Packaging and the Shelf Life of Vegetable Oils

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17.1 INTRODUCTION

The word oil is derived from the Latin word oleum, originally used for olive oil, but nowadays it means any of numerous combustible and unctuous substances that are liquid at room temperature (this distinguishes them from fats) and soluble in many organic solvents but not in water. Vegetable oils are derived from plants and chemically are composed of triglycerides and several other minor components, which may be very important for different aspects. This chapter deals exclusively with edible, vegetable oils. Lipids in general, and edible vegetable oils in particular, are very important in foods. They are, however, vulnerable to quality deterioration and must be adequately protected by packaging throughout their commercial life.

Sources of edible vegetable oils are many and varied, and their quality attributes such as nutritional properties, health benefits, lipid composition, odor, and color are very important. A precise knowledge of these attributes and their changes throughout the supply chain is required to guide shelf life testing and estimation. Oils are generally stable microbiologically due to very low moisture content. However, they are subject to important chemical and physical changes. Specific indices of failure (IoFs) of these products will be discussed, as will the role that different packaging materials and packages may have on their shelf lives.

17.1.1 VEGETABLE OIL SOURCES AND MARKETS

Vegetable oils are derived from both annual (such as sunflower and soybean) and perennial (such as palm and olive) plants, and oil accumulates both in seeds (such as palm kernels and cottonseeds) and in fruits (such as olive, avocado, palm, and coconut). More detailed information on edible oils sources and their features can be found in specialized books such as those by Gunstone (2002) and Bockisch (1998).

Vegetable oils are produced and commercialized worldwide in very large quantities; global production of the major oilseeds is estimated at over 400 million tonnes per year. The two most widely produced edible oils are soybean and palm, with about 30 million tonnes of each produced annually worldwide; about 8–10 million tonnes of rapeseed and sunflower seed oils are produced annually, and 2.5–5 million tonnes each of oils such as olive, peanut, or cottonseed. Approximate world consumption of different vegetable oils is shown in Figure 17.1.

The greatest amounts of soybean and palm oils are used for cooking, as well as for margarine and soap production and even biofuel generation. The oils mainly or exclusively used for direct consumption and cooking or frying, such as olive, corn, and peanut oils, are produced in relatively
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Small quantities commercially but are the ones for which package protection and strategies for shelf life extension are probably more crucial.

17.1.2 Vegetable Oil Chemical Composition

Several factors can affect the composition of a vegetable oil; many of them are related to the technological processes used for obtaining the oil but the majority are related to the vegetable oil source. Together with extrinsic factors coming from the packaging and the environment, the oil’s compositional aspects primarily influence its shelf life, giving it more or less sensitivity to light, O\textsubscript{2}, temperature, enzymes, and all the potential causes of shelf life reduction. The main components of vegetable oils (and of all edible lipids) are triglycerides, that is, esters of glycerin and free fatty acids, normally present as 98–99% of the total mass. The first and greatest variability in oil composition depends on which fatty acids are linked and with which of the three possible hydroxyls of glycerin. The simplified compositions of various vegetable oils are presented in Table 17.1.

The sensitivity to possible oxidation phenomena, that is, the level of unsaturated acids, and the degree of natural resistance to oxidation, that is, the level of antioxidant tocopherols (vitamin E), is very important. The antioxidant effects of several tocopherols, and vitamin E in particular, have been evaluated on the oxidative stability of virgin olive oils (Baldioli et al., 1996), as well as soybean oils (Jung and Min, 2006).

Vitamin E, in spite of its importance, may be considered a minor component of edible vegetable oils. Equally, other lipophilic constituents are present in low or very low concentrations, for

![Figure 17.1](http://www.soystats.com/2005/page_35.htm)  

<table>
<thead>
<tr>
<th>Vegetable Oil</th>
<th>Saturated Fatty Acid (%)</th>
<th>Monounsaturated Fatty Acid (%)</th>
<th>Polyunsaturated Fatty Acid (%)</th>
<th>Vitamin E (mg/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut oil</td>
<td>85.2</td>
<td>6.6</td>
<td>1.7</td>
<td>66</td>
</tr>
<tr>
<td>Cotton seed oil</td>
<td>25.5</td>
<td>21.3</td>
<td>48.1</td>
<td>42.77</td>
</tr>
<tr>
<td>Wheat germ oil</td>
<td>18.8</td>
<td>15.9</td>
<td>60.7</td>
<td>136.65</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>14.5</td>
<td>23.2</td>
<td>56.5</td>
<td>16.29</td>
</tr>
<tr>
<td>Olive oil</td>
<td>14.0</td>
<td>69.7</td>
<td>11.2</td>
<td>5.10</td>
</tr>
<tr>
<td>Corn oil</td>
<td>12.7</td>
<td>24.7</td>
<td>57.8</td>
<td>17.24</td>
</tr>
<tr>
<td>Sunflower seed oil</td>
<td>11.9</td>
<td>20.2</td>
<td>63.0</td>
<td>49.0</td>
</tr>
</tbody>
</table>

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example, vitamin K, carotenoids, phytosterols, hydrocarbons, polyphenols, alcohols, pigments, free fatty acids, flavoring, and aromatic substances. These are not directly related to oil stability over time, as is the case with unsaturated glycerides or antioxidant tocopherols, but they are important for their nutritional implications and sensory appreciation and, therefore, definitely pertinent to shelf life studies.

17.1.3 Vegetable Oil Processing

When fruits or seeds are separated from plants, the specificity of the cultivar, the degree of maturity, and climatic effects have already affected oil composition and its sensitivity to aging; however, these intrinsic aspects of the future product’s shelf life are not definitely established yet. Other factors related to the handling operations and processing can still strongly influence oil stability.

Possible crushing or bruising of the vegetable sources during delivery to the extraction plants can directly modify the chemical composition and increase the product sensitivity to microbial attacks and enzymic degradation (Loew, 1973; Pritchard, 1983). Generally speaking, all possible measures that can reduce or avoid mechanical damage to seeds or fruits along the supply chain must be put into practice as a guarantee of longer shelf lives of the extracted oils.

The main technological problem in producing oil from a vegetable source, both fruits and seeds, is lipid extraction from the solid and heterogeneous material. Triglycerides reside in specialized locations in seeds and fruits (mainly in cotyledons and endosperm cells in seeds and in mesocarp vacuoles in fruits) and must be extracted in the most selective and safest way. The first unit operation, which follows preliminary cleaning steps, is always size reduction; that is, by crushing or milling the raw material, the oil extraction is made easier, but at the same time, the sensitive lipids are obviously exposed to light, heat, and O₂ and thus become susceptible to oxidation during their processing. After size reduction, the processes differ according to the vegetable source, the tradition, and the final results expected.

The traditional way of extracting oils (still largely used for olives) is physical extraction by pressure; an innovative form of physical extraction is the use of centrifuges, which have the great advantage, compared with the traditional way, of quickly separating the oil from the aqueous phase, thereby avoiding potential damage to the quality and stability of the oil.

Chemical extraction, which is faster, less expensive, and achieves higher yields, is the modern way of processing vegetable sources, particularly seeds. Hexane or similar petroleum-derived solvents are used. Chemical extraction makes it possible to recover about 99% of the oil contained in the seeds and avoids the overheating of the oil and meal that often occurs with mechanical extraction.

The crude oils must be refined before they can be considered edible. Filtration removes contaminants that could contribute to microbial, enzymic, and chemical deterioration. Distillation at low temperature is used to eliminate residual solvents. Winterizing (filtering the oil at near-freezing temperatures) is used in the preparation of some oils (particularly salad oils) to remove triglycerides that might cause them to become turbid. Some oils may be partially hydrogenated to produce cooking oils or various ingredient oils. Light hydrogenation makes the oil more resistant to rancidity, particularly those oils very rich in polyunsaturated triglycerides. Bleaching is one more possible operation in the refining process, particularly of seeds oils; it removes coloring matter and other minor components that are adsorbed on inorganic adsorbents such as montmorillonite clay or activated carbon. The last operation is the deodorizing step, which removes unwanted flavors and odors.

17.2 Vegetable Oil Quality Attributes

For vegetable oils the expected final uses and destinations drive the definition of quality attributes. Vegetable oils come from very different raw materials and can be used as foods, as ingredients and for cooking. For these reasons their quality attributes are numerous and very different. A short
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overview of the quality attributes of vegetable oils will be given under three headings: sensory, nutritional, and technological characteristics.

17.2.1 SENSORY CHARACTERISTICS

17.2.1.1 Color
Color plays an important role in specifications for commercial oils, even if the expectations can be very different. For seed oils generally, a clear, almost colorless product is desired, whereas for olive and other common plant oils, more intense shades are well accepted. The color is deeply affected by the vegetable source (e.g., the fruit maturity) as well as by the extraction and refining processes, which can, in general, reduce the coloring substances originally present.

17.2.1.2 Odor
Volatiles in oils come straight from the vegetable source used, but they are also a consequence of the process applied to produce the oil. They are responsible for the odor of the oil that can be a positive and typical attribute of the product, but may also indicate a negative change in the oil, frequently related to oxidation and rancidity development. There are many different substances that are volatile and have sensory effects; some of them have extremely low perception thresholds in the range of ppb or even less, for example, hexanal, one of the main final products of the autoxidation of unsaturated fatty acids.

17.2.1.3 Flavor
Taste and flavor are sensory attributes particularly relevant for salad or ingredient oils (e.g., for mayonnaise production or fish canning). Criteria for the organoleptic assessment of virgin oils have been available in Europe since 1991 (EEC, 1991), making virgin oil the first food item in Europe for which a sensory panel analysis is mandatory for legal compliance.

17.2.2 NUTRITIONAL CHARACTERISTICS

17.2.2.1 Polyunsaturated Fatty Acids
The polyunsaturated fatty acid (PUFA) content of oils is that fraction of fatty acids with more than one double bond within the molecule. Although general agreement on the role of PUFAs has not yet been achieved, omega-3 and omega-6 fatty acids appear to reduce the risk of cardiovascular disease and heart attacks. Omega-3 fatty acids can also reduce prostate cancer growth and slow histopathological progression. However, other studies show that the consumption of high amounts of PUFAs slightly increases low density lipoprotein (LDL) levels, and omega-6 fatty acids can contribute to allergies and inflammation, and may increase the risk of developing breast cancer in postmenopausal women and prostate cancer in men. All the supposed negative effects of PUFAs are related to their oxidation products, to free radical accumulation, and to the possible presence of trans-isomer fatty acids.

Partially hydrogenated vegetable oils can show a high proportion (up to 45%) of trans-fatty acids. This is a peculiarity of PUFAs, which can assume a cis or trans conformation depending on the geometry of the double bond. Trans-fatty acids give the triglycerides properties similar to saturated fatty acids in many respects, including increasing LDL and reducing high density lipoprotein (HDL) cholesterol. Ortega-Garcia et al. (2006) demonstrated that deodorization is the main step that increased the levels of trans-fatty acids, with the extent depending on temperature and heating time.

17.2.2.2 Essential Fatty Acids
Essential fatty acids (EFAs) are those fatty acids that cannot be synthesized by any known chemical pathways within humans but must be obtained from the diet. Many vegetable oils are excellent
sources of EFAs, particularly soybean, rapeseed, safflower, and sunflower seed oils. Initially (1930–1950) only two PUFAs were defined as essential, namely arachidonic (20:4) and linolenic (18:3) acids; later studies demonstrated that any omega-3 and omega-6 fatty acid can remedy fatty acid deficiency. EFAs are particularly useful in the central nervous system. Nowadays it is recognized that some PUFAs are essential in some pathological states and in particular life phases such as lactation.

17.2.2.3 Fat-Soluble Vitamins
The fat-soluble vitamins A, D, E, and K are essential for the normal growth and development of humans, and their deficiency is associated with specific disease states. Recommended daily dietary allowances are in the range of 10–100 µg, except for vitamin E, of which at least 15 mg is required. They are present to different extents in vegetable oils in active forms or as precursors, with vitamin E always being the most abundant and important for its antioxidant activity.

17.2.2.4 Natural Antioxidants
For a long time the topic of antioxidants in oils has been approached only in terms of possible additives for protecting the product against rancidity. More recently, however, the presence of natural antioxidants in vegetable oils has been emphasized; their presence is both a nutritional attribute relevant to the consumer and a protective aid to the product. Antioxidants are compounds that extend the induction period of oxidation or slow down the oxidation rate.

Besides tocopherols and tocotrienols (both occur in alpha, beta, gamma, and delta forms, each form having slightly different vitamin E activity), other interesting antioxidants are always present in vegetable oils. Polyphenols (e.g., hydroxytyrosol, caffeic, protocatechuic, and syringic acids) are largely present in olive oil (Papadopoulos and Boksou, 1991). Phospholipids, which like lecithin, come from membrane constituents of vegetal cells, are widely diffused. Beta-carotene has been found both in seed and fruit oils. Lignans, which are polyphenols such as pinoresinol, podophyllotoxin, and staganacin, have been found in several oils coming from seed oils, particularly flax, sesame, and soybean. Among antioxidants, tocopherols are the most important group in various vegetable oils.

17.2.3 TECHNOLOGICAL CHARACTERISTICS
There are few technological characteristics that are important for the possible use of oils as ingredients, or for cooking or frying. These attributes rarely change significantly unless very long or very bad storage conditions are assumed.

17.2.3.1 Heat Stability
The ability to withstand high temperatures such as those encountered in canning, frying, or cooking operations, without thermal decomposition or other negative side-effects, has been termed heat stability and is an important attribute of commercial oils. Frying and baking temperatures are often 200°C or higher, and at these temperatures polymers are formed via autoxidative pathways or thermal polymerization, which increases the viscosity and contributes to foam production.

17.2.3.2 Oil Crystallizability
The winterizing operation has been already mentioned as an important step in the preparation of salad oils, conducted in order to prevent the possible crystallization of the heaviest triglycerides that might cause turbidity. Crystallization of oils depends on their triglyceride composition, which determines their melting temperature (Sato, 1988). Crystallization is also a process used by the vegetable oil industry to obtain specific fractions with given properties. At subzero temperatures, a lipid is frequently a mixture of a liquid phase entrapped in a solid phase made of triglyceride crystals (Calligaris et al., 2004); this has consequences for the oxidative stability of oils as explained later.
17.2.3.3 Emulsification Ability
In several food preparations, oils have to be emulsified with an aqueous phase; manufacture of margarine, ice cream, and mayonnaise are typical examples. The approach to emulsification largely depends on oil composition (the fraction of polar lipids, in particular), which, in turn, affects surface energies, viscosities, and other rheological properties that influence the emulsification ability of different oils.

17.3 DETERIORATIVE REACTIONS AND INDICES OF FAILURE FOR VEGETABLE OILS
The stability of a vegetable oil must be regarded as the ability to maintain the original sensory and texture characteristics that are present immediately after manufacture for as long a time as possible despite the ongoing changes in its molecular structure (Kristott, 2000). The main deteriorative reactions that influence the quality of packaged vegetable oils during their shelf life are described in the following text and the IoFs to quantify the extent of deterioration are also defined.

17.3.1 Enzymic Reactions
Enzymes are involved in many different ways in deteriorative reactions of vegetable oils, and the final products of their activity may often be considered IoFs. The action of three main classes of enzymes will be discussed: lipases, lipoxygenases, and polyphenol oxidases.

17.3.1.1 Lipases
The cleavage of fatty acids from the triglyceride molecule in the presence of moisture is a reaction that leads to the formation of undesired acidity and, possibly, unpleasant off-flavors, particularly if short- and medium-chain length fatty acids are released. Lipases have both endogenous and microbiological origins. They can catalyze the hydrolysis of fatty acids at specific positions on triglyceride molecules, leading to the so-called lipolytic rancidity.

A special type of lipolytic rancidity development is the so-called ketonic rancidity. Molds of the genera *Penicillium*, *Aspergillus*, and *Citromyces* can release enzymes called desmolases, which catalyze the production of methyl ketones and alcohols from the liberated fatty acids. The methyl ketones formed by such enzymes have very characteristic sweet and fruity odors that resemble that of perfume (Kristott, 2000).

Because enzymes are usually inactivated at temperatures above 60°C and by the processes of refining and deodorization, lipolytic rancidity development can only occur in vegetable oils that have not been processed at high temperatures, such as the cold-pressed oils. The liberation of free fatty acids from triglycerides during storage makes an oil unpalatable and, therefore, shortens its shelf life. Spontaneous hydrolysis of triglycerides can also be triggered by heat in the presence of moisture, but this type of reaction is not of practical relevance to the stability of edible oils because these are usually stored at or below ambient temperature (Kristott, 2000).

17.3.1.2 Lipoxygenases
Lipoxygenases are nonheme iron-containing enzymes that catalyze the oxygenation of the 1,4-pentadiene sequence of PUFAs to produce their corresponding mainly 9 and 13 isomers, which are unstable and rapidly transformed into a variety of volatile and nonvolatile substances (Salas et al., 1999). The basic stoichiometry of the lipoxygenase oxidation reaction is the same as for autoxidation, but, in common with many enzyme reactions, it is both regiospecific and stereospecific about the substrate. The flavor components formed, such as aldehydes and alcohols, can be directly responsible for off-flavor genesis (Amirante et al., 2006). Virgin olive oil is a singular case because this enzymic pathway is also responsible for the genesis of its genuine and appreciated flavor. In addition, it has been suggested that lipoxygenase plays a role in the oxidation of pigments of the olive fruit (Georgalaki et al., 1998).
17.3.1.3 Polyphenoloxidases

The enzymic oxidation of polyphenols may be an important deteriorative reaction for some vegetable oils, in particular olive oils that have a high polyphenol content. The presence of such enzymic activities results in browning of olive fruits and may influence the oxidative stability of the oil during storage. Georgalaki et al. (1998) found that significant polyphenoloxidase and lipoxygenase catalytic activities were present in virgin olive oil samples, which could not be correlated with the moisture content of the oil samples. Filtration of oil samples resulted, in several cases, in up to a threefold increase in both activities, suggesting that the filtration process removed some inhibitory components.

17.3.2 Oxidative Rancidity

Oxidative stability is one of the most important indicators of the quality of edible oils. Oxidative rancidity is a complex of chemical changes that imply a series of reactions between unsaturated fatty acids or acylglycerols with O₂. The off-flavor compounds released make oil less acceptable or unacceptable to consumers or for industrial use as a food ingredient (Choe and Min, 2006). For this reason, oxidative stability is an important IToF to determine oil quality and shelf life because low molecular weight off-flavor compounds are produced during oxidation. Oxidation of oil also destroys EFAs and produces toxic compounds and oxidized polymers. Therefore, oxidation of oil is very important in terms of palatability, nutritional quality, and toxicity of edible oils. The process is complex because of the influence of multiple factors such as light, heat, composition of fatty acids, enzymes, metals, and antioxidants. Moreover, the type of O₂ influences the mechanism of oxidation of edible oils.

17.3.2.1 Autoxidation Pathway

The autoxidation pathway of oils proceeds through three steps: initiation, propagation, and termination. Heat, UV, and visible light can act as initiators and accelerate the formation of free radicals from fatty acids or acylglycerols. In the propagation step, the free radicals can react with triplet O₂ to form a reactive lipid peroxy radical, which can further react with another lipid molecule to generate hydroperoxide and another lipid alkyl radical (Angelo Allen, 1996). In the termination phase, two radicals react to give products that do not sustain the propagation phase; termination also occurs when antioxidants react with free radicals generated during propagation.

The hydroperoxides of unsaturated fatty acids (primary products) are intermediate products that, in the presence of metals or at high temperatures, are readily decomposed to alkoxy radicals that then form aldehydes, ketones, esters, acids, alcohols, and short-chain hydrocarbons. The presence of transition metals such as iron and copper in edible oils is due both to endogenous factors linked to plant metabolism and to exogenous factors such as fruit or seed contamination (Bendini et al., 2006). All the secondary products are much more volatile than the starting fatty acids and are responsible for the development of rancid off-flavors. The time for secondary product formation from the primary oxidation product varies with different oils. Secondary oxidation products are formed immediately after hydroperoxide formation in olive oil and rapeseed oils. However, in sunflower and safflower oils, secondary oxidation products are formed when the concentration of hydroperoxides is appreciable (Choe and Min, 2006).

17.3.2.2 Photo-oxidation Route

The exposure of vegetable oils to light accelerates oxidation through a mechanism called photo-oxidation. This is based on the generation of highly reactive singlet O₂ (¹O₂) from atmospheric triplet O₂. Chlorophylls and their degradation products (pheophytins and pheophorbides) act as sensitizers to produce ¹O₂ in the presence of light and atmospheric O₂ and accelerate the oxidation of oil. Virgin olive oil and rapeseed oil contain chlorophyll at 10 ppm and 5–35 ppm, respectively (Salvador et al., 2001). Chlorophylls are generally removed during oil processing, especially by the
bleaching process. Suzuki and Nishioka (1993) found that chlorophyll \(a\) in canola oil was 1.88 ppm and the concentration decreased to 0.22 ppm after refining.

Storage of virgin olive oil in the dark does not necessarily ensure the stability of the oil under conditions promoting photo-oxidation (Terao and Matsushita, 1977). Thus, the virgin olive oil photo-oxidation rate is not expected to depend on a high level of oleic acid to the extent observed in autoxidation but on the presence of photosensitizers and singlet \(O_2\) quenchers. Although chlorophyll pigments act as photosensitizers, carotenoids are effective inhibitors of photo-oxidation by quenching singlet \(O_2\) and excited triplet states of photosensitizers. The antioxidant activity of carotenoids is related to a light-filtering effect due to the extended conjugation system (Psomiadou and Tsimidou, 2002).

### 17.3.2.3 Oxidation-Derived Products

The primary oxidation products are (odorless and flavorless) monohydroperoxides that are precursors of unpleasant odors and flavors that diminish the quality of oils. The volatile aldehydes obtained from various unsaturated fatty acid monohydroperoxides and the vinyl ketones are mainly responsible for potent off-flavors because their threshold levels are very low. Other volatile oxidation products such as furan derivatives, vinyl alcohols, ketones, alcohols, alkynes, and short-chain fatty acids also contribute to undesirable flavors to varying extents (Kanavouras et al., 2006).

Morales et al. (1997) found that the volatile compounds identified in virgin olive oil off-flavor were quite different from those identified in virgin olive oil off-flavor. The explanation could be their different origins, mainly biochemical for flavors and chemical for off-flavors. The main differences that characterize off-flavors are the absence of C6 aldehydes and alcohols (produced from linolenic acid), which contribute to the green flavor of virgin olive oil, the absence of esters contributing to fruity flavor, and the presence of many aldehydes with low odor thresholds contributing to the typical rancid odor of oxidized oils. On the other hand, the amount of hexanal does not allow oxidized olive oils to be distinguished from virgin ones, as this compound can come from lipoxygenase cascade and oxidative pathways. The measurement of nonanal has clearly demonstrated its usefulness, as it does not appear in virgin olive oils but does appear in oxidized olive oils.

### 17.3.3 Loss of Natural Antioxidants

The presence and importance of natural antioxidants in vegetable oils have been mentioned previously; the reactions leading to loss of tocopherols and polyphenols are the main causes of quality deterioration of oils.

#### 17.3.3.1 Tocopherols

In the case of cold-pressed oils and, in particular, of extra-virgin olive oils (EVOO), \(\alpha\)-tocopherol is the major antioxidant, representing about 90% of the total tocopherols. These natural antioxidants, widely present in all vegetable oils, are not stable during oil refining and their content decreases during each processing step. Ortega-Garcia et al. (2006) found that the refining process removed 28.5% of the tocopherols of safflower oil. The major losses occur during deodorization where the tocopherols are removed with the stripping steam.

#### 17.3.3.2 Polyphenols

Polyphenols in vegetable oils are always a complex mixture of compounds. Olive oil is particularly rich in these natural antioxidants, with aglycones derived from secoiridoid compounds present in olives being the most abundant phenolic compounds in virgin olive oil. Secoiridoid derivatives play an important role in oil stability and extend the shelf life of olive oil (Montedoro et al., 1992; Owen et al., 2000).

The presence of antioxidants in vegetable oils is also an important factor in the stabilization of free fatty acids. The higher oxidative stability of virgin olive oil compared to that of other vegetable...
oils is due to both the low PUFA content of the triacylglycerols and the level of natural phenolic components with antioxidant activity. Phenolic compounds in vegetable oils are strong free radical scavengers because they are able to donate a hydrogen atom to the lipid radical formed during the propagation phase of lipid oxidation. Similarly, polyphenols are effective stabilizers of α-tocopherol during olive oil heating, thus contributing to the nutritional value of cooked foods.

17.3.4 Oil Crystallization

The partial crystallization of triglycerides that causes a cloudy aspect to the oil has been already mentioned. This is a reversible defect that can be observed during winter storage and which progressively disappears with increasing temperature. Kristott (2000) reported that crystallization of oils and fats and subsequent transition of crystal type could promote oxidation reactions. In fact, the liquid phase surrounding fat crystals is expected to contain a high proportion of unsaturated fatty acids in addition to the concentrated dissolved O₂. Calligaris et al. (2006) highlighted that the relative concentration of reactants (unsaturated fatty acids and polyphenols) in the liquid phase surrounding fat crystals is, besides temperature, the main variable affecting the oxidation rate in partially crystallized EVOO.

17.3.5 Absorption of Flavor and Migration of Substances from Packaging

Scalping and migration are interactions that can occur between oil and packaging material and affect the quality and safety of oils (Kanavouras et al., 2006). In order to avoid alteration of the flavor profile or to reduce chemical contamination of oil during storage, knowledge of oil–package–environment interactions is required. Some mass transfer can occur between the environment and the food and some between the food and the packaging material.

17.3.5.1 Scalping

In recent years, plastics have been increasingly employed to package vegetable oils, due to their low weight, ease of handling, and competitive cost (Gambacorta et al., 2004; Kaya et al., 1993; Maloba et al., 1996). Plastic packaging materials can absorb different compounds from the food, a phenomenon called scalping (sorption). In particular, flavor scalping is a term used to describe the loss of quality of a packaged food due either to its volatile flavors being absorbed by the package or the food absorbing undesirable flavors from the packaging material. Sorption of food aromas, particularly by plastic packaging materials, is usually perceived as a major factor contributing to the quality alteration of most foods during storage. Also, nonvolatile compounds may be absorbed by packaging materials, but in this case, they primarily affect the packaging itself—its characteristics such as permeability and mechanical properties.

Kanavouras et al. (2004a, 2004b) studied the role of plastic materials as potential flavor sorbents for olive oil. Flavors dissolved in the oil were readily absorbed by low density polyethylene (LDPE), with the flavor concentration and storage temperature affecting the absorption of aroma compounds. Sorption of oil into packaging materials, especially olefins, causes swelling of the polymer, which in turn increases migration. The sorption of fatty acids increases with increased chain length due to increased van der Waals bonds between polymer and fatty acid. The sorption of olive oil flavor compounds by polymeric plastic materials during storage can result in a considerable decrease in oil quality due to losses of desirable organoleptic characteristics.

Several investigations have shown that considerable amounts of aroma compounds can be absorbed by plastic packaging materials, resulting in loss of aroma intensity or unbalanced flavor profile (e.g., van Willige et al., 2000a, 2000b). However, sorption may also indirectly affect food quality by causing delamination of multilayer packages (Olafsson and Hildingsson, 1995) or by altering the barrier and mechanical properties of plastic packaging materials (Tawfik et al., 1998). Oxygen permeability through the packaging can increase as a result of these interactions,
but unfortunately, little information is available in the literature on this subject. Van Willige et al. (2002) studied the influence of flavor and off-flavor absorption on the O$_2$ permeability of LDPE, PP, PC, and poly(ethylene terephthalate) (PET). Absorption of some volatile substances (limonene, decanal, 2-nonenone, and hexyl-acetate) increased O$_2$ permeability of PP and LDPE; O$_2$ permeability of PET was not influenced by the presence of flavor compounds, meaning that PET remained a good O$_2$ barrier.

17.3.5.2 Migration
Migration is an important safety aspect to be considered when selecting food packaging materials. Plastic additives and residual monomers or oligomers are not chemically bound to the polymer molecules and can, therefore, move freely within the polymer matrix. Consequently, at the interface between the packaging material and food they can dissolve in the food product and thus adversely affect the flavor and acceptability of the food. The chemical nature of the packaging material has a notable influence on oil quality. A review by Kanavouras et al. (2006) suggested that edible oils should not be stored in PVC plastic materials as vinyl chloride monomer (VCM) and plasticizers can migrate into fatty foods, leading to the contamination of the oils. Castle et al. (1991) investigated the preferential migration by the size of oligomers from PVC into olive oil. The smaller oligomers migrated 90-fold more readily than the bulk of the plasticizer. PET is one of the most inert plastics and in recent years packing of oil into PET bottles has increased. Nevertheless, PET monomers, oligomers (cyclic trimers, pentamers, heptamers), plasticizers, colorants, stabilizers, and different additives used for flexibility purposes (adipic and phthalic acid esters) as well as degradation products are all prone to migration.

The migration of acetaldehyde from PET bottles is a major problem, as its presence may affect the organoleptic properties of oil (Tsimis and Karakasides, 2002). Migrating PET oligomers have been measured and the cyclic trimer was the most dominant. Little data concerning the influence of migration processes on the quality of olive oil are available; in general, PET bottles are usually considered suitable to contain not only seed oil but also olive oil (Cecchi et al., 2006; Kaya et al., 1993).

17.3.6 Indices of Failure of Vegetable Oils
Once the most relevant quality attributes and major deteriorative modes of vegetable oils are known, the subsequent task is to identify the IoFs that indicate that the product is no longer acceptable. To define shelf life, it is also necessary to establish a critical limit for each IoF beyond which the food product is no longer acceptable, and decide which one is the most relevant or reaches the critical limit first. The critical limit may vary from country to country as people from different locations have different preferences (Lee et al., 2008a). The presentation of the main IoFs for vegetable oils follows.

17.3.6.1 Triglyceride Hydrolysis
The level of free acidity during storage of oils measures the liberation of fatty acids as a result of hydrolytic rancidity development. Acidity values are used for classifying different categories of olive oil although, according to Kiritsakis et al. (2002), acidity is not the best criterion for evaluating olive oil quality, as one oil with relatively high acidity may have a good aroma while another one with low acidity may not. For EVOO the maximum acidity is 1%, increasing as the quality category of the oil changes. For seed oils, the critical value of acidity is much less and in several countries the legal level is 0.5%.

17.3.6.2 Enzymic and Chemical Oxidation
Because lipid oxidation is one of the most undesirable yet common deteriorative reactions, several IoFs related to this phenomenon are known and regularly used. The peroxide value (PV) determines the quantity of hydroperoxides that are formed during the early stages of oxidative rancidity
development. As hydroperoxides are decomposed in subsequent oxidation reactions, a low PV in an oil does not necessarily mean that it is fresh and IoFs related to the amount of secondary oxidation products are also necessary. The anisidine value (AnV) and thiobarbituric acid (TBA) test are common indices for detecting advanced lipid oxidation (Kristott, 2000).

The advance of oxidation processes in refined vegetable oils is indicated by the increase in total volatiles and the concentration of some specific volatile compounds such as hexanal. Morales et al. (1997) investigated the volatile components during the thermo-oxidation process and proposed the hexanal:nonanal ratio as an indicator of the level of oxidation of olive oil. In other words, as the amount of hexanal diminished in the olive oil headspace, the amount of nonanal increased and the oil moved toward higher oxidation levels and consequently lower acceptability. For quality control purposes, the presence of rancid off-flavors is also measured through sensory analysis. Basic flavor compounds, among other oxidation indicators, were investigated by Kanavouras et al. (2004a) as a useful tool to evaluate the tolerance of oil to oxidation or its oxidation level at a certain point, and to extrapolate the results for predicting the shelf life of the product under various conditions.

Another characteristic affected during oil oxidation is color. The color of olive oil, for example, is due to the solubilization of chlorophyll and carotenoid pigments present in the source fruit. The influence of extraction technology and the role of oxidative spoilage on chromatic characteristics of edible oils have been studied by Ranalli et al. (1994, 1996).

As oxidative deterioration proceeds, the level of important antioxidants such as tocopherols and polyphenols inevitably decreases. Therefore, the concentrations of natural antioxidants could theoretically be a valuable IoF to reveal early deterioration, but so far no significant literature is available on this subject.

17.3.6.3 Oil–Package Interactions

Both scalping and migration are time-related phenomena. In many cases legal limits to migration of packaging constituents already exist and analytical procedures for determining such potential migrants are known; diffusion equations to model the interactions are now readily available (CRL-FCM, 2008). Scientific knowledge on migration from packaging materials could provide some useful markers or IoFs for shelf life studies. For vegetable oils in plastic packaging, this seems to be a realistic perspective due to the strong chemical affinity that exists between the synthetic polymers used and the oils, making migration phenomena quite rapid and important.

17.4 HOW PACKAGING MIGHT IMPACT INDICES OF FAILURE

Many different kinds of packaging are used for vegetable oils: tinplate cans, glass bottles, PET, or HDPE plastic bottles, and paper-based cartons are most common. The selection of the kind of package to be used is generally done on the basis of marketing and economic criteria; however, proper packaging will in many cases provide conditions to assure adequate shelf life for distribution and marketing (Kanavouras et al., 2006). Even though oils are quite stable products, physicochemical characteristics of packaging materials may significantly affect oil quality during their shelf life. Furthermore, besides the specific properties of the materials, the packaging geometry (Del Nobile et al., 2003b) and the techniques of filling and closing the containers (de Oliveira et al., 2001) may also be very important.

17.4.1 Oxygen Permeability and Light Transmission

As far as physicochemical characteristics of the materials are concerned, the O\textsubscript{2} permeability and the UV/visible light transmission of the packaging walls are the major ones, due to the oxidative sensitivity of vegetable oils. Oxygen permeability is a property of plastic materials only, whereas light transmission is important both for glass and plastics. Different polymers may have very different permeabilities; for instance, the ratio of the highest O\textsubscript{2} permeability coefficient to the lowest
can be greater than 5000 (Lee et al., 2008b). Light transparency is a less investigated property that depends mainly on the chemical nature of materials, their crystallinity, the presence of specific additives, color, and thickness. Thickness, however, is less relevant than molecular structure in comparisons between PET and glass. Only 25 µm of PET makes a better filter than 2.2 mm of glass (Lee et al., 2008c). El-Shattory et al. (1997) reported that the flavor of cottonseed and palm oils was preserved better in metal cans than in white plastic bottles, that is, in a container totally impermeable to gas and light. In recent times the effects of light on food stability and the role of packaging in protecting against light have been investigated (Bosset et al., 1994; Piergiovanni and Limbo, 2004; Wold et al., 2005). Many additives are available today for both plastics and glass to reduce UV transmission. It is also essential to take into account the light-emitting spectrum, which can be quite different in different circumstances as Torri et al. (2007) showed in a survey of the lighting conditions in large-scale food retail stores.

17.4.2 Packaging Geometry

The geometry of packaging can act in different ways in providing protection to the product. As discussed in Chapter 1, the size and shape of plastic packages can affect the ratio between permeable surface area and product volume, modulating the O₂ ingress per unit volume of product. For both plastic and glass or metal packages, shape and size can influence the headspace and, consequently, the amount of O₂ available. Del Nobile et al. (2003b) proposed a two-dimensional mathematical model to predict the time course of hydroperoxides and O₂ concentration profiles inside bottled virgin olive oil during storage. They showed that the quality decay kinetics of oil greatly depended on container geometry, material used, and initial value of the O₂ partial pressure in the bottle headspace (Figure 17.2).

17.4.3 Packaging Inertness

As already mentioned, oil–package interactions can affect product shelf life, reducing nutritional value and stability (by scalping) or increasing the level of chemical contamination (by migration). Therefore, the selection of packaging materials may also be done on the basis of their interaction with oils. Generally speaking, glass is the most inert material, followed by metals and plastics. However, large differences exist among the different materials, and consideration must be given to closures and their liners (often made of plastics even for metal and glass containers) when assessing the global inertness of a package.

**FIGURE 17.2** Predicted average hydroperoxide concentration versus time of virgin olive oil bottled in different PET containers. (From Del Nobile M.A., Bove S., La Notte E., Sacchi R. 2003b. Influence of packaging geometry and material properties on the oxidation kinetic of bottled virgin olive oil. *Journal of Food Engineering* 57: 189–197, with permission.)
17.4.4 FILLING AND CLOSING TECHNOLOGIES

The filling and capping steps are very relevant in the process of oil packaging, affecting the quality perceived by consumers. In order to reduce the O2 residual inside the bottles, the oil is generally stripped with gaseous N2, to lower the initial level of residual O2 to below 0.5 ppm. Gaseous N2 can be pressurized by injecting liquid N2 into the headspace prior to closing (de Oliveira et al., 2001). In order to reduce O2 ingress during shelf life, the effectiveness of the closures is also very important. The efficiency of closures is related to several factors: material used, design, and liner adopted. All these factors must guarantee, at the same time, hermeticity, easy opening, and the possibility of reclosing. As these goals are sometimes contradictory, efforts to develop new devices is ongoing, including the use of active and intelligent packaging.

17.5 SHELF LIFE OF VEGETABLE OILS IN DIFFERENT PACKAGES

As described previously, O2, light, temperature, and the presence of heavy metals greatly influence the quality of oil. Therefore, all these factors must be taken into account when selecting packaging materials. The majority of shelf life research has focused on comparative evaluations using key IOFs of edible oil stored in different packaging materials. The conclusion is that oil stability can be enhanced by selection of a suitable package. Little information is available about light exposure of samples and the characteristics of the packaging materials in the UV and visible range. Moreover, most shelf life studies are conducted at constant temperature, relative humidity (RH), or lighting conditions; it would be of real interest to evaluate the shelf life of edible oils simulating the fluctuating temperature (or lighting conditions) during the whole distribution chain, that is, from producer to consumer. Ramirez et al. (2001), for instance, clearly showed the very negative effects on sunflower oil of exposing bottles to light for half a day; the shelf life was halved in comparison with bottles stored in the dark as shown in Figure 17.3A and 17.3B. Finally, packages used in end-point studies should have the same size and shape as the original containers for product distribution. This means that the contribution of the closure system or the volume of the headspace should always be taken into account in the quality evolution of the oil.

A limited number of mathematical models have been presented in the literature concerning the role of packaging in influencing oil shelf life. In the majority of these studies, the main focus was to predict the shelf life of packaged oil in new package designs after taking into consideration the role of O2, the geometrical and structural characteristics of the plastic container, and the volume of oil. Del Nobile et al. (2003a, 2003b) developed a mathematical model to assess the effectiveness of plastic containers to prolong the shelf life of virgin olive oil assuming average hydroperoxide concentration as a measure of oil quality. The mathematical model combined the mass balance equations of O2 with those describing the rate of hydroperoxide formation and decomposition; it was validated by monitoring oil in glass and PET containers at 40°C. Couteliers and Kanavouras (2006) proposed a simple model based on the evolution of hexanal in order to estimate the reaction constants under various storage conditions of light, temperature, and O2 availability. A mathematical predictive model was introduced to describe the mass transport from and to the oil phases through various packaging materials.

17.5.1 METAL PACKAGING

Metal containers for vegetable oils are manufactured using tinplate or aluminum and in two different ways:

a. Bottom and top closed at the metal fabrication plant with an orifice on the top for subsequent filling and capping.

b. Bottom seamed onto the body blank and the top closed only after filling at the bottling plant.
Tinplate containers have been used for a long time for oil packaging and are still well appreciated because of their many advantages (Tsimis and Karakasides, 2002). They provide total protection against light, O$_2$, water vapor, and microorganisms, and are resistant to several types of mechanical abuses. In addition, the inside of the container is protected with food-approved special enamels (lacquers) that protect the metal from the corrosiveness of the product. Edible oils are generally packed in tinplate containers of different capacities, typically from 500 g to 15 kg. Grover (1982) studied the shelf life of several vegetable oils (mustard oil, groundnut oil, sesame oil, etc.) when packaged in new and reused tinplate containers. The quality of oil packed in new containers did not change during 1 year, whereas the quality of oils packed in containers reused several times remained intact for only 4–5 months. The reuse of containers, in fact, increases corrosion of the tin coating and the

![Graph A](image1.png)

![Graph B](image2.png)

**FIGURE 17.3** Estimated shelf lives for sunflower oil stored at 45°C kept in the dark (A) and exposed to light for 12 hours a day (B). (From Ramirez G., Hough G., Contarini A. 2001. Influence of temperature and light exposure on sensory shelf-life of a commercial sunflower oil. *Journal of Food Quality* 24: 195–204, with permission.)
exposed steel base readily reacts with the free fatty acids in oil, leading to oxidative rancidity and organic tin salts with high toxicity (Tsimis and Karakasides, 2002).

Aluminum is also employed as a packaging material for edible oils as it is light and very resistant to corrosion. In order to increase its mechanical resistance, aluminum alloys with small amounts of Mg, Mn, and Si/Mg are recommended.

All these metallic containers are considered inert against oils, even though trace levels of metal ions such as Fe and Cu are known to have adverse effects on the oxidative stability of olive oil. In fact, transition metals catalyze the decomposition of hydroperoxides, contributing to off-flavor production (Sahan and Basoglu, 2008).

17.5.2 Glass Bottles

Glass containers are widely used for bottling olive oils and virgin olive oils in particular. This is due not only to marketing requirements but also because glass containers prevent the permeation of O₂ molecules into the bottle, slowing down the autoxidation rate of PUFA:s. Transparent glass, however, leads to photo-oxidation of olive oil and reduction of its shelf life. The use of colored glass bottles prevents or slows down the oxidation process: green bottles, for instance, protect oil from wavelengths of 300–500 nm (Kiristakis et al., 2002). Rastrelli et al. (2002) found that α-tocopherol represents the first target of EVOO autoxidation stored in half-empty clear bottles after 12 months of storage at room temperature and under diffused lighting, with a reduction greater than 90%; in filled clear bottles, the vitamin E reduction was lower (about 25%). Results concerning the study of the effect of storage on secoiridoid and tocopherol contents and antioxidant activity of monovarietal EVOO showed that, despite antioxidant depletion, oils with high antioxidant content were still excellent after 240 days of storage at 40°C in closed dark bottles. These data led to the conclusion that the beneficial properties of extra-virgin olive oils due to antioxidant activity can be maintained throughout their commercial life if properly packaged and stored (Lavelli et al., 2006). In order to reduce light transmission, aluminum foil can be used to cover glass containers. This practice is used especially for EVOO that has high nutritional and sensory properties.

Metal and glass are the only packaging materials that provide a virtually total barrier to moisture and gases. The word “virtually” is used because such containers require a closure that incorporates other materials such as polymeric sealing compounds in cans and in closures, through which O₂ can easily permeate and promote oxidation (de Oliveira et al., 2001). The shelf life of edible oils packaged in metal containers or nontransparent glass bottles can be considered product-dependent because deteriorative reactions are driven by intrinsic stability of the product, not by environmental factors or packaging (Lee et al., 2008d). In other words, intrinsic stability is dictated by initial quality of the oil, processing conditions, and filling operations.

17.5.3 Plastic Bottles and Containers

Plastic containers are a relatively new means of edible oil packaging due to their comparatively low price and low weight. The polymers most frequently used are PET, HDPE, and PVC. Although they do not provide as long a shelf life as metal containers, they are economical compared to tinplate and therefore suitable for use where a very long shelf life is not required.

PET is one of the most used plastics in food packaging covering a wide range of packaging structures. PET satisfies many important requirements: good aesthetic aspect (brilliance and transparency); suitability for coloring; good mechanical, thermal, and chemical resistance; low production cost; good barrier properties against CO₂; suitability for prolonged storage, easy recyclability, and low weight with respect to glass bottles. The trend toward incorporating modifier compounds into PET packaging resins has grown in order to produce containers with a high degree of clarity, in a wide variety of custom shapes, and free from residual acetaldehyde (Kanavouras et al., 2006).
Also, the incorporation of antioxidant stabilizers in PET increases its application in the food area, particularly for vegetable oil storage.

The influence of PET bottle weight, closure performance, and filling technique on the O<sub>2</sub> content of soya cooking oil was investigated by Coltro et al. (2003). The experiment considered a PET bottle of standard weight (27 g) and two PET bottles of reduced weight (20 g), differently filled (flushed with gaseous N<sub>2</sub> or pressurized with liquid N<sub>2</sub>). Considering the bottles without closures, results highlighted that PET bottles with reduced weight had a 20% increase in oxygen transmission rate (OTR). The differences in OTR decreased significantly (less than 14%) if closures were considered during the permeability measurements. Therefore, the closure system of PET containers for vegetable cooking oil is of critical importance to the overall barrier properties of the packaging system. This fact drastically diminishes the importance of the effect of weight reduction on the level of protection provided by the package to the oil.

Cecchi et al. (2006) assessed the role of clear PET bottles and dark-green glass bottles on the quality of EVOOs during 2 months storage. Samples stored in PET bottles developed a pungent and offensive off-flavor compared to samples stored in glass bottles. The PV of samples stored in glass bottles was always lower than those stored in PET bottles. Kucuk and Caner (2005) studied sunflower oil packaged in both PET and glass bottles, both with and without headspace and stored in conditions of light and darkness for 9 months. Oil stored in glass and PET in the dark showed very little oxidation and maintained its original profile for a long period (Table 17.2). De Oliveira et al. (2001) referred to an experiment on soya oil stored in biaxially oriented PVC. In the dark, the shelf life was 360 days at 23°C and 135 days at 35°C; stored under light, shelf life was reduced to less than 60 days at 23°C. The shorter shelf life of the oil in PVC compared to metal and glass packages, when stored at 23°C and 35°C in the presence of light, was attributed to the higher OTR of PVC and the type of closure used.

Kakuda et al. (2008) studied the effect of packaging and light exposure on vitamin A stability in fortified vegetable oil. Three packaging materials (PET, PVC, and HDPE) and exposure to light and dark conditions were variables in the experimental design. The major factors affecting vitamin A stability was exposure to light and the type of packaging material. After 37 days of storage in clear PET bottles, the levels of vitamin A dropped to 17–33% when exposed to light. Samples stored in brown PET bottles and exposed to light retained 72–88% vitamin A. When completely protected from light, vitamin A in the clear and brown PET bottles was very stable (81–91% remained after 6 months). Similar results were obtained with clear PVC, opaque HDPE, and brown HDPE bottles. The clear and opaque bottles showed rapid loss of vitamin A (13–36% remained) when exposed

### TABLE 17.2
Effect of Packaging Materials and Storage Time on Mean Peroxide Values

<table>
<thead>
<tr>
<th>Package</th>
<th>With–Without Headspace (Air)</th>
<th>Dark/Light</th>
<th>Storage Time (Months)</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td></td>
<td></td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>Light</td>
<td>0.230</td>
<td>0.800</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dark</td>
<td>0.230</td>
<td>0.400</td>
</tr>
<tr>
<td></td>
<td>Without air</td>
<td>Light</td>
<td>0.230</td>
<td>0.800</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dark</td>
<td>0.230</td>
<td>0.400</td>
</tr>
<tr>
<td>Glass</td>
<td></td>
<td>Light</td>
<td>0.230</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dark</td>
<td>0.230</td>
<td>0.310</td>
</tr>
<tr>
<td></td>
<td>Without air</td>
<td>Light</td>
<td>0.230</td>
<td>0.776</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dark</td>
<td>0.230</td>
<td>0.300</td>
</tr>
</tbody>
</table>


Note: Means with different letters are significantly different (p < 0.01); standard error 0.0764.
to light for 49 days, whereas brown HDPE bottles retained 79–88% vitamin A after 3 months. Vegetable oil is an effective carrier for vitamin A and may retain high potency if protected from light or packaged in nontransparent plastic containers.

HDPE is largely used as a packaging material because of its tensile strength and hardness and good chemical resistance. Blow-molded HDPE containers in the form of bottles, jars, and jerry cans are used for packaging edible oils. Coltro et al. (2003) investigated the quality deterioration of soya oil in 1-L plastic bottles made of HDPE, coextruded with a layer containing black pigment, during storage at 23°C. Soya oil stored in a metal container was used as a control. No differences were found between the organoleptic properties of the oil contained in the metal and plastic containers throughout the total storage time investigated (113 days). Over the same period, the chemical quality of the oil remained within the limits of stability.

PVC is a popular packaging material for edible oils in many countries, mainly due to its transparency, adaptability to all types of closures, total compatibility with existing packaging lines, and potential for personalized design features (Kanavouras and Coutelieris, 2005). Mainly driven by issues such as the protection of the environment, PET has been supplanting PVC in the edible-oil market. As with other transparent plastic materials, PVC increases light exposure of the oil, enhancing oxidation. UV absorbers can be added to plastic materials in order to reduce their light transmission. Azeredo et al. (2004) studied the oxidation of refined soybean oil during 6 months storage at 25°C under a constant illumination (1720 lux) as affected by combining different primary antioxidants to oil or PVC resin. In particular, tert-butylhydroquinone (TBHQ), β-carotene, and citric acid were added to the oil while an UV absorber (Tinuvin P) was in the PVC bottles. The results highlighted that, among the compounds used to reduce oxidation rates of soybean oil, TBHQ was the most effective, followed by Tinuvin P. Moreover, the latter solution allowed the protection of oil without modification of oil color.

17.5.4 Multilayer Pouches and Paper-Based Cartons

In recent years, the adoption of multilayer pouches for oil storage has increased due to consumer preference for unit packages. Generally, limited quantities of edible oil are packed in flexible pouches (up to 500 g). Flexible pouches may be manufactured from laminates or multilayered films of different compositions and the pouches may be in the form of a pillow or stand-up pouch. The selection of a laminate or multilayer film is governed primarily by the compatibility of the contact layer, heat sealability, heat seal strength, and shelf life required, together with machinability and physical strength parameters.

Mahadevaiah et al. (1992) studied the storage of double-filtered groundnut oil in different multilayer film pouches. The materials were based on polyolefins, nylon, and PET layers, and after filling, the pouches were stored at 27°C/65% RH and 38°C/90% RH. The groundnut oil kept better in multilayer film pouches consisting of nylon and PET films than in non-nylon-based film pouches under both conditions. Packaging and storage studies of palm oil in seven different flexible pouches were carried out in order to design a suitable package for oil (Narasimhan et al., 2001). Pouches containing 200 g of oil were stored under three conditions representative of different climatic conditions. The quality deterioration was comparatively less in films containing polyamide (PA) as one of the layers, and leakage rates were minimal in films containing ethylene-acrylic acid copolymer (EAA) as the sealant layer.

Recently, new packaging formats have been introduced in the market including bag-in-box systems, lined cartons, and paperboard laminate cartons. In particular, Tetra Brik® cartons have been used in Spain, Brazil, and other countries and are considered more suitable for packaging olive oil (Kiritsakis et al., 2002).

17.5.5 Active Packaging

In order to reduce the diffusion of O₂ into bottled oil, various solutions have been tried; the most popular involve the use of “oxygen scavengers” (OS), which remove O₂ dissolved in the oil and...
provide a barrier to O$_2$ diffusion from the atmosphere. These scavengers can be easily incorporated into the packing material without altering its other properties. Sacchi et al. (2008) studied the oxidation of EVOO and sunflower oil (SO) stored in PET bottles with two different OS concentrations (1% and 5%). The shelf life test was carried out for 6 months at 25 ± 4°C under a constant illumination of 400 lux. During the first 3 months of storage, the effect of scavengers was evident: oils bottled in PET loaded with 5% of OS showed a dissolved O$_2$ (DO) content lower than oils bottled in PET with 1% OS and in standard PET. Between 3 and 6 months, the level of DO remained almost constant in all packages, indicating that the O$_2$ consumed during storage was nearly limited to the initial content in the oil (Figure 17.4).

Maloba et al. (1996) measured the oxidative stability of sunflower oil during storage at two temperatures (23°C and 37°C) in the presence of a novel OS film that contained polyfuryloxirane (PFO). Commercially refined and deodorized sunflower oil was stored in a lighted room in sealed transparent packages containing either PFO film or the antioxidant butylated hydroxytoluene (BHT) at 0.02%. Sunflower oil stored in the presence of the OS film was more stable than oil stored without the film, or than film stored with 0.02% BHT. The PFO film scavenges O$_2$ through energy transfer sensitization of singlet O$_2$.

Gambacorta et al. (2004) studied the shelf life of EVOO stored in five different materials: PET, PET including 1% and 3% OS, PET coated with high-barrier resin, and PET coated with high-barrier resin including an O$_2$ scavenger. Glass was used as a reference material. The packaged oil was stored in the dark at room temperature and at 37°C for 12 months. A significant influence of the package on the quality decay kinetics was found, suggesting that PET bottles coated with a high-barrier resin and those including an OS could replace traditional glass bottles.

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