A water-soluble form of enzyme treated oat flour containing beta-glucan soluble fiber and used as a fat replacer, bodying and texturizing ingredient. Reduced calorie (1–4 calories/g) as used in baked goods, fillings and frostings, frozen desserts, dairy beverages, cheese, salad dressings, processed meats and confections.

Polydextrose (Litesse®, Sta-Lite™)

Reduced-calorie (1 calorie/g) fat replacer and bulking agent. Water-soluble polymer of dextrose containing minor amounts of sorbitol and citric acid. Approved for use in a variety of products including baked goods, chewing gums, confections, salad dressings, frozen dairy desserts, gelatins and puddings.

Polyols (many brands available)

A group of sweeteners that provide the bulk of sugar, without as many calories as sugar (1.6–3.0 calories/g, depending on the polyol). Due to their plasticizing and humectant properties, polyols also may be used to replace the bulk of fat in reduced-fat and fat-free products.

Starch and modified food starch (Amalean®I & II, Fairnex™VA15, & VA20, Instant Stellar™, N-Lite, OptaGrade®#, Perfectamyl™AC, AX-1, & AX-2, PURE-GEL®, STA-SLIM™)

Reduced-calorie (1–4 calories/g as used) fat replacers, bodying agents, texture modifiers. Can be derived from potato, corn, oat, rice, wheat or tapioca starches. Can be used together with emulsifiers, proteins, gums and other modified food starches. Applications include processed meats, salad dressings, baked goods, fillings and frostings, sauces, condiments, frozen desserts and dairy products.

Z-Trim

A calorie free fat replacer made from insoluble fiber from oat, soybean, pea and rice hulls or corn or wheat bran. It is heat stable and may be used in baked goods (where it can also replace part of the flour), burgers, hot dogs, cheese, ice cream and yogurt.

#Appears as corn starch on the ingredient statement, others appear as food starch modified.

(Calorie Control Council—http://www.caloriecontrol.org)

Some Carbohydrate-Based Fat Replacers on Food Labels

Carrageenan, *cellulose*, *gelatin*, *gellan gum*, *gels*, *guar gum*, *maltodextrins*, *polydextrose*, *starches*, *xanthan gum*, *modified dietary fibers*.

The ingredient may be used for reasons OTHER than fat replacement.

Fat-Derived Fat Replacements

Fat-derived fat replacements, such as Olestra, offer 0 calorie/g. Other replacements offer less than 9 kcal/g of fat. The majority are *emulsifiers*, *emulsions with little fat*, *or analogs*—triglycerides or similar, with a changed configuration (see the underlined items listed below as examples). It is reported by the International Food Information Council (IFIC) that "Some fat-based ingredients, such as Caprenin and Salatrim, are actually fats tailored to contribute fewer calories and less available fat to foods. Others such as olestra, are structurally modified to provide no calories or fat" (Calorie Control Council, CalorieControl.org).

Olestra, marketed under the brand name Olean®, differs from fats and oils in its chemical composition and properties. Olestra is a sucrose polyester (SPE), predominantly sucrose octaester, which is synthesized by reacting six to eight fatty acids with the eight free hydroxyl groups of sucrose. (Recall that fats are a glycerol backbone with three fatty acids attached.) Each fatty acids may be 12–20 or more carbons in length and may be either saturated or unsaturated. Fatty acids may be derived from corn, coconut, palm, or soybean sources.

Olestra became the latest of several food ingredients approved without generally recognized as safe (GRAS) status [others are TBHQ (1972), aspartame (1981), polydextrose (1981), and acesulfame K (1988) (Chap. 17)]. Its chemical makeup and configuration make olestra

indigestible and it is not absorbed. Its numerous fatty acids are attached to the sucrose in a manner that cannot be easily penetrated by digestive enzymes in the length of time it is in the digestive tract. As a result, olestra provides *no* calories.

Unlike *protein-derived* fat replacements, which by their nature *cannot* be exposed to high heat, olestra is used for frying applications. It was first patented in 1971 and sought FDA approval as a cholesterol-lowering drug. Approval was denied, because such use was not shown.

A subsequent petition in 1987 requested use of olestra as a direct food additive. It was to be used as a fat replacement for (1) up to 35 % of the fat in home-use cooking oils and shortenings and (2) up to 75 % of the fat in commercial deep-fat frying of snack foods. The petition was amended in 1990 and approved in 1996 to allow the Procter & Gamble Olean® to be used as a 100 % replacement for fats in savory snacks (salty, piquant, but not sweet, such as potato chips, cheese puffs, and crackers), including the frying oil and any fat sources in the dough (conditioners, flavors, etc.). All other uses of olestra require separate petitions.

The FDA conclusions regarding the major chemical changes in frying and baking applications of olestra are that changes are similar to triglycerides. The fatty acid chains oxidize in both cases. In baking, there is slower degrading of the fatty acids, but the same by-products are produced. Olestra has baking and frying applications and may be used in dairy-based or oil-based foods.

A distinctive label statement is required for all Olean®-containing products. Labels must state "This Product Contains Olestra. Olestra may cause abdominal cramping and loose stools. Olestra inhibits the absorption of some vitamins and other nutrients. Vitamins A, D, E, and K have been added." In three small test markets, the major user of Olean® has not observed nor has there been evidence of severe abdominal cramps and loose stools resulting from the consumption of products containing Olean® (Frito-Lay).

Health concerns regarding the use of olestra have been addressed in part by over 150 Procter & Gamble studies.

Caprenin® (Procter & Gamble) is another fat replacement that contains 5 calories/g. It contains a glycerol backbone with three fatty acids. Two of the fatty acids are medium chain, caprylic and capric, which are metabolized similarly to carbohydrates, and the other chain consists of a long fatty acid—behenic acid—that is incompletely absorbed. These fatty acids are selected on the basis of specific, desired properties.

Nabisco Foods has developed a proprietary family of low-calorie **salatrim** fats—named for **s**hort **a**nd **l**ong **a**cyl**tri**glyceride **m**olecule. Salatrim is a patented ingredient of conventional glycerol backbones to which long-chain fatty acids and short-chain fatty acids are added. The long-chain stearic acid is combined with the short-chain acetic, propionic, and butyric acids on a glycerol molecule.

Nabisco states that salatrim is different from other fat replacers because it is made from real fat, whereas other fat substitutes are made from protein and carbohydrates.

Salatrim received GRAS status by the FDA in 1994. It was approved for use in baked products, chocolates and confections, dairy products, and snacks, but it cannot be used successfully in frying applications.

A nutritional advantage of using these fat replacers is that they contain 5 kcal/g, instead of the normal fat amount of 9 kcal/g. This calorie reduction may be due to hydrolysis of short-chain fatty acids that are rapidly hydrolyzed to carbon dioxide and long-chain fatty acids that are incompletely absorbed.

Examples of <u>fat-derived</u> FDA-approved *or* currently researched fat replacers:

Examples of Fat-Based Fat Replacers

Emulsifiers (Dur-Lo®, EC^T-25)

Examples include vegetable oil mono- and diglyceride emulsifiers which can, with water, replace all or part of the shortening content in cake mixes, cookies, icings, and numerous vegetable dairy products. Same caloric value as fat (9 calories/g) but less is used, resulting in fat and calorie reduction.

Sucrose fatty acid esters also can be used for emulsification in products such as those listed above. Additionally, emulsion systems using soybean oil or milk fat can significantly reduce fat and calories by replacing fat on a one-to-one basis.

Salatrim (Benefat[T])

Short and long-chain acid triglyceride molecules. A 5 calories/g family of fats that can be adapted for use in confections, baked goods, dairy and other applications.

Lipid (fat/oil) analogs

– **Esterified propoxylated glycerol (EPG)**

Reduced-calorie fat replacer. May partially or fully replace fats and oils in all typical consumer and commercial applications, including formulated products, baking and frying.

– **Olestra** (Olean[®])

Calorie-free ingredient made from sucrose and edible fats and oils. Not metabolized and unabsorbed by the body. Approved by the FDA for use in replacing the fat used to make salty snacks and crackers. Stable under high heat food applications such as frying. Has the potential for numerous other food applications. For more information on olestra, check out the new olestra brochure.

– **Sorbestrin****

Low-calorie, heat stable, liquid fat substitute composed of fatty acid esters of sorbitol and sorbitol anhydrides. Has approximately 1.5 calories/g and is suitable for use in all vegetable oil applications including fried foods, salad dressing, mayonnaise and baked goods.

*Brand names are shown in parentheses as examples.

**May require FDA approval.

(Calorie Control Council, CalorieControl.org) www.caloriecontrol.org/fatreprint.html

Protein-Derived Fat Replacements

Proteins may be used in place of fat. They contribute 1–4 kcal/g, instead of 9. An easily recognized type is gelatin; however, there are others. The International Food Council states that "Some protein-based ingredients, such as Simplesse[®], are made through a process that gives fat-like textural properties to protein. Other proteins are heated and blended at high speed to produce tiny protein particles that feel creamy to the tongue. ... protein-based fat reducers cannot be used as substitutes for oils and other fats in frying" (International Food Information Council, IFIC.org).

Simplesse[®] is a natural fat substitute developed by the NutraSweet Company and approved by the FDA in 1990. It is a *microparticulated protein* (*MPP*). Simplesse[®] uses a patented process that heats and intensely blends naturally occurring food proteins such as *egg white and milk* proteins, along with water, pectin, and citric acid. The protein remains chemically unchanged, yet aggregates under controlled conditions that allow formation of small aggregates or microparticles.

The *blending* process produces small, round uniformly shaped protein particles—about 50 billion per teaspoon—that create the creamy mouthfeel of full fat. The microparticulated particle size is near the lower range of *MPPs* that naturally occur in milk, egg white, grains, and legumes. For example, casein (milk protein) micelles range in size from 0.1 to 3.0 mm in diameter and are perceived as creamy to the tongue. In comparison, a larger particle size, 10–30 mm in diameter, is found in powdered (confectionery) sugar, which is perceived as more powdery and gritty.

Initially, Simplesse[®] was an ingredient approved by the FDA for use in dairy-based frozen desserts. Today, it has many more food applications in products such as butter spreads, cheese (creamed, natural, processed, baked cheesecakes), creamers, dips, ice cream, and sour cream. It is also successfully incorporated into oil-based products such as margarine spreads, mayonnaise, and salad dressings. Many are Kosher approved, and with proper storage, they have a shelf life of 9 months (The Academy of Nutrition and Dietetics, Eatright.org).

Due to its milk and egg protein composition, individuals *allergic* to milk or eggs *cannot* eat

this fat substitute. It contains 1.2 calories/g (*not a* 0-calorie food), approximately one-third the calories of protein, and significantly lowers fat intake. Simplesse® is a GRAS substance.

Whey protein concentrates (WPCs), and *isolates* (WPIs), and isolated soy protein (legumes) are proteins that can be used to provide some of the functional properties of fat without the same number of fat calories. Dairy-Lo® is an example of a WPC and uses include dairy products, baked goods, frostings, mayonnaise-type products, and salad dressings.

Soy may be used for emulsification or gelling and is approved for addition of up to 2 % in cooked sausage and cured pork. It may be used at higher levels in ground meat and poultry.

Examples of <u>protein-derived</u> FDA-approved *or* currently researched fat replacers:

Examples of Protein-Based Fat Replacers

Microparticulated protein (Simplesse®)
Reduced-calorie (1–2 calories/g) ingredient made from whey protein or milk and egg protein. Digested as a protein. Many applications, including: dairy products (e.g., ice cream, butter, sour cream, cheese, yogurt), salad dressing, margarine- and mayonnaise-type products, as well as baked goods, coffee creamer, soups and sauces.

Modified whey protein concentrate (Dairy-Lo®)
Controlled thermal denaturation results in a functional protein with fat-like properties. Applications include: milk/dairy products (cheese, yogurt, sour cream, ice cream), baked goods, frostings, as well as salad dressing and mayonnaise-type products.

Other (K-Blazer®, ULTRA-BAKE™, ULTRA-FREEZE™, Lita®)
One example is a reduced-calorie fat substitute based on egg white and milk proteins. Similar to MPP yet made by a different process. Another example is a reduced-calorie fat replacer derived from a corn protein. Some blends of protein and carbohydrate can be used in frozen desserts and baked goods.

(Calorie Control Council—caloriecontrol.org. http://www.caloriecontrol.org/articles-and-video/feature-articles/glossary-of-fat-replacers)

Beyond the scope of this discussion is more information that defines fat replacers and extenders. For example, fat substitutes, fat analogs, fat mimic, fat extender, and fat barriers are terms better defined elsewhere in the literature.

Nutritive Value of Fats and Oils

Most health authorities in the United States take the stance that fat should be limited—yet, not *all* currently agree with this recommendation. Fats are needed for numerous functions in the human body, and two PUFAs are essential—linoleic and linolenic acid are required for human growth. In addition to the many roles fat plays in functionality of foods, fats are a very concentrated energy source—providing 9 calories/g. This is 2¼ times as many calories per gram as either carbohydrates or protein.

The health-conscious consumer may make choices of reducing certain foods that are major contributors of less desirable fatty acids, and, as well, substitute foods, possibly *increasing* fats that are major contributors of the fatty acids that are desired (Pszczola 2000). The food industry may have a major impact in reducing heart disease, as they have *changed* formulations. See health and nutrition article "Feeling better about fat" (Decker 2012).

Similar to the role of cholesterol in animal cell membranes, *phytosterols* and *phytostanols* perform the same role in *plants*. Phytostanols are the saturated form of plant sterols. The structures are similar to cholesterol, differing only in the side chain (Fig. 12.4). *Plant sterols* are commercially available in margarines (such as Benecol®, which contains stanols, and Take Control ®, which contains sterols) and salad dressings, and although there are several theories suggested, and the precise mechanism is unknown, these phytonutrients have been shown for many decades to significantly reduce low-density lipoprotein (LDL) or "bad" cholesterol. They inhibit the uptake of endogenous and dietary cholesterol

(ISEO Technical Committee 2006). More recently, it has been shown that *dietary* cholesterol does not bear a direct negative influence on *serum* cholesterol in the healthy individual.

The cost factor continues to be a challenge, as is the marketing of any "healthy food" that incorporates new ingredients. Benecol® and Take Control® are much more expensive than other types of margarines or spreads.

Research is ongoing regarding the type and amount of fats as a part of optimal nutrition.

OILS (ChooseMyPlate.gov)

What Are "Oils?"

Oils are fats that are liquid at room temperature, like the vegetable oils used in cooking. Oils come from many different plants and from fish. Oils are NOT a food group, but they provide essential nutrients. Therefore, oils are included in USDA food patterns. Some oils are used mainly as flavorings, such as walnut oil and sesame oil. A number of foods are naturally high in oils.

Foods that are mainly oil include mayonnaise, certain salad dressings,

and soft (tub or squeeze) margarine with no *trans* fats. Check the Nutrition Facts label to find margarines with 0 g of *trans* fat. Amounts of *trans* fat are required to be listed on labels.

Most oils are high in monounsaturated or polyunsaturated fats, and low in saturated fats. Oils from plant sources (vegetable and nut oils) do not contain any cholesterol. In fact, no plant foods contain cholesterol.

A few plant oils, however, including coconut oil, palm oil, and palm kernel oil, are high in saturated fats and for nutritional purposes should be considered to be solid fats.

Solid fats are fats that are solid at room temperature, like butter and shortening. Solid fats come from many animal foods and can be made from vegetable oils through a process called hydrogenation.

Safety of Fats and Oils

Safety of the original fats and oils may be compromised. For example, rancidity due to lengthy or improper storage conditions, including temperature, may destroy fats and oils. Of course, the presence of harmful, foreign substances in any food material, as well as skin burns from hot oil products, poses severe dangers in the workplace.

Conclusion

Fats and oils add or modify flavor, aerate batters and doughs, contribute flakiness and tenderness, emulsify, transfer heat, and provide satiety. They are composed of a glycerol molecule with one, two, or three fatty acids attached creating mono-, di-, or triglycerides, respectively. Minor components of fats and oils include phospholipids, sterols, tocopherols, and pigments. Fatty acid chains of even number may exist as geometric or positional isomers. Nomenclature may be

according to a common name, systemic or Geneva name, or omega system.

Fats and oils exist in several crystalline forms and have different melting points. Solid fats have higher melting points than oils. Fats and oils may be processed by being deodorized or rendered. They are modified by hydrogenation, interesterification, acetylation, or winterization.

The deterioration of fats and oils occurs as they absorb odors or become rancid. Hydrolytic rancidity releases free fatty acids, and oxidative rancidity produces shorter, off-odor free radicals catalyzed by heat, light, metals, or enzymes. Prevention of oxidation by avoiding catalysts in the environment or by the addition of sequestering agents or antioxidants may be useful in extending shelf life.

Monoglycerides and diglycerides have uses as emulsifiers, permitting fats and liquids to mix. Fats and oils are useful as shorteners; they tenderize and produce flakes in baked products. They may also be used in the preparation of salad dressings and for frying applications. Foods may contain reduced-fat, low-fat, or no-fat formulations using a variety of fat replacers derived from carbohydrates, proteins, or fats.

The cost factor continues to be a challenge, as is the marketing and healthy value of any "healthy food" that incorporates new ingredients.

Plant breeders are researching the development of healthier fats. A variety of vegetable oils continue to be available to food processors and, to a lesser extent, to the consumer. Stability without increased saturation is the goal of processors. Advanced hybridization of vegetable sources of oil may reduce saturated fatty acids, and thus improve nutritional value. Fats and oils should be used sparingly in the daily diet.

Notes

CULINARY ALERT!

Glossary

Acetin fat A triglyceride with one or two fatty acids on a triglyceride replaced by acetic acid; this decreases the melting point.

Acetoglyceride Acetin fat.

Antioxidant Prevents, delays, or minimizes the oxidation of unsaturated bonds by donating an H atom to the double bond in a fatty acid.

Autoxidation Progressive oxidative rancidity in an unsaturated fatty acid promoted by heat, light, the metals iron and copper, and lipoxygenases.

BHA Butylated hydroxyanisole; an antioxidant.

BHT Butylated hydroxytoluene; an antioxidant.

Cis **configuration** A double-bond formation when H atoms attach to the C atoms of the double bond on the same side of the double bond.

Continuous phase The phase or medium in which the dispersed phase is suspended in an emulsion.

Deodorized oils Oils that have undergone the process of removing odors by heat and vacuum or by adsorption onto charcoal.

Dispersed phase A phase that is disrupted or finely divided in the continuous phase of an emulsion.

Emulsifier Bipolar substance with a hydrophilic and hydrophobic end, which reduces surface tension and allows the ordinarily immiscible phases of a mixture to combine.

Fat replacement A substance used to replace fat in a formulation; these may be protein-, carbohydrate-, or fat-based.

Flakiness Thin, flat layers formed in some dough products desirable in biscuits or piecrusts.

Hydrocolloid Long-chain polymers; colloidal material that binds and holds water.

Hydrogenation Process of adding H to unsaturated fatty acids to reduce the number of double bonds; an oil becomes more solid and more stable in storage.

Hydrolytic rancidity Reaction of fats with water to liberate free fatty acids.

Hydrophilic Water-loving substance attracted to water.

Hydrophobic Water-fearing substance attracted to fat.

Interesterification Rearrangement as fatty acids migrate and recombine with glycerol in a more random manner.

Interfacial tension See surface tension.

Isomer Fatty acids have the same number of carbons, hydrogens, and oxygens, but form different arrangements that create different chemical and physical properties.

Lecithin Phospholipid of two fatty acids esterified to glycerol and a third group of phosphoric acid and choline as the N group; useful as an emulsifier.

Maltodextrin Hydrocolloid; starch derivative of tapioca, potato, corn, rice, oats, or barley that may be used to replace fat in a formulation.

Oxidative rancidity Fat is oxidized and decomposes into off-odor compounds with shorter-chain fatty acids, aldehydes, or ketones.

Phospholipid A lipid containing two fatty acids and a phosphoric acid group esterified to glycerol.

Phytosterols and phytostanols Natural substances obtained from plants, which are related to cholesterol, but are able to reduce blood cholesterol levels. Stanols are the saturated form of plant sterols. These substances are contained in margarines such as Benecol (contains stanols) and Take Control (contains sterols).

Plastic fat Able to be molded and hold shape; contains both liquid and solid triglycerides in various ratios.

Polymorphism Fats existing in different crystalline forms: α, β' intermediate, and β.

Rearrangement Interesterification of fatty acids on glycerol, i.e., modified lard.

Rendered Fat freed from connective tissue and reduced, converted, or melted down by heating; for example, lard is rendered hog fat.

Sequestering agent Binds metals, thus preventing them from catalyzing autoxidation; for example, EDTA and citric acid.

Smoke point The temperature at which fat may be heated before continuous puffs of blue smoke come from the surface of the fat.

Sterols A lipid containing a steroid nucleus with an 8–10 C side chain and an alcohol group; cholesterol is the most well known.

Surface tension (Interfacial tension) force that tends to pull molecules at the surface into the bulk of a liquid and prevents a liquid from spreading. Reduction of surface tension enables a liquid to spread more easily.

TBHQ Tertiary butylhydroquinone; an antioxidant.

Tenderization Easily crushed or chewed, soft, fragile, baked dough.

Tocopherols Minor component of most vegetable fats; antioxidant; source of vitamin E.

Trans **configuration** A double-bond formation in fatty acids where the H atoms attach to the C atoms of the double bond on opposite sides of the double bond.

Winterized Salad oil that is pretreated prior to holding, to control undesirable cloudiness from large, high-melting-point triglyceride crystals.

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Food Emulsions and Foams
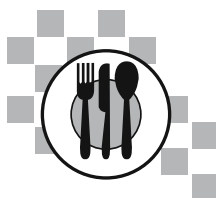
Introduction

Many convenience foods, such as frozen desserts, meat products, margarine, and some natural foods, such as milk and butter, are emulsions. That is, they contain either water dispersed in oil or oil dispersed in water. These water and oil liquids do not normally mix, and so when present together, they exist as two separate layers. However, when an emulsion is formed, the liquids are mixed in such a way that a single layer is formed with droplets of one liquid dispersed within another. Food emulsions need to be stable; if they are not, the oil and water will separate out. Stability is usually achieved by adding a suitable emulsifier. In some cases, a stabilizing agent is also required.

Food foams, such as beaten egg white, are similar to emulsions except that instead of containing two liquids, they contain a gas (usually air or carbon dioxide) dispersed within a liquid. The factors affecting stability of emulsions also apply to foams. Some foods, such as ice cream and whipped cream, are highly complex being both an emulsion and a foam.

Understanding of food emulsions and foams is complex, yet is important if progress is to be made in maintaining and improving the stability and hence the quality of these types of foods. This chapter will discuss the principles of formation and stability of emulsions and foams and the characteristics of the ingredients necessary to stabilize them.

Emulsions

Definition

An *emulsion* is a *colloidal system* containing droplets of one liquid dispersed in another, the two liquids being immiscible. The droplets are termed the *dispersed phase*, and the liquid that contains them is termed the *continuous phase*. In food emulsions, the two liquids are oil and water. If water is the continuous phase, the emulsion is said to be an *oil-in-water* or *o/w emulsion*, whereas if oil is the continuous phase, the emulsion is termed a *water-in-oil* or *w/o emulsion*. Oil-in-water emulsions are more common and include salad dressings, mayonnaise, cake batter, and frozen desserts. Butter, margarine, and some icings are examples of water-in-oil emulsions.

An emulsion must also contain an *emulsifier*, which coats the emulsion droplets and prevents them from *coalescing* or recombining with each other. Emulsions are colloidal systems because of the size and surface area of the droplets (in general, around 1 μm, although droplet size varies considerably, and some droplets may be a lot larger than this). Emulsions are similar to colloidal dispersions or sols, except that the dispersed phase is liquid and not solid. Colloidal dispersions are mentioned in Chap. 2.
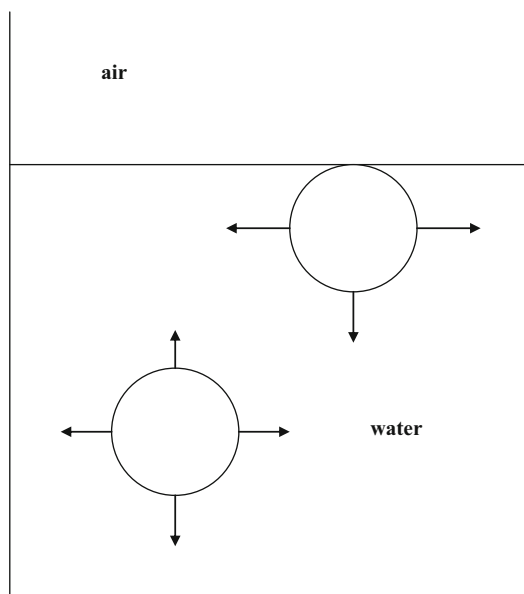
Surface Tension

To form an emulsion, two liquids that do not normally mix must be forced to do so. To understand how this is achieved, we must first consider the forces between the molecules of a liquid. Imagine a beaker of water placed on a desk (Fig. 13.1).

The water molecules are attracted to one another by hydrogen bonds as described in Chap. 2. A molecule in the center of the beaker has forces acting on it in all directions, because water molecules surround it. The net force on this molecule due to attraction by other water molecules is zero, because these forces are acting in all directions. However, this is not the case for a water molecule on the surface. Since there are no water molecules above it, there is a net downward pull on the molecule. This results in the molecule being pulled in toward the bulk of the liquid.

This downward pull can be seen when one fills a narrow tube such as a pipette or a burette with water. The surface of the liquid curves downward at the center, and the curve is called the meniscus. The greater the attractive forces between the liquid molecules, the greater the depth of the meniscus. Water molecules have strong attractive forces among them, and so it is relatively hard to penetrate the surface, or to get the water to spread. Try placing a needle gently on the surface of clean or distilled water. It will float, because the attractive forces between the water molecules keep it on the surface. (To make it sink, see below.)

If there are strong attractive forces among the molecules of a liquid, the force required to pull the molecules apart, to expand the surface, or to spread the liquid will be high. This force is known as **surface tension**. A liquid such as water, with strong attractive forces between the molecules, has a high surface tension. This makes it hard to spread. You can see this if you put water on a clean surface. It will tend to form droplets rather than spreading evenly as a thin film across the surface. (A droplet has minimal surface area and maximal internal volume, and so it is the most energetically favorable shape for liquids with a high surface

Fig. 13.1 Schematic diagram of the forces acting on water molecules in the bulk and at the surface of the liquid

tension, where the molecules are being pulled into the interior.)

The term surface tension is normally used when a *gas* (usually air) surrounds the *liquid* surface. When the surface is between two *liquids*, such as water and oil, the term **interfacial tension** is used.

A high surface or interfacial tension makes it hard to mix the liquid either with another liquid or with a gas. This is a drawback when making an emulsion or foam and needs to be overcome. So how can surface tension be reduced?

Surface-Active Molecules

To reduce the surface or interfacial tension, something must be done to decrease the attractive forces between the liquid molecules, so that it is easier to spread them. This can be achieved by adding a **surface-active** molecule, or a **surfactant**. As their name suggests, surface-active molecules are active at the *surface* of a liquid, rather than at the bulk of it. Surfactant molecules prefer to exist at the surface of a liquid rather than at the bulk because of their structure. In all cases, a section of
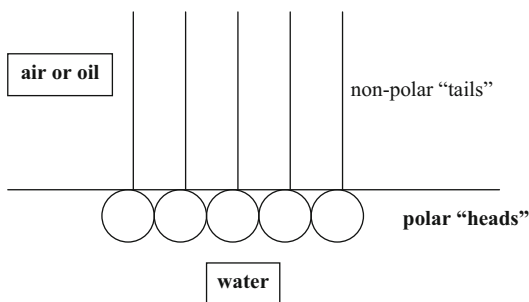
Fig. 13.2 Orientation of amphiphilic molecules at an interface

the molecule is water-loving or **hydrophilic** because it is polar or charged, and a section is water-hating or **hydrophobic** because it is apolar. In other words, the molecules are **amphiphilic**.

The apolar section has little or no affinity for water, and so it is energetically favorable for this section to be as far away from the water as possible. However, the polar section is attracted to the water and has little or no affinity for the oil. Therefore, the molecule orients at the surface with the polar section in the water, with the apolar section either in the air or in the oil (see Fig. 13.2).

Due to the fact that the molecule *adsorbs* at the surface, it reduces the attractive forces of the water molecules for themselves and makes it easier to expand or spread the surface. In other words, it reduces the surface or interfacial tension.

Detergent is an example of a surfactant. When detergent is added to water, it enables the water molecules to spread much more easily, so that they wet a surface more readily. After adding detergent, water will flow over a surface, forming a thin sheet, instead of tending to gather into droplets. Going back to the example of the needle floating on water (see above), if a small drop of detergent is added, the needle will sink. The surface tension is reduced, allowing the water molecules to spread more easily, and so the needle no longer stays on the surface.

Obviously, detergents are not used as food ingredients! (However, they are used when washing dishes, because they enable the water to spread across the surface and remove food particles more easily.) There are many food ingredients that are

surfactants. Polar lipids such as lecithin, which has a polar "head" and an apolar "tail," are surfactants and may be used as food additives to increase the wettability and aid in mixing of products like hot chocolate mix.

Proteins are surface-active because they contain both hydrophilic and hydrophobic sections. The nature and extent of these sections depend on the specific amino acid sequence of each protein, and some proteins orient at the surface more readily than others do (Proteins are discussed in Chap. 8).

Some spices, such as dry mustard and paprika, are also used as surface-active ingredients. These finely divided powders tend to gather at the surface rather than the bulk of the liquid.

Molecules that are either hydrophilic or hydrophobic do not orient at an interface. The molecules remain in the bulk of the liquid. For example, sugars, which are hydrophilic, or salt, which dissociates into ions, will be located in the bulk water phase. These types of molecules are not surface-active and will not decrease the interfacial tension. In fact, they may increase it, depending on their ability to bind the water molecules, hence increasing molecular attraction.

Emulsion Formation

An emulsion is formed when oil, water, and an emulsifier are mixed together. Although there are different food emulsions, they *all* contain these three components. To form an emulsion, it is necessary to break up either the oil or the water phase into small droplets that remain dispersed throughout the other liquid. This requires energy and is usually carried out using a mixer or a homogenizer. As the oil and water are mixed, droplets are formed. (They may be oil or water, yet are usually oil droplets.) An emulsifier is adsorbed at the surface of new droplets, decreasing the interfacial tension and allowing formation of more and smaller droplets. The lower the surface or interfacial tension of the oil and water, the more easily one liquid can be disrupted to form droplets and the more easily the other liquid will flow around the droplets.

The liquid with the higher interfacial tension will tend to form droplets, and the other liquid will flow around the droplets to form the continuous phase. The emulsifier generally determines the liquid that would form the continuous phase. Emulsifiers that are more easily dispersed in water (and therefore are more hydrophilic overall) tend to reduce the interfacial tension of the water more than that of the oil, promoting formation of o/w emulsions. Emulsifiers that disperse more readily in the oil phase tend to form w/o emulsions. The emulsifier is usually dispersed in the preferred phase before the oil and water are mixed together.

> **Principles of Formation of a Stable Oil-in-Water Emulsion**
> - Emulsifier is dispersed in the aqueous phase.
> - Oil is added and the interfacial tension of each liquid is reduced by the emulsifier.
> - Energy is supplied by beating or homogenizing the mixture.
> - The oil phase is broken up into droplets, surrounded by water.
> - Emulsifier adsorbs at the freshly created oil droplet surfaces.
> - Small droplets are formed, protected by an interfacial layer of emulsifier.
> - The interfacial area of the oil becomes very large.
> - The aqueous phase spreads to surround each oil droplet.
> - The emulsion may become thick due to many small oil droplets surrounded by a thin continuous phase.
> - If the interfacial film is strong, the emulsion will be stable.

An emulsifier does not simply reduce interfacial tension. It must also form a stable film that protects the emulsion droplets and prevents separation of the emulsion. The droplets are continually moving through the continuous phase, and so they constantly encounter or collide with each other. When two droplets collide, one of three things happens, as shown in Fig. 13.3:

(a) The emulsifier film stretches or breaks, and the droplets combine to form one larger droplet (or in other words, they *coalesce*). This ultimately leads to separation of the emulsion.
(b) The two emulsifier layers surrounding the droplets interact and an aggregate is formed. This occurs when a cream layer develops on top of fresh milk.
(c) The droplets move apart again.

Which of these three events occurs depends on the nature of the emulsifier molecules and on their ability to completely coat all the emulsion droplets with a stable, cohesive, *viscoelastic* film. A viscoelastic film tends to flow to coat any temporarily bare sections of the surface and is also able to stretch instead of breaking when, for example, another droplet bumps into it. Therefore, it is less likely to break when droplet collisions occur. As the droplets are formed, their surface or interfacial area increases dramatically, and sufficient emulsifier must be present to completely coat all the droplet surfaces. Incompletely coated droplets will coalesce resulting in larger droplets and ultimately in separation of the emulsion.
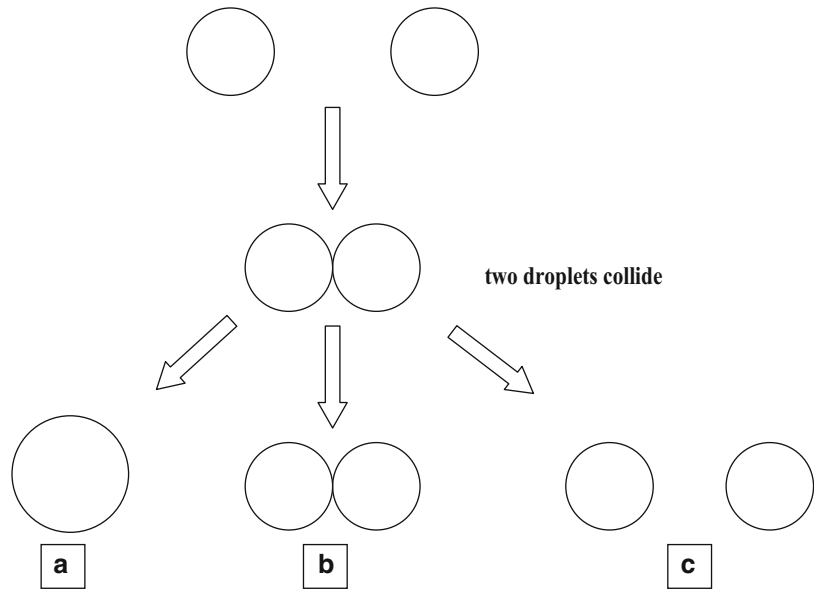
Emulsifiers

Emulsifiers must be able to:
- Adsorb at the interface between two liquids such as oil and water
- Reduce the interfacial tension of each liquid, enabling one liquid to spread more easily around the other
- Form a stable, coherent, viscoelastic interfacial film
- Prevent or delay coalescence of the emulsion droplets

Reduction of the interfacial tension facilitates emulsion formation, because it reduces the amount of energy needed to break up one liquid into droplets and to spread the other liquid around them. Formation of a film that prevents coalescence promotes emulsion stability.

All emulsifiers are surfactants, because all emulsifiers adsorb at the surface and reduce

Fig. 13.3 Diagram to illustrate what may happen after two droplets collide: (*a*) coalescence, (*b*) aggregation, and (*c*) droplets move apart again

two droplets collide

a

b

c

interfacial tension. However, all surfactants do *not* make good emulsifiers, because not all surfactants are able to form a stable film at the interface and prevent coalescence. The stability of the film is important in determining the stability and shelf life of the emulsion. Some emulsifiers work better than others do, in terms of forming a stable emulsion.

In general, large macromolecules such as proteins form stronger surface films than smaller surfactant molecules such as lecithin because of their greater ability to extend over the droplet surface. They also have a greater ability to interact with other groups within the same molecule or on different molecules and are able to form viscoelastic surface films.

Small molecules are not usually able to form stable interfacial films by themselves, and their role is normally that of a surfactant rather than an emulsifier, in that they lower interfacial or surface tension and promote spreading or wettability. Although they do not make good emulsifiers, they are often called emulsifiers. Many food scientists do not differentiate between surfactants and emulsifiers, and so the words may be used interchangeably in some cases. However, in the

world of a colloid scientist, there is a clear distinction between the two!

Characteristics of an Emulsifier
- Contains hydrophilic and hydrophobic sections (amphiphilic)

Functions of an Emulsifier

- Adsorbs at the oil/ water interface
- Reduces interfacial tension

   facilitates formation emulsion

- Forms a stable interfacial film
- Prevents coalescence

   promotes emulsion stability

Natural Emulsifiers

The best emulsifiers are proteins, which uncoil or denature and adsorb at the interface, and interact
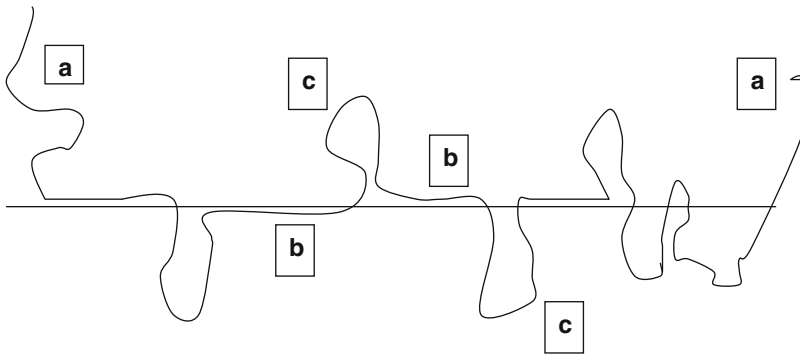
Fig. 13.4 Schematic diagram of a protein adsorbed at an interface: (*a*) tails, (*b*) trains, and (*c*) loops

to form a stable interfacial film. Proteins tend to uncoil such that their hydrophobic sections are oriented in oil, and their hydrophilic sections are oriented in water. Hence, a series of loops, trains, and tails may be envisioned at the interface, as shown in Fig. 13.4.

The loops and tails are able to interact with each other, thus forming a stable film that resists rupture. The proteins of *egg yolk* tend to be the best emulsifiers, as exemplified by their use in mayonnaise. These proteins are lipoproteins and are associated with each other and with phospholipids such as lecithin, in structures known as micelles. These micellar structures appear to be responsible for the excellent emulsifying properties of egg yolk proteins.

The *caseins* of milk are also excellent emulsifying agents. They are important emulsifiers in homogenized milk and in dairy desserts. In fresh (unhomogenized) milk, the caseins are associated with each other in structures known as casein micelles. Electron micrographs have shown that after homogenization, intact micelles are present at the fat globule surfaces, as well as individual protein molecules. It is thought that the micelles are responsible for the stability of homogenized milk, rather than the individual protein molecules.

Other food proteins used as emulsifiers include *meat* proteins and *soy* proteins. Lecithin is often considered to be an emulsifier. Lecithin is a surfactant and is useful for promoting wettability and aiding mixing of products such as hot drink mixes. It is also an essential ingredient in chocolate, where it aids in dispersion of the sugar and fat.

Lecithin does not usually form strong interfacial films by itself and so would not be the emulsifier of choice unless other emulsifiers or stabilizers were added.

However, proteins are usually present in food emulsions, which may allow for formation of a strong interfacial film involving lecithin. Soy lecithin may be added to emulsions containing egg yolk, in order to reduce the amount of egg yolk needed, since soy lecithin is cheaper than egg yolk.

Synthetic Emulsifiers or Surfactants

Most synthetic emulsifiers would more correctly be termed *surfactants*, because they are relatively small molecules compared with proteins, and they are used mainly to aid in dispersion of fat, rather than to stabilize emulsions.

Surfactants such as *mono-* and *diglycerides* are added to shortening and to cake mixes, to aid in dispersion of the shortening. Cakes are complex, in that they contain fat droplets and air bubbles, and so are both emulsions and foams. (Foams are discussed later in this chapter.) The mono- and diglycerides enable the shortening to be dispersed into smaller particles, and this promotes incorporation of a large number of air cells, which increases cake volume and promotes a more even grain in baked products (Chap. 15).

Glycerol monostearate is an example of a monoglyceride that is commonly used in foods. Acids may be esterified with monoglycerides to give another group of surfactants, including

sodium stearoyl-2-lactylate, which is often used in baked products. Two other groups of manufactured surfactants include the *SPANS*, which are fatty acid esters of sorbitan, and the *TWEENS*, which are fatty acid esters of polyoxyethylene sorbitan. Although all surfactants are amphiphilic, they have different degrees of hydrophobic (*lipophilic*) and hydrophilic character. This can be expressed as the **hydrophilic/lipophilic balance**, or **HLB**.

An HLB scale has been developed, which goes from 1 to 20. Surfactants with a low HLB (3–6) have more hydrophobic or lipophilic character. These would be used to form a w/o emulsion. Examples include glycerol monostearate and sorbitan monostearate (SPANS 60). Surfactants with a high HLB (8–18) have more hydrophilic character and form w/o emulsions. Examples would be polyoxyethylene sorbitan monostearate (TWEENS 60) or sodium stearoyl-2-lactylate. SPANS usually have a low HLB and form w/o emulsions, whereas TWEENS have a high HLB and form o/w emulsions. Use of the HLB scale may be going out of favor, yet is useful to food scientists to help them in determining which emulsifier is most suited to their needs.

Examples of Emulsions

French dressing is an example of a *temporary emulsion*, or in other words, an unstable emulsion that separates fairly soon after formation. The basic ingredients of French dressing are oil (the dispersed phase), vinegar (the continuous phase), dry mustard, and paprika. Other ingredients may be added for flavor. The "emulsifiers" used here are the mustard and paprika. Combining the ingredients and shaking them vigorously forms the emulsion. The mustard and paprika adsorb at the interface and reduce interfacial tension as the dressing is shaken, thus facilitating formation of an emulsion, yet they do not interact at the interface to form a stable film. Hence, when shaking is stopped, the oil droplets are not protected, and so they soon coalesce, and the oil and vinegar layers separate.

Mayonnaise is an example of a **permanent emulsion**, since it is stable and does not separate under normal handling conditions. The main ingredients of mayonnaise are oil (the dispersed phase), vinegar (the continuous phase), and egg yolk. The egg yolk proteins, being excellent emulsifiers, protect the oil droplets against coalescence. Mayonnaise usually contains about 75 % oil, which exists as stable droplets surrounded by a thin aqueous film. It is unusual in that it contains so much more dispersed phase than continuous phase. Generally, the continuous phase of an emulsion is present in greater quantity.

Mayonnaise is made by slowly pouring small amounts of oil at a time into the vinegar and egg yolk mixture and continuing to beat to break up the oil into droplets and form the emulsion. As more oil is added, more droplets are formed, and the surface area increases dramatically. The continuous phase spreads out to surround the oil droplets and becomes a thin film. It is hard for the droplets to move around, since they are packed tightly together, and separated only by a thin film of aqueous phase, and so the mayonnaise becomes very thick and may even be stiff enough to cut. Some salad dressings may be similar to mayonnaise, except that they contain less oil and have a thinner consistency. Adding stabilizers such as gums or starches often enhances the stability of the emulsion.

Milk is an example of an emulsion that occurs in nature (Chap. 11). Milk contains about 3.5 % fat in emulsified form. In fresh (unhomogenized) milk, the fat droplets are stabilized by a complex protein membrane known as the milk fat globule membrane. Fresh milk is a stable emulsion; however, it will cream fairly quickly if left to stand. The fat droplets vary in size from about 0.1 to 10 μm. There are many more small droplets than large ones; however, because of their size, the larger ones account for most of the fat. Because of the density difference between the milk fat and the aqueous phase, the fat droplets tend to rise though the milk. This is especially true for the larger droplets.

Milk fat globules are unique in that as they rise, they tend to cluster together. This results in larger fat particles, which rise even faster. Hence,

after a few hours, a cream layer can be seen at the top of the milk. This is not a true separation of oil and water, since the cream layer is still an emulsion and the interfacial film is still intact. The milk has separated into a concentrated emulsion and a dilute one. The cream can be removed and either used as cream or made into butter.

Homogenizing the milk, which breaks up the fat globules into much smaller ones, prevents this creaming effect. By Stokes law, the smaller particles would take almost infinite time to coalesce and aggregate, thus remaining as small droplets.

Factors Affecting Emulsion Stability

Obviously, the main factor affecting emulsion stability is the *emulsifier* itself. As has been discussed, emulsifiers that form stable interfacial films produce stable emulsions. There must also be sufficient emulsifier to completely coat the surface of all the droplets in order to ensure stability. *Droplet size* is also important because larger droplets are more likely to coalesce. Also, because of the density difference between oil and water, large oil droplets will tend to rise through the emulsion more quickly, creating a more concentrated emulsion closer to the surface, as is seen in milk. This may cause the emulsion to break.

Changing the *pH* by adding acid or changing the *ionic strength* by adding salts may reduce the stability of the interfacial film, especially if it is made of protein. Such changes may denature the protein, as explained in Chap. 8, and cause the emulsion to separate.

Another factor affecting emulsion stability is the *viscosity* of the emulsion. The thicker the emulsion, the slower the movement of the molecules within the system and the longer it will take for the two phases to separate. Emulsions can be made thicker by adding ingredients such as gums, pectin, or gelatin. If gums are added to French dressing, a permanent emulsion may be formed without the need for egg yolk as the emulsifier.

Gums are often added to emulsions as stabilizers. They are not emulsifiers themselves, and they do not normally adsorb at an interface, because they are hydrophilic. However, they act by increasing the viscosity of the system, which slows movement, and hence reduces the number of collisions between droplets. This slows down and may even prevent separation of emulsions.

Storage and *handling* affect emulsion stability. Although some emulsions are termed permanent, it should be noted that all emulsions are delicate systems that are inherently unstable, because they contain two immiscible liquids, and the wrong handling conditions can cause emulsion breakage.

Temperature also affects emulsion stability. When emulsions are warmed, the oil droplets become more fluid and coalescence is more likely. On the other hand, cooling an emulsion to refrigeration temperatures may cause some solidification of the oil droplets, depending on the composition of the oil. This may enhance stability. Most emulsions do not survive freezing conditions. This is usually because the proteins at the interface become denatured, or because the interfacial film is physically disrupted by the formation of ice crystals. *Gums* are often added to emulsions that are to be frozen to enhance their stability.

Heat and *violent shaking* are also likely to disrupt emulsions. For example, cream is converted to butter by churning the warm emulsion. The emulsion breaks, the aqueous phase is drained off, and a water-in-oil emulsion is formed, with water droplets (approximately 18 %) dispersed throughout the butterfat.

Factors Affecting Emulsion Stability
- Type of emulsifier
- Concentration of emulsifier
- Droplet size
- Changing pH or ionic strength
- Viscosity
- Addition of stabilizers
- Heating, cooling, freezing, and/or shaking

Foams

Foams make a vital contribution to the volume and texture of many common food products. They give volume and a distinctive mouthfeel to

products such as whipped cream and ice cream and they give a light, airy texture to baked goods. Improperly formed or unstable foams result in dense products with a low volume, which are unacceptable to consumers. Foams are inherently unstable, and it is imperative that food scientists increase their knowledge of the factors affecting foam stability, in order to enhance the quality and shelf life of these products.

A foam contains gas bubbles dispersed in a liquid continuous phase. The liquid phase may be a simple dispersion, as in egg white, which is a dilute protein dispersion, or it may be complex, containing emulsified fat droplets, ice crystals, and/or solid matter. Examples of complex food foams include ice cream, angel food cake, marshmallows, and yeast-leavened breads. Foams such as meringue and baked goods are heat-set, which denatures the protein and converts the liquid phase to a solid phase. This gives permanence to the foam structure.

Comparison Between Foams and Emulsions

Foams are similar to emulsions, in that the gas bubbles must be protected by a stable interfacial film otherwise they will burst. Therefore, the factors affecting emulsion formation and stability also apply to foams, and, in general, good emulsifying agents also make good foaming agents. However, there are some important differences between emulsions and foams. The bubbles in foams are generally much bigger than the droplets in emulsions, and the continuous phase surrounding the gas bubbles is very thin.

In fact, it is the continuous phase that has colloidal dimensions, rather than the dispersed phase. The density difference between the two phases is much greater in a foam, and there is a tendency for the liquid continuous phase to drain due to gravity, and for the gas bubbles to escape. The factors affecting formation are similar for both emulsions and foams. However, there are additional factors involved in foam stability.

Foam Formation

In order to produce a foam, energy must be supplied (by whipping) to incorporate gas into the liquid, to break up large bubbles into smaller ones, and to spread the liquid phase around the gas bubbles as they form. The foaming agent, which is contained in the liquid phase, adsorbs at the surface of the liquid, reducing surface tension and also forming a film around the gas bubbles. It is important that the surface tension is low, so that the liquid will spread rapidly around the gas bubbles during whipping. If newly formed gas bubbles are not immediately coated with foaming agent, they will burst or coalesce and be lost.

The amount of energy supplied during whipping is also important; the higher the energy, the smaller the bubbles and the greater the foam volume, provided that sufficient foaming agent is present to completely coat and stabilize the bubbles.

Foam Stability

The stability of a foam may be measured in terms of loss of foam volume over a period of time. When a liquid is whipped to form a foam, the volume of the liquid increases due to incorporation of air. If the foam is stable, the volume does not change very much. However, loss of air from an unstable foam may cause a considerable reduction in volume.

Foam stability may be *reduced* due to the following factors:

- The tendency of the liquid film to drain due to gravity. As it drains, a pool of liquid gathers at the bottom of the container, and the film surrounding the gas bubbles becomes very thin. This may allow the gas to escape and the volume of the foam to shrink.

- The tendency for the film to rupture and allow coalescence or escape of gas bubbles.
- Diffusion of gas from small bubbles to larger ones. This results in fewer bubbles and the foam shrinks.
- Evaporation of the continuous phase also affects foam stability, but to a lesser extent. If the liquid evaporates, gas bubbles burst and foam volume is reduced.

If gas bubbles are lost due to any of these factors, a more dense, low-volume foam is produced, which is not usually desirable, especially in foods such as angel food cake or ice cream.

To produce a *stable* foam with a high volume, film rupture, liquid drainage, and evaporation must be prevented or at least minimized. As with emulsions, the gas bubbles must be stabilized by the presence of a stable interfacial layer, which resists rupture. However, the composition of the continuous phase is also very important in determining foam stability. The liquid phase must have a low vapor pressure, so that it does not evaporate readily at storage and handling temperatures.

More importantly, drainage of the continuous phase must be minimized. Thick liquids drain more slowly than thin ones, and so increasing the viscosity of the continuous phase will reduce drainage. A high viscosity is essential if a stable foam is to be produced.

Foaming Agents

The two most important characteristics of a foam are foam *volume* and foam *stability*. Foam volume depends on the ability of the foaming agent to adsorb at the interface and rapidly reduce interfacial tension and on the level of energy input during whipping. Foam stability depends on the ability of the foaming agent to produce a stable interfacial film and a viscous continuous phase. Although all surfactants are able to reduce surface tension and produce foams, not all are able to form stable foams. In fact, some may act as foam suppressants!

A good foaming agent has the same characteristics as an emulsifier, in that it is able to adsorb at the interface, reduce interfacial tension, and form a stable interfacial film that resists rupture. As might be expected, the best foaming agents used in foods are proteins. Although many proteins are able to produce foams, egg white proteins are superior foaming agents and are used in food foams such as meringues, angel cake, and other baked goods. Other proteins used as good foaming agents include gelatin and milk proteins.

When egg white is whipped (Chap. 10), the proteins denature at the interface and interact with one another to form a stable, viscoelastic, interfacial film. Some of the egg white proteins are glycoproteins containing carbohydrate. When these proteins adsorb at the interface, the carbohydrate sections orient toward the aqueous phase. Being hydrophilic, they bind water and increase the viscosity of the liquid. This helps to reduce drainage, thereby contributing to foam stability.

Gelatin is a good foaming agent, and a warm gelatin sol can be whipped to three times its original volume. When cooled, the gelatin solidifies or forms a gel, which traps the air bubbles and stabilizes the foam; marshmallows are gelatin foams.

The Effect of Added Ingredients on Foam Stability

Many food foams have additional ingredients added to *enhance stability*. For example, egg white foams, such as meringue or angel food cake, also have sugar added. The *sugar* increases the viscosity of the liquid, aiding stability. It also protects the proteins from excessive denaturation and aggregation at the interface. Too much interaction results in an inelastic film which is not resistant to rupture, and in reduced foam volume. Therefore it is important to guard against this when making egg white foams.

Factors Affecting Foam Stability

- Drainage of the liquid film between gas bubbles
- Rupture of the interfacial film around gas bubbles
- Diffusion of gas from small to large bubbles
- Evaporation of the continuous phase

Factors Promoting Foam Stability

- Stable viscoelastic surface film
- Very viscous continuous phase
- Low vapor pressure liquid

Effects of Added Ingredients

Foam stabilizers	Foam destabilizers
Gums	Lipids
Thickeners	Phospholipids
Sugar	Small molecule surfactants
Acid	Salts
Solid particles	

Acid, such as cream of tartar or lemon juice, may also be used to increase foam stability. Addition of acid reduces the pH, which reduces the charge on the protein molecules and usually brings them closer to their isoelectric point. This generally results in a stronger, more stable interfacial film. When added to egg whites, acid prevents excessive aggregation at the interface. However, acid delays foam formation. It may therefore be added toward the end of the whipping process. In the case of egg whites, it is often added at the "foamy" stage. Whipping is not complete until the egg whites have formed stiff peaks. (Egg white foams are discussed in more detail in Chap. 10.)

Other ways to increase viscosity of the continuous phase include addition of *gums* and other *thickening agents*. Also, addition of *solid matter* may promote stability. Whipped cream, for example, is stabilized by solidified fat globules that are oriented in the continuous liquid film. The emulsified fat increases viscosity and is responsible for the stability of whipped cream. To form a stable foam, cream to be whipped must contain at least 30 % fat. Creams with lower fat contents may be whipped successfully if thickening agents such as carrageenan are added. If the cream is warm and too much of the butterfat is liquid, then whipping will not produce a stable foam. Instead, the emulsion will break and the cream will be converted to butter.

Ice cream is another example of a complex foam, which is stabilized by emulsified fat droplets and small ice crystals oriented within the continuous phase. Angel food cake contains solid particles, in the form of flour, which are folded into the egg white/sugar foam. The flour contributes to stability by increasing the viscosity of the liquid, which minimizes film drainage. The increased viscosity and presence of solid particles also reduces breakage of the interfacial film, hence minimizing loss of foam volume.

Anti-foaming Agents and Foam Suppressants

As all cooks know, egg whites will not whip to a stable foam if there is any egg yolk present (Chap. 10). This is because the phospholipids and lipoproteins in the yolk adsorb at the surface, in competition with the egg white proteins, and interfere with formation of a stable egg white protein film. Unlike the egg white glycoproteins, which are hydrophilic, the phospholipids and lipoproteins are unable to increase the viscosity of the continuous phase, because they are hydrophobic, and so orient away from the water. This prevents formation of a stable foam.

Such molecules are termed ***foam suppressants***. They suppress foam volume because they adsorb at the interface, thus suppressing adsorption of the desired foaming agent and preventing it from forming a stable foam. They do not have the properties required to form a stable film or to sufficiently increase the viscosity of the continuous phase. Hence, their presence makes formation of a stable foam impossible. Typical foam

suppressants include fats, phospholipids, and other small amphiphilic molecules.

Salts also tend to act as foam suppressants, because they weaken interactions between the protein molecules at the surface, thus weakening the interfacial film around the gas bubbles. However, their effect is not as important as surfactant molecules, because they do not adsorb at the interface.

Anti-foaming agents are able to break up foams or prevent them from forming. Anti-foaming agents are added to fats and oils used in frying, to prevent foaming during the frying process. Like foam suppressants, they act by adsorbing at the air/liquid interface in place of the foaming agents, and because they do not have the characteristics of a foaming agent, they prevent foam formation.

Other Colloidal Systems

Although this chapter covers emulsions and foams, gels should be mentioned, since they are also colloidal systems. A **gel** consists of a liquid dispersed phase held within a solid continuous phase. Gels are formed when conditions allow the solid dispersed phase of a colloidal dispersion or sol to bond at strategic points, forming a three-dimensional network that traps liquid within itself. Conditions that are likely to cause formation of such a network include heating, cooling, addition of calcium or other divalent ions, and/or change of pH. Important food gels include starch gels (discussed in Chap. 4), pectin gels (Chap. 5), and gelatin, egg white, and other protein gels (Chap. 8).

Conclusion

Food emulsions and foams are complex colloidal systems, and understanding of their formation and stability is important if the quality and shelf life of these products is to be improved.

Emulsions contain liquid droplets stabilized by an interfacial layer of emulsifier and dispersed throughout a liquid continuous phase. Foams are similar, although the dispersed phase consists of large gas bubbles surrounded by a very thin, continuous, liquid film. The nature of the emulsifier or foaming agent is crucial in determining stability. It must adsorb at the interface, reduce surface tension, and form a stable, viscoelastic interfacial layer that resists rupture, so that coalescence of liquid droplets or loss of gas bubbles is avoided. Additional factors are important in foam stability; it is important that the liquid film between the gas bubbles is very viscous, so that drainage due to gravity is minimized. Evaporation of the liquid must also be prevented during normal storage and handling conditions.

Both natural and synthetic emulsifying agents are available to food companies. The best emulsifiers and foaming agents are proteins. Egg yolk proteins are known as the best emulsifiers, whereas egg white proteins are considered to be the best foaming agents used in food products.

Notes

CULINARY ALERT!

Glossary

Adsorb To bind to a surface.

Amphiphilic A molecule containing both hydrophobic and hydrophilic sections.

Coalescence (coalescing) Two liquid (or gas) droplets merge (merging) to form one larger droplet.

Colloidal system Emulsions, foams, dispersions (or sols), and gels are all colloidal systems. A colloidal system contains one phase (usually the dispersed phase) with dimensions ranging mainly from 0.1 to 10 μm. The dispersed phase contains large numbers of small droplets or particles, and so the surface or interfacial area of this phase is very large. This is an important characteristic of colloidal systems.

Continuous phase The phase or substance that surrounds the liquid droplets or gas bubbles in an emulsion or foam.

Dispersed phase The discrete bubbles (air, carbon dioxide, or liquid) that are surrounded by liquid in an emulsion or foam.

Emulsifier A substance that enables two normally immiscible liquids to be mixed together without separating on standing.

Emulsion An emulsion contains liquid droplets stabilized by a layer of emulsifier and dispersed throughout a liquid continuous phase.

Foam A foam contains gas bubbles coated with a stable interfacial layer and surrounded by a thin, viscous liquid continuous phase. In food foams, the gas is usually air or carbon dioxide.

Foaming agent A molecule that is able to promote foam formation. Useful foaming agents in foods are also able to promote foam stability by forming a stable interfacial layer and also by increasing the viscosity of the continuous phase.

Foam suppressant A molecule that prevents or hinders foaming, generally by adsorbing to the interface in place of the desired foaming agent and interfering with the action of the foaming agent.

Gel A two-phase system consisting of a solid continuous phase and a liquid dispersed phase. A gel may be considered to be a three-dimensional network with liquid trapped within its spaces.

Hydrophilic Water-loving. Hydrophilic molecules are either charged or polar and have an affinity for water.

Hydrophilic/lipophilic balance or HLB A scale that goes from 1 to 20 and indicates the ratio of hydrophilic and hydrophobic groups on a molecule. It is used to determine the suitability of emulsifiers when formulating an emulsion. A high HLB indicates a molecule with more hydrophilic groups, which is suitable for o/w emulsions. A low HLB indicates that there are more lipophilic groups, and the molecule has a greater affinity for oil and is more suited for w/o emulsions.

Hydrophobic Water-hating. Hydrophobic molecules are nonpolar and have an affinity for apolar solvents.

Interfacial tension The force required to increase the interfacial area of a liquid, or to spread it over a surface such as oil. See also, surface tension.

Lipophilic Fat-loving, or water-hating. Lipophilic molecules are nonpolar and have an affinity for lipids and other apolar solvents.

Oil-in-water or o/w emulsion An emulsion containing oil droplets dispersed in water. Oil is the dispersed phase and water is the continuous phase.

Permanent emulsion A stable emulsion that does not separate over time.

Surface tension The force required to increase the surface area of a liquid, or to spread it over a surface. Surface and interfacial tension are often used interchangeably. Generally, surface tension applies at the surface of a liquid (i.e., when it is in contact with air), whereas

interfacial tension applies when two liquids are in contact with each other.

Surface-active A molecule that adsorbs at the surface of a liquid. Surface-active molecules contain both hydrophobic and hydrophilic sections, and it is energetically favorable for them to exist at the interface rather than in the bulk phase of a liquid.

Surfactant A surface active molecule (see above).

Temporary emulsion An unstable emulsion, which separates into two layers on standing.

Viscoelastic Exhibits both viscous (liquid) and elastic (solid) properties. In other words, the material will flow if force is applied, but it will also stretch. When the force is removed, the material does not return completely to its original position. It is important for an emulsifier film to flow around droplets to cover temporary bare patches, and also to be able to stretch, so that when disrupted, it does not break.

Water-in-oil or w/o emulsion An emulsion containing water droplets dispersed in oil. Water is the dispersed phase and oil is the continuous phase.

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