Packaging of Cereals, Snack Foods and Confectionery

20.1 INTRODUCTION

Cereals are the fruits of cultivated grasses, members of the monocotyledonous family *Gramineae*. The principal cereal crops are wheat, barley, oats, rye, rice, maize, sorghum and the millets. Cereals have been important crops for thousands of years and the successful production, storage and use of cereals has contributed in no small measure to the development of modern civilization. Today, cereals and cereal-based products are an important part of the diet in most countries, and each year new products based on cereals are developed and marketed to increasingly sophisticated consumers.

20.2 GRAINS

The cereals of commerce and industry are harvested, transported and stored in the form of grain. The anatomical structure of all cereal grains is basically similar, differing from one cereal to another in detail only.

The mature grain of the common cereals consists of carbohydrates, nitrogenous compounds (mainly proteins), lipids, mineral matter and moisture, together with small quantities of vitamins, enzymes and other substances, some of which are important nutrients in the human diet. Carbohydrates are quantitatively the most important constituents, forming 77%–87% of the total dry matter. The lipids in milled cereal products are liable to undergo two types of deterioration: hydrolysis from endogenous lipases and oxidation from endogenous lipoxygenases or molecular O_2 . The products of lipid hydrolysis are glycerol and free fatty acids, which give rise to unpleasant odors. The products of lipid oxidation cause the odor and flavor of rancidity. Damage to the grain and the fragmentation that occurs in milling promote deterioration by bringing the lipid and the enzyme together (Kent and Evers, 1994).

20.2.1 WHEAT

The wheat grain is a living, respiring organism, which usually carries endemic fungi. Respiration is slow at 14% moisture content and 20°C, but rises as moisture content and temperature increase. The process of respiration generates heat (which is difficult to remove because wheat is a poor conductor) as well as CO_2 and water vapor, resulting in a loss in weight. Unless the grain is turned over to allow evaporation of the moisture, it will sweat and become caked in the bin.

Wheat at moisture contents between 16% and 30% can support fungal growth and there is thus the risk of mycotoxin production. Above 30% moisture content, wheat is susceptible to bacterial attack, leading to spoilage, excessive heat production and possibly charring. Insect life also becomes more active as the temperature rises and, because of their respiration, live insects in grain also raise the grain temperature. Deterioration during storage is aggravated by mechanical damage during harvesting because microorganisms attack damaged grains more readily than intact grains (Kent and Evers, 1994).

The shelf life for wheat as a function of moisture content and temperature is presented in Table 20.1. This table shows the importance of drying grain in that a drop of 3% in moisture content

TABLE 20.1
Safe Storage Life (Days) for Grains as a Function of Moisture Content and Temperature

	Grain Moisture (%)		
Grain Temperature (°C)	14	15.5	17
10.0	256	128	64
15.5	128	64	32
21.1	64	32	16
26.7	32	16	8
32.2	16	8	4
37.8	8	4	2

Source: Adapted from Bailey, J.E., Whole grain storage, in: Storage of Cereal Grains and Their Products, 4th edn., Sauer D.B. (Ed.), American Association of Cereal Chemists, St. Paul, MN, pp. 141–169, 1992.

increases the shelf life by a factor of four. The major problems at higher moisture contents include accelerated wheat enzyme activities and microbial spoilage.

20.2.2 FLOUR

Wheat flour is the product prepared from grain by grinding or milling processes in which the bran and germ are partly removed and the remainder is comminuted to a suitable degree of fineness (Cauvain and Young, 2008). It has been recommended that for long storage periods, flour should be stored in a closed atmosphere. Under these conditions, flour acidity increases due to the accumulation of linoleic and linolenic acids.

Flour is stored commercially in bags or bulk bins. The storage hazards for flour are similar to those of wheat in storage, which include mold and bacterial attack, insect infestation, oxidative rancidity and eventual deterioration of baking quality. The expected shelf life of plain white flour packaged in paper bags and stored in cool, dry conditions and protected from infestation is 2–3 years. The rate of increase in acidity increases with storage temperature and decreasing flour grade (i.e., as the ash residue increases). Thus, the shelf life of brown and wholemeal flours is shorter than that of white flour. Freedom from insect infestation during storage can be ensured only if the flour is free from insect life at the time of packing and if the storage area is free from infestation.

The optimum moisture content for the storage of flour is related to the intended shelf life, the barrier properties of the packaging material, as well as the ambient temperature and humidity. For use within a few weeks, flour can be packaged at 14% moisture content, but at moisture contents higher than 13%, mustiness resulting from mold growth may develop over time. At moisture contents lower than 12%, the risk of lipid oxidation and the development of rancidity increases (Kent and Evers, 1994). A moisture content of 12% corresponds to approximately $0.5 \, a_{\rm w}$.

As with wheat and other grains, the moisture content is an unreliable guide to stability and will vary depending on the type of grain as well as the variety. To determine the moisture content that corresponds to the maximum $a_{\rm w}$ for stability at a particular storage temperature, moisture sorption isotherms at various temperatures are required. Published data on both the shelf life of flour at various $a_{\rm w}$ s and values for critical moisture contents are lacking, and it is therefore difficult to specify precisely the type of water vapor barrier required in a package. Notwithstanding the lack of information about critical moisture contents and shelf lives as a function of $a_{\rm w}$, bags made from cotton twill or paper have been used successfully for decades for consumer packs of flour. Kraft paper bags with an LDPE liner would provide additional protection and therefore a longer shelf life, but this does not seem to be justified.

20.2.3 RICE

Cultivated on every continent except Antarctica, rice is a crop that feeds half of the world's population and has fed more people over a longer period of time than any other crop. Brown (unmilled) rice is more nutritious than milled rice, but storage stability problems and a traditional consumer preference for whole (milled) rice have limited the quantities of brown rice packaged and sold for direct consumption. A major deterrent to greater user of brown rice is the accumulation of free fatty acids in rice stored under warm and humid conditions. Fatty acids can be released by lipases present in the rice aleurone (bran) layer of damaged grains and by high lipase-containing bacteria and fungi adhering to rice.

20.3 BREAKFAST CEREALS

Breakfast cereal foods can be classified according to the amount of domestic cooking required, the form of the product and the cereal used as raw material. All cereals contain a large proportion of starch, which, in its natural form, is insoluble, tasteless and unsuited for human consumption. It must be cooked to make it digestible and acceptable. In the case of hot cereals, the cooking is carried out in the home, while ready-to-eat cereals are cooked during manufacture (Fast and Calwell, 2000).

If the cereal is cooked with excess moisture and moderate heat as in boiling, then the starch gelatinizes and becomes susceptible to starch-hydrolyzing enzymes in the human digestive system. If the cereal is cooked with a minimum of moisture (or without moisture) but at higher temperatures as in toasting, then nonenzymic browning between protein and reducing sugars may occur and there may be some depolymerization of the starch.

20.3.1 MANUFACTURE

Ready-to-eat cereals probably owe their origin to the Seventh Day Adventist Church whose members, preferring an entirely vegetable diet, experimented with the processing of cereals in the midnineteenth century. A granulated product called "Granula," made by J.C. Jackson in 1863, may have been the first commercially available ready-to-eat breakfast cereal. A similar product called "Granola" was made by J.H. Kellogg by grinding biscuits made from wheatmeal, oatmeal and maize meal (Kent and Evers, 1994).

Ready-to-eat cereals comprise flaked, puffed, shredded and granulated products, generally made from wheat, maize or rice, although oats and barley are also used. The basic cereal may be enriched with sugar, honey or malt extract. All types are prepared by processes which tend to cause hydrolysis (dextrinization) rather than gelatinization of the starch.

Flaked products are made from wheat, corn, oats or rice. After cooking (often at elevated pressure) and the addition of flavorings such as malt, sugar and salt, the cereal is dried to 15%–20% moisture content and conditioned for 1–3 days. It is then flaked, toasted, cooled and packaged.

Puffed products are prepared from conditioned whole grain wheat, rice, oats or pearl barley, or dough made from corn meal or oat flour with the addition of sugar, salt and sometimes oil. It is cooked for 20 min under pressure, dried to 14%–16% moisture content and pelleted by extrusion through a die. A batch of the conditioned grain or pelleted dough is fed into a heated pressure chamber which is injected with steam. The starch becomes gelatinized and expansion of water vapor on release of the pressure causes a several-fold increase in volume. The puffed product is dried to 3% moisture content by toasting and then cooled and packaged.

Shredded products are made from whole wheat grains which are cooked to gelatinize the starch. After cooling and conditioning, the grain is fed through shredders. The shreds are baked for 20 min at 260°C, dried to 1% moisture content, cooled and packaged.

Granulated products are made from yeast dough consisting of wheat flour and salt. The dough is baked as large loaves, which are then broken up, dried and ground to a standard degree of fineness.

Flaked or puffed cereals are sometimes coated with sugar or candy to provide a hard, transparent coating that does not become sticky even under humid conditions. The sugar content of cornflakes increases from 7% to 43% as a result of the coating process, and that of puffed wheat from 2% to 51% (Kent and Evers, 1994).

20.3.2 INDICES OF FAILURE

There are five indices of failure to be considered when selecting suitable packaging materials for breakfast cereals. They are as follows:

- 1. Moisture gain resulting in loss of crispness
- 2. Lipid oxidation resulting in rancidity and off-flavors
- 3. Loss of vitamins
- 4. Breakage, resulting in an aesthetically undesirable product
- 5. Loss of aroma from flavored product

The shelf life of breakfast cereals depends to a large extent on the content and quality of the oil contained in them. Thus, products made from cereals with a low oil content such as wheat, barley, rice and maize grits (oil content: 1.5%–2.0%) have a longer shelf life than products made from oats (oil content: 4%–11%, average 7%). Although whole corn has high oil content (4.4%), most of the oil is contained in the germ, which is removed in making grits (Kent and Evers, 1994).

20.3.3 PACKAGING

The materials used for the packaging of ready-to-eat breakfast cereals are discussed later in relation to the major indices of failure.

20.3.3.1 Loss of Crispness

Data on the permissible increase in moisture content or $a_{\rm w}$ before loss of crispness occurs is required so that the water vapor barrier required to achieve the desired shelf life can be calculated. Sauvageot and Blond (1991) reported a slight decrease in crispness intensity of commercial samples of cornflakes ($m_{\rm i}$ 6.0%) and rice crispies ($m_{\rm i}$ 6.9%) between 0 and 0.50 $a_{\rm w}$ or 7% water content, after which there was a very rapid decrease. However, it is important to note that the effect of hydration on crispness of cereal-based products varies with the formulation. For example, Valles-Pamies et al. (2000) reported that extruded waxy maize starch products exhibited a loss of crispness at 0.40 $a_{\rm w}$, whereas the critical $a_{\rm w}$ was 0.75 when the starch contained 20% sucrose (Figure 20.1).

A particular challenge arises with breakfast cereals where dried fruit such as raisins are blended with the cereal prior to packaging. These so-called multidomain foods are dynamic systems in which moisture gain or loss occurs continuously from one domain to another until thermodynamic equilibrium between the food components and the surrounding gaseous environment is reached. Water migration and the resulting changes in moisture content affect the shelf life through undesirable modifications of their physical, sensory and microbial qualities. A simulation of moisture transfer in a cereal-raisin system stored in an impermeable package was developed by Sapru and Labuza (1996). Risbo (2003) included the package permeability properties in his shelf life calculations on a cereal-raisin system. Roca et al. (2008) developed a more general model to predict moisture transfer and shelf life in multidomain foods over the temperature range 5°C–30°C.

Packaging of breakfast cereals has traditionally been in fiberboard boxes with a supercalendered, waxed and glassine liner. As well as providing a barrier to water vapor, the liner must also confine cereal aromas within the packaged product and simultaneously prevent foreign odors entering. It should also be reclosable to protect the cereal remaining in the package (Monahan, 1988). The glassine liner has been largely replaced by various plastic materials, in particular thin gauge HDPE. HDPE coextruded

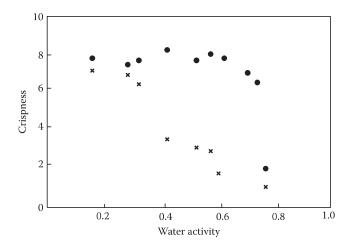


FIGURE 20.1 Sensory crispness of expanded starch-based extrudates versus $a_{\rm w}$ (\bullet without sucrose; x with 20% sucrose). (From Valles-Pamies, B. et al., *J. Sci. Food Agric.*, 80, 1679, 2000.)

with a thin layer of EVA copolymer is also used, where the EVA copolymer permits a lower heat seal temperature while offering the consumer an appealing and peelable seal (Monahan, 1988).

In a few cases where the cereal product is not hygroscopic and/or retains a satisfactory texture when in equilibrium with the ambient atmosphere, a liner may not be needed for moisture protection and may even serve to entrap rancid aromas. Where this is the case, either no liner or one which is vapor permeable may be used (Monahan, 1988). Some shredded wheat products are in this category and are discussed in the following.

20.3.3.2 Lipid Oxidation

The primary mode of chemical deterioration in dry cereals is lipid oxidation and two reasons have been advanced for this (Labuza, 1982). First, the $a_{\rm w}$ of dry cereals is at or below the monolayer, which essentially stops all other types of deteriorative reactions. Second, unsaturated fats are required in lipid oxidation, and the grains used in breakfast cereals have a high ratio of unsaturated to saturated fats.

To minimize oxidative rancidity, it is important that the package exclude light and most cereals are packed with an outer paperboard carton mainly for this reason. Excluding O_2 may be of limited assistance in extending shelf life although O_2 is almost never rate limiting (Labuza, 1982). For this reason, most companies do not bother to use packaging which is a good O_2 barrier. However, in a study of the storage stability of a flaked oat cereal product packaged in materials of different O_2 barrier properties with and without the addition of an O_2 absorber, Sakamaki et al. (1988) observed that the absorber retarded or delayed lipid oxidation provided that it was used with a packaging material that was a good O_2 barrier such as PVdC copolymer-coated PP-LDPE. Larsen et al. (2003) studied the effect of package OTR (including the use of an O_2 absorber), light and temperature (23°C and 38°C) on the sensory stability of extruded oat pellets packaged in O_2 over a period of 3 months. Oats stored under light developed a high degree of paint odor (rancidity) at both temperatures when in medium and high OTR packages, while those stored in the dark only did so at 38°C. Extruded oat in packages with low OTR, with and without an O_2 absorber, did not develop paint odor during 3 months of storage at either temperature, even when exposed to light; the headspace O_2 concentration in these packages did not exceed 1%.

Although the use of synthetic antioxidants in the package liner has been shown to be successful in extending shelf life, it is not generally permitted in most countries. Paradiso et al. (2008) showed that natural tocopherols limited the development of off-flavors in cornflakes during storage at room temperature for a year.

20.3.3.3 Loss of Vitamins

The vitamin and mineral fortification of cereals is widely practiced in many countries and there are usually associated nutritional labeling requirements. The major factor influencing vitamin loss in packaged cereals is the temperature of storage. In a study on the effects of processing and storage on micronutrients in breakfast cereals, it was concluded that micronutrient loss would not be a major factor in determining the shelf life of dry cereals. There were no substantial losses of added vitamins during normal shelf lives with the possible exception of vitamin A and, to a slight extent, vitamin C. Vitamin A survived six months (the average distribution time) at room temperature with no measurable loss (Labuza, 1982).

20.3.3.4 Mechanical Damage

The rigidity of the carton stock and the compression resistance of the finished carton must together provide the necessary resistance to product breakage throughout production line operations, warehouse storage and distribution from the manufacturer to the retailer and consumer. Rigidity also prevents the bulging of the carton. Protecting breakfast cereals from breakage does not appear to be a problem using currently available carton stock and carton designs.

20.3.3.5 Loss of Flavor

This can be a problem with certain cereal products to which fruit flavors have been added prior to packaging. In these situations, loss of flavor results in the product being considered to be at the end of its shelf life by the consumer. A study (Mohney et al., 1988) evaluating two typical cereal liner materials (HDPE and glassine) found that the permeability coefficients of *d*-limonene (a common flavor component in citrus products) in the HDPE liner were three to four orders of magnitude higher than those in glassine. It was also found that the solubility of *d*-limonene in the glassine liner was substantially lower than in the HDPE liner for the same vapor pressures. Thus, equilibrium distribution of the limonene vapor between a product such as a fruit-flavored cereal and the respective liners will result in a much lower limonene concentration within the glassine liner and "scalping" of the cereal flavor can be assumed to be much more significant in the HDPE liner.

20.4 PASTAS

Although the word "pasta" is traditionally associated with Italy and with durum wheat semolina, Italy cannot claim to have invented this popular food and semolina (the coarsely ground grain of durum wheat with particles mostly between 0.25 and 0.75 mm in diameter) is not the original raw material. The Chinese invented pasta that was produced as noodles from rice and legume flours several thousand years BCE. Today, pasta consumption is increasing in many countries to the extent that pasta can be classed as a truly international food.

Part of the appeal of pasta products (macaroni, spaghetti, vermicelli, noodles) is that they may be prepared from several raw materials according to countless formulations, and cooked and served in numerous ways to various tastes. Durum wheat semolina is considered to be the best raw material for pasta making because of the functional characteristics of its proteins, low lipoxygenase activity and high yellow pigment content. The limited availability and high cost of durum wheat compared with other cereals has lead to the use of flours and starches from rice, maize, barley, soft wheat, cassava and potato in pasta formulations in various parts of the world (Fuad and Prabhasankar, 2010).

The original composition of Italian pasta (water, durum wheat semolina and egg) has altered considerably to include vitamin supplements, iron salts, powdered vegetables, tomato concentrate, milk protein, other cereal flours and meat and cheese in filled pasta in order to satisfy the tastes and food habits of different populations. The introduction of MAP has enabled certain types of pasta (particularly the fresh and filled varieties) to progress from being a small-scale manufacturing operation to an established position in the food industry where, for example, fresh product is distributed across the United States.

Pasta can be subdivided into two categories. The first, macaroni, has come to represent a generic family of over 140 items in the United States and includes spaghetti, macaroni and vermicelli. This class of product is made from semolina, water and, in most cases, added vitamins and minerals, and contains about 1.5% fat.

The second broad category of pasta is noodles, which are discussed in the following.

20.4.1 Dried Pasta

Dried pasta is produced by the reduction of dough moisture content from 30% to about 11% by means of a dehydration process, the length of which is determined by the temperature used. The drying of pasta products at temperatures above 60°C has become widely accepted by pasta manufacturers, with benefits of this approach including control of bacteria in egg products and shorter drying cycles. If the drying stage of pasta manufacture is not properly controlled, then extensive growth of microorganisms such as *Salmonella* spp. and *Staphylococcus aureus* can occur, resulting in a potential hazard to public health (Aureli et al., 1986).

Two modes have been identified for dried pasta product failure: moisture gain or loss and color loss. The major mode is moisture gain, with the optimum moisture content for pasta storage appearing to be 10%–11%. If the pasta moisture content increases to 13%–16%, then mold growth (which makes the pasta unfit for consumption) and starch recrystallization or retrogradation (which makes the pasta unacceptably tough when cooked) occur (Labuza, 1982). As with other dried products, the optimum moisture content for stability is derived from the maximum "safe" a_w ; that is, a moisture content that is in equilibrium with 70% relative humidity or an a_w of 0.70.

For macaroni, a moisture content of 12.8% corresponds to an $a_{\rm w}$ of 0.70 at 25°C, while for egg noodles, the corresponding moisture content is 14.7% at 25°C and 13.3% at 27°C for vermicelli. The $a_{\rm w}$ corresponding to a moisture content of 10%–11% is about 0.56 at 25°C for macaroni, 0.44 for egg noodles at 25°C and 0.45 at 27°C for vermicelli, thus providing a margin for moisture increase during storage before the critical moisture content $m_{\rm c}$ is reached. If the moisture content of the pasta is allowed to fall to less than a certain level (9.5% in the case of vermicelli, which corresponds to 0.32 $a_{\rm w}$) it becomes too fragile and unacceptable in quality.

A second mode of deterioration is color loss through oxidation of carotene pigments by lipoxidase enzymes found naturally in semolina flour. These enzymes oxidize lipids and the peroxides formed attack the pigments. Light accelerates the oxidation process. An associated mode of deterioration is staling, which results from the oxidation of the lipids in the product. An analysis of published shelf life data suggests that the basic mode of failure in dried pasta is lipid oxidation rather than moisture gain (Labuza, 1982).

Manufacturers of pasta claim shelf lives of macaroni and spaghetti products ranging from 6 months to indefinite, and noodle shelf life claims range from 1 to 6 months. The exact shelf life depends on the storage temperature, RH and packaging material, none of which are well defined. The traditional packaging material for dried pasta was the paperboard carton, which frequently contained a plastic window so that the customer could view the contents. Today, most pasta products are packaged in plastic films such as OPP or LDPE-PET laminate.

20.4.2 Fresh Pasta

The production of fresh pasta involves kneading of the dough, followed by extrusion or lamination and then drawing. In the case of special pasta, this latter stage is accompanied by filling, using a cooked meat or vegetable-cheese mixture, thus resulting in a variety of potential microbiological flora. The moisture content of fresh pasta is >24% and requires refrigerated storage at <4°C (Costa et al., 2010).

Fresh pasta products are refrigerated for retail distribution and may be pasteurized. The micro-biological quality of fresh pasta will thus depend on the quality of the raw materials, the cleanliness

and hygiene of the processing environment and equipment and the handling of the product during production and packing. In addition, the temperature of the product during storage, distribution and retailing is crucial with respect to microbiological quality. Pasta is typically pasteurized by passing through a chamber on a perforated conveyor belt using injected steam at a temperature of 91°C and for a time of 9 min, followed by cooling to 4°C within 15 min inside a forced circulating air freezer (Sanguinetti et al., 2011).

The use of MAP has become widespread for fresh pasta products and a range of N₂ and CO₂ gas compositions are used. A survey for *Staphylococci* spp. and their enterotoxins in wet pasta packaged in a MA of CO₂:N₂ 20:80 from five processors showed that 12% of fresh products were contaminated with *S. aureus* (Park et al., 1988). The pasta had a recommended shelf life of 4 weeks when stored at 4°C. The results showed that proper refrigeration was essential to ensure the safety of MAP wet pastas.

Fresh pasta packaged in a MA of CO₂:N₂ 22:78 was compared with a control air package and monitored by Lee et al. (2001) for quality changes during storage at 8°C. The MAP suppressed the microbial growth of total aerobic bacteria, yeasts and molds with a concomitant reduction in the rates of physical and chemical quality changes. The shelf life was successfully extended from 20 days in air packs to 40 days in MAP based on a microbial criterion for end of shelf life of 10⁶ cfu g⁻¹. The shelf life extension was greater when the initial microbial quality of the product was better.

Mold growth is a major problem in the shelf life of fresh filled pasta. Pasteurized, fresh cheese-filled pasta was packaged in a MA of $CO_2:N_2$ 50:50 or in air and changes in microbial growth, chemical and physical parameters and sensory attributes were monitored by Sanguinetti et al. (2011) for 42 days at 4°C. MAP allowed a mold-free shelf life of 42 days, whereas air-packaged samples spoilt between 7 and 14 days.

The influence of chitosan (1–3 g kg⁻¹ dough), gas headspace and film barrier properties on the microbiological and sensory shelf life of fresh pasta was studied by Costa et al. (2010). Results suggested that the sensory quality, in particular the odor of the packaged product, played a significant role in determining product acceptability. MAP (CO₂:N₂ 70:30), chitosan and high barrier packaging acted in a synergistic way to control the quality loss of fresh pasta during refrigerated storage at 4°C from both microbial and sensory points of view, giving a shelf life of almost 18 days compared to 10 days in low barrier packaging.

The actual packaging materials used for fresh pasta products depend on whether or not the product is pasteurized (in which case, the package must be able to withstand the pasteurization process without deforming) and whether or not the product is to be heated in its package in a microwave oven by the consumer (in which case, the package must be able to withstand domestic microwave temperatures). For products which are not pasteurized nor intended to be heated in their package, a rigid tray of PVC-LDPE onto which is sealed a PA-LDPE film is common. However, if microwave heating is used, then the rigid tray is usually made from CPET or PS-EVOH-LDPE, and the film may be based on PVdC copolymer-coated PET, OPET-EVOH-LDPE or PP.

20.4.3 Noodles

Wheat flour noodles are staple foods in many Asian countries and account for the end use of at least one-eighth of global wheat production. Noodles have now become more widely adopted for everyday use and storage has been facilitated by the introduction of dried noodles and boiled and packaged long shelf life noodles. Consumption of noodles, particularly instant noodles, has been expanding very rapidly during recent decades. The primary ingredient of Asian noodles is refined flour milled from bread wheat (*Triticum aestivum*, also known as common wheat), in contrast to pasta where semolina from durum wheat (*Triticum durum*) is the primary ingredient.

Asian noodles are made in a wide variety of types that are categorized based on formulation (particularly the presence or absence of alkali), cross-sectional dimensions and postcutting processes such as steaming, frying, drying or boiling. For consumers of these products, the quality

of the noodles themselves is primarily defined by texture and appearance. Other factors are also important, for example, for instant fried noodles, rehydration rates during final preparation and the absence of rancid taste after extended storage. The first instant noodle, called *chicken ramen*, was produced by Nissin Foods of Japan in 1958 (Fu, 2008). Another milestone was reached in 1971 when Nissin introduced cup noodles: instant noodles in a foam PS cup to which boiling water could be added to rehydrate and heat the noodles.

The three main styles of Asian wheat noodles are white salted, yellow alkaline and instant. The ingredients of Asian noodles include wheat flour, water and either common salt (sodium chloride) or alkaline salts (typically mixtures of sodium and potassium carbonates). It is believed that the original purpose of including alkaline salts in noodles was to extend the shelf life by inhibiting mold growth (Fu, 2008). Generally speaking, a white, soft and elastic noodle texture is characteristic of white salted noodles, while a bright, clear yellow color with a firm, chewy texture and a smooth surface is typical of yellow alkaline noodles. The alkaline salt in yellow alkaline noodles inhibits enzyme activity and changes the flour pigments (flavonoids) to yellow. This results in a product with a desirable bright yellow color, favorable noodle strength and palatability. The processing of instant noodles involves precooking of the fresh noodle strands by steaming and then deep frying which gives a texture distinct from that of white salted and yellow alkaline noodles. Instant noodles are increasingly popular due to their ease of preparation.

Asian noodles may be sold as a fresh product, in the moist form following partial cooking or dried prior to packaging. The moisture content of fresh noodles ranges from 32% to 40%. The main disadvantage of fresh noodles is their relatively short shelf life, ranging from one to several days, depending on the packaging and storage conditions (Fu, 2008). The final moisture content of dried noodles is usually less than 14%.

Starch noodles, produced from purified starch from various plant sources, are a major category of Asian noodles. Starches derived from the mung bean, yellow peas and potato are widely used in the production of these noodles (Tan et al., 2009). Rice noodles (the second principal form of rice product after cooked rice grains) are also widely consumed in Asia. Traditionally, rice noodles are made from long-grain rice with high amylose content (>22% amylose).

For deep fried instant noodles, oxidation leading to rancidity (instant noodles are 15%–22% fat) is the major reason for end of shelf life. Rancidity development is a minimum at $a_{\rm w}=0.3$ (corresponding to the monolayer) and shelf life is typically 4–5 months. Addition of antioxidants to the frying oil extends shelf life, for example, 200 ppm of TBHQ and 500 ppm EDTA quintuples shelf life. Other deteriorative reactions in instant noodles are moisture uptake (instant noodles have 3%–6% moisture content) and nutrient degradation (especially B group vitamins such as riboflavin).

Ling (2010) reported the following data for retail Asian noodles presumably purchased in Canada:

- 1. Dried noodle sticks $a_{\rm w}$ 0.550–0.614 and fat 0.4%–2.0%
- 2. Instant noodles in bags a_w 0.140–0.626 and fat 12%–17%
- 3. Instant noodles in cups a_w 0.481–0.504 and fat 20%–37%

No indication was given as to the age of the samples or how much of their shelf life remained at the time of testing.

Rachtanapun and Tangnonthaphat (2011) evaluated the effects of packaging type and storage temperatures on the sensory and microbial shelf life of fresh rice noodles packed in four different packages: HDPE film (OTR 1372 mL m⁻² day⁻¹ at 25°C and 52.5% RH); HDPE pouch (OTR 1773), PET pouch (OTR 37) and PA-LDPE pouch (OTR 19) under vacuum conditions. Noodles in the PA-LDPE pouch had the longest shelf life (13 days) when stored at 25°C. When stored at 4°C, the shelf life was 29 days with end of shelf life being starch retrogradation; low temperatures inhibited microbial growth and slowed down the decrease in pH.

Li et al. (2011) added humectants to fresh noodles to lower their $a_{\rm w}$ from 0.94 to 0.85 and combined this with irradiation at 4 kGy to extend the microbial (TPC < 10^6 cfu g⁻¹) and sensory shelf life

at 37°C more than sevenfold from 2 to 16 days. A trained panel of 10 evaluated the noodles for odor and color, and samples that scored <5 on a 10 point scale were considered unacceptable. No mention was made of any packaging of the noodles.

20.5 BAKERY PRODUCTS

Bakery products have been an important part of a balanced diet for thousands of years. Flour and its principle baked product, bread, are the cheapest and most important staple foods for many nations of the world. The function of baking is to present cereal flours in an attractive, palatable and digestible form. A wide variety of bakery products can be found on supermarket shelves including breads, unsweetened rolls and buns, doughnuts, sweet and savory pies, pizza, quiche, cakes, pastries, biscuits, crackers and cookies. It is useful to classify bakery products on the basis of their $a_{\rm w}$ and pH, because these parameters are a good indication of the spoilage problems likely to be encountered. The $a_{\rm w}$ and pH of a range of bakery products is presented in Table 20.2.

20.5.1 Bread

20.5.1.1 Manufacture

The production of bread and other fermented products accounts for the greater volume proportion of all manufactured baked products (Cauvain and Young, 2011). Although breads come in a wide variety of forms and apparently different processes, the underlying principles involved in their manufacture are similar. Bread is made by mixing wheat flour, water, yeast and salt. Other ingredients which may be added include flours of other cereals (e.g., malt flour and soy flour), fat, yeast foods, emulsifiers, milk and milk products, fruit and gluten. After mixing, the individual dough pieces are shaped, expanded through fermentation and then heat-set in the baking process.

TABLE 20.2
Water Activity and pH of Typical Bakery Products

Water Activity (a_w)	рН	Products
0.99		Creams, custards
0.97	6.0	Crumpets
0.95-0.99	5.6	Breads, fermented products
0.90-0.95		Moist cakes (e.g., carrot cake)
0.91	6.3	Yeasted pastries (e.g., Danish, croissant)
0.84	4.2	Fruit pies
0.82-0.83	6.3	Chocolate-coated doughnuts
0.80-0.89		Plain cakes (e.g., Madeira, sponge cakes)
0.70-0.79		Fruit cakes
0.65-0.66	5.6	Bread crumbs, biscuit crumbs
0.60-0.69		Some dried fruits or fruit cakes
0.61		Biscuits, chocolate, some dried fruits
0.3		Pastries

Source: Adapted from Cauvain, S.P. and Young L.S., Bakery Food Manufacture and Quality: Water Control and Effects, 2nd edn., Wiley-Blackwell, Oxford, England, 2008; Smith, J.P. et al., Crit. Rev. Food Sci. Nutr., 44, 19, 2004.

20.5.1.2 Indices of Failure

Although several indices of failure are possible in bakery products, the four most important are now discussed in turn.

20.5.1.2.1 Microbial Spoilage

Microbial growth, particularly mold growth, is the major factor limiting the shelf life of bakery products. Spoilage types for typical bakery products are shown in Table 20.3. Chemical preservatives are used by the bakery industry in many countries to prevent or retard microbiological spoilage; chemicals used include calcium and sodium propionate, sorbic acid, potassium sorbates, sodium diacetate, methylparaben, propylparaben, sodium benzoate and acetic acid at levels of 0.005%–0.5% w/w (Smith et al., 2004). The extension of shelf life resulting from the use of preservatives is limited by the development of off-odors and flavors or effects on product quality (Seiler, 1998). As well, the trend toward foods free of preservatives is driving the development of alternative methods to overcome the problem. Principal among these is MAP, using mainly CO₂.

It has been mentioned earlier in this book (see, in particular, Chapter 16) that CO_2 has an inhibitory effect on the growth of certain microorganisms, where its effectiveness increases as the product storage temperature is reduced. Microorganisms tend to vary in their tolerance of CO_2 , with molds generally being more affected than bacteria or yeasts.

For bakery products with an $a_{\rm w}$ of 0.86 or above, the *Penicillium* group of molds tend to govern mold-free shelf life, but as the $a_{\rm w}$ falls below this level, the *Aspergillus glaucus* group of molds predominate. These latter organisms are more susceptible to the effects of ${\rm CO}_2$ than *Penicillium* species, although certain of the latter species (in particular *Penicillium roqueforti*, a common contaminant of rye bread) are much more ${\rm CO}_2$ resistant than others. The type of molds present, rather than the $a_{\rm w}$, is a more important factor affecting the antimold activity of ${\rm CO}_2$. Bakery products such as cakes, which have an $a_{\rm w}$ of 0.85 or below, can be expected to show a large increase in mold-free shelf life by packaging in ${\rm CO}_2$ (Smith et al., 2004).

With high $a_{\rm w}$ bakery products, the shelf life is sometimes limited by the growth of yeasts or lactic acid bacteria rather than molds. These microorganisms are resistant to the effects of ${\rm CO}_2$ and cause spoilage either in the form of visible growth or by the generation of quantities of ${\rm CO}_2$, which cause the package to expand. Of particular importance is the group of filamentous yeasts known as *chalk molds* (usually *Pichia burtonii*). Chalk molds produce a white powdery spreading growth which tends to be more obvious on the surfaces of dark-colored breads. Lactic acid bacteria (particularly

TABLE 20.3 Spoilage Types for Typical Bakery Products

Water Activity (a_w)	Products	Spoilage Types
0.99	Creams, custards	Bacterial spoilage (e.g., "rope" mold growth and "chalk molds")
0.90-0.97	Breads, crumpets, part-baked yeasted products	Bacterial spoilage (e.g., "rope" mold growth and "chalk molds")
0.90-0.95	Moist cakes (e.g., carrot cake)	Mold and yeast, bacterial spoilage (e.g., "rope")
0.8-0.89	Plain cakes	Molds and yeasts
0.7-0.79	Fruit cakes	Xerophilic molds and osmophilic yeasts
0.6–0.69	Some dried fruits or fruit cakes	Specialized xerophilic molds and osmophilic yeasts, sugar-tolerant yeasts
< 0.6	Biscuits, chocolate, some dried fruits	No microbial spoilage

Source: Cauvain, S.P. and Young L.S., Bakery Food Manufacture and Quality: Water Control and Effects, 2nd edn., Wiley-Blackwell, Oxford, England, 2008.

Leuconostoc mesenteroides) have been found to be responsible for spoilage of gas-packaged crumpets. Fortunately, post-baking contamination with yeasts and lactic acid bacteria is uncommon and can be controlled by the adoption of appropriate hygienic precautions (Seiler, 1998).

20.5.1.2.2 Staling

Staling is the common description of the decreasing consumer acceptance of bakery products as they age, caused by changes in crumb other than those resulting from the action of spoilage organisms; it is the major mode of deterioration. Bread staling falls into two categories: crust staling and crumb staling. Crust staling is generally caused by moisture transfer from the crumb to the crust, resulting in a soft, leathery texture and is generally less objectionable than crumb staling. Crumb staling is more complex, more important and less well understood (Pateras, 2007). The firmness of bread varies with position within a loaf, with maximum firmness occurring in the central portion of the crumb. The most widely used indicator of staling is measurement of the increase in crumb firmness (Gray and Bemiller, 2003). Most white bread in the United States has a commercial shelf life of 2 days after which it is no longer considered fresh because of the staling process. As a consequence, large quantities of bread are discarded or returned to the manufacturer, posing an economic burden to both the baking industry and consumers.

Bread staling is a complex phenomenon in which multiple mechanisms operate, and neither the bread system nor the staling process is well understood at the molecular level. The most plausible hypothesis is that retrogradation of amylopectin occurs, and because water molecules are incorporated into the crystallites, the distribution of water is shifted from gluten to starch/amylopectin, thereby changing the nature of the gluten network (Gray and Bemiller, 2003). The formation of complexes between starch polymers, lipids and flour proteins is thought to inhibit the aggregation of amylose and amylopectin, so that, for example, cookies and biscuits (which have a higher lipid content than bread) tend to stale more slowly. Staling can be prevented if bread is stored above 55°C or below -18°C (Kent and Evers, 1994). Antistaling enzymes or carbohydrases, which work by hydrolyzing the amylopectin fraction and thereby preventing retrogradation and hence staling, increased shelf life of white pan bread by over two days (Gil et al., 1999).

An interesting aspect of the staling of bread is that the rate has a negative temperature coefficient, so that as the temperature increases up to 55°C, the rate of staling decreases. The staling rate passes through a maximum close to 4°C and decreases as the temperature declines below this point. From a packaging point of view, nothing can generally be done through the selection of different packaging materials to either accelerate or impede the rate of staling, although an exception is pita bread, which is discussed in the next section on gas packaging.

Evidence for the effect of CO_2 on the rate of staling is conflicting. Rasmussen and Hansen (2001) found no significant effects of 100% CO_2 or 50:50 $CO_2:N_2$ during storage of bread for 7 days at $20^{\circ}C$ compared to control bread in air. The development of bread firmness during storage in 100% CO_2 for 49 days was correlated to amylopectin retrogradation and to changes in the freezable water fraction of the breads in a nonlinear manner, suggesting that bread firmness is influenced by both the crystallization behavior of starch and by changes in hydration.

20.5.1.2.3 Moisture Loss/Gain

The cooling of bread can create problems, particularly when the bread is to be sliced and packaged before sale. Bread leaves the oven with the crumb at a temperature of about 98°C and a moisture content at the center of about 45%. The crust is hotter (about 150°C) but much drier (1%–2% moisture content) and cools rapidly. During cooling, water moves outward from the interior toward the crust and then to the atmosphere. Excessive drying during cooling results in weight loss and poor crumb characteristics. If the moisture content of the crust rises considerably during cooling, then the texture of the crust becomes leathery and tough and the attractive crispness of freshly baked bread is lost (Kent and Evers, 1994).

After cooling, the moisture content of white bread is 36% and the $a_{\rm w}$ is 0.96. Packaging has a major influence over whether or not a bakery product will gain or lose moisture during storage, although clearly the difference between the $a_{\rm w}$ of the product and the RH of the ambient

atmosphere will be the primary driving force. Softness or resistance to deformation and recovery from deformation are important crumb characteristics and are directly affected by the level of water remaining in the product, coupled with a fully developed and resilient crumb structure (Cauvain and Young, 2008).

The loss of crust crispness is an important and beneficial change in sandwich bread types because it adds to the perception of freshness by the consumer. When purchasing bread, consumers can only assess freshness by squeezing the loaf, knowing that fresh bread has little resistance to squeezing and will rapidly spring back to its original shape (Cauvain and Young, 2008).

Although loss of crust crispness as a result of moisture gain is, at least in theory, a possible cause of end of shelf life for bread, such an occurrence is rare and can generally be overcome by selecting a more permeable package. An associated problem with moisture gain is an increase in crust $a_{\rm w}$ and an increased likelihood of mold growth. Conversely, excessive moisture loss can also be easily controlled by selecting a less permeable packaging material.

20.5.1.2.4 Rancidity

The development of oxidative rancidity in bread is not normally considered to be a problem as bread has relatively high oxidative stability. However, changes in aroma and flavor attributes such as "acidic," "off," "rancid" and "dust" together with the taste attributes "sweet" and "bitter" have been found to increase during storage of whole wheat bread. Jensen et al. (2011) reported small but significant differences in oxidative stability for whole wheat bread crumb and crust stored in plastic bags with $100\%~N_2$ at room temperature. The overall antioxidative capacity was reduced during storage with the accumulation of lipid hydroperoxides peaking after 2–3 weeks of storage. Bread crust was generally found to be more stable to oxidation compared to the crumb. They suggested that the quality of bread with extended shelf life may be improved by minimizing oxidation through the use of antioxidants.

20.5.1.3 Packaging

The objective in packaging bread is to maintain the bread in a fresh condition by preventing too rapid drying out, without providing too good a moisture barrier which would promote mold growth on a soggy crust. The most commonly used material is an LDPE bag in which the end is twisted and sealed with a PS tag. This form of packaging helps retard one mode of deterioration in bread; namely, moisture loss. However, the moisture which tends to migrate from the crumb to the crust is prevented by the package from passing freely into the atmosphere, and results in a crust with a tough, leathery consistency. Some specialty breads such as French and Italian are packaged in OPP or PET bags perforated with small holes which allow moisture to escape and thus retain a crisp crust. Several hole sizes and densities are available, depending on the particular product and its surface area:volume ratio.

An assessment of the risk of physical contamination of bread packaged in perforated OPP films and sold in self-service retail outlets found a correlation between the risk and the geometrical characteristics of the film including the size of the holes and the area of the holes as a percentage of the total surface area (Piergiovanni et al., 2003). Pagani et al. (2006) investigated variations in the moisture content inside the loaf during storage and their influence on changes in crumb softness over 48 h when packaged in perforated OPP films of varying hole diameter and density. Moisture loss varied from 10% to 25% of the initial moisture content. The best performing film had a mean hole diameter of 0.54 mm and hole density of 21.4 holes cm⁻² (corresponding to an open surface of 5%) and allowed both crust crispness and crumb softness to be maintained, something that cannot be achieved with, for example, paper bags.

Vacuum packaging is not a suitable technology to extend the mold-free shelf life of most soft bakery products because the product is crushed under a vacuum. However, it has been used to prevent mold problems in flat breads such as naan and pita, and pizza crusts. An alternative to vacuum packaging is to modify the atmosphere inside the package and the three approaches that have been investigated are discussed in the following.

20.5.1.3.1 Gas Packaging

The idea of modifying the gas atmosphere inside a package of bread in order to extend the product shelf life is not new. In fact, it was shown as early as 1933 that the storage of bread in atmospheres containing at least 17% CO₂ delayed the appearance of mold (Skovholt and Bailey, 1933). At a concentration of 50% CO₂, the mold-free shelf life of bread was doubled under storage conditions favoring mold development.

Extensive research on the use of CO_2 for extending the shelf life of bakery products was undertaken by Seiler in the United Kingdom in the 1960s (Seiler, 1998). In detailed studies with bread and cake stored at 21°C and 27°C and CO_2 concentrations of 0%–60%, it was shown that the mold-free shelf life increased with increasing CO_2 concentrations, with the effect (not unexpectedly) being greater at lower temperatures. Subsequent studies with mixtures of CO_2 and N_2 and with 100% CO_2 confirmed the need for CO_2 in the package headspace, where simply displacing headspace O_2 with N_2 alone was insufficient to prevent mold growth.

A range of gas mixtures has been used to extend the shelf life of bakery products, from 100% CO₂ to 50:50 CO₂:N₂. The optimum blend of gases for a specific product cannot be determined by trial and error but only through a detailed, systematic study of the variables influencing product shelf life. Extensions of 3 weeks to 3 months at room temperature are achievable using appropriate mixtures of CO₂ and N₂ (Smith et al., 2004).

Degirmencioglu et al. (2011) added potassium sorbate to bread dough at concentrations of 0%, 0.15% and 0.30% and packed the sliced bread in expanded APET-EVOH-LDPE trays sealed with a PA-LDPE film and six different gas concentrations (air, $100\%~N_2$, $70:30~N_2:CO_2$, $50:50~N_2:CO_2$, $30:70~N_2:CO_2$ and $100\%~CO_2$). The packaged bread samples were stored for 21 days at $20^{\circ}C$ and 60%~RH. None of the samples showed signs of mold growth after 21 days, and $100\%~CO_2$ with 0.30% potassium sorbate was the most effective treatment for the inhibition of bacteria.

Pita bread (also called Arabic, Egyptian baladi, flat or pocket bread) is made from flour, water and yeast and has a shelf life of only a few hours, mainly due to its large surface area:volume ratio. Hardening caused by staling and drying is the main factor limiting shelf life, with the moisture content and $a_{\rm w}$ of unpackaged pita bread reducing from 55.5% and 0.95 to 40.3% and 0.92, respectively, in 6h. Using a laminate film containing EVOH as a barrier layer, a gas atmosphere of 99.5% $\rm CO_2$ or a mixture of 73:27 $\rm CO_2$: $\rm N_2$ enabled the shelf life of pita bread to be extended to 14 days at which time yeast growth terminated shelf life. Staling, as determined by means of a penetrometer, was delayed in MAP pita bread (Avital and Mannheim, 1988). Black et al. (1993) prevented microbial spoilage for up to 28 days in packs containing EVOH and flushed with 100% $\rm CO_2$, but stale flavors developed after 21 days and no clear pattern of firming over time or between treatments was found.

In a review on the use of MAs for the packaging of bakery products, Smith et al. (2004) concluded that MAP may not be suitable for all types of bakery products and that knowledge of a product's physical, chemical and microbiological characteristics are critical to the success of this technology. Furthermore, the importance of combining technologies such as O₂ absorbers and ethanol vapor generators with MAs to increase the shelf life of bakery products was emphasized.

20.5.1.3.2 Alcohol Vapor

It has been known for many years that ethanol is a powerful bactericide. Indeed, ethanol is still used in this application for the sterilization of surgical instruments and working surfaces. Ethanol is also a very effective antifungal agent and, as such, has the potential to extend the shelf life of bakery products. In 1976, a U.S. patent was granted to cover the use of ethanol for retarding mold growth in partially baked pizza crust. The data presented demonstrated that where pizza bases were sprayed on all surfaces with 95% ethanol to give a concentration of 2% based on product weight, the shelf life was increased by up to fivefold. Subsequently, the U.S. FDA affirmed the GRAS status of

ethanol as a direct human food ingredient and permitted its use for spraying prebaked pizza bases at concentrations up to 2% by weight (Seiler, 1998).

Extensive tests were carried out in the United Kingdom to determine the effectiveness of treatment with 95% ethanol in increasing the mold-free shelf life of a range of bakery products (Seiler, 1998). At a given level of treatment, the antimold activity of ethanol was greater when the products were tightly packed in film than when loosely packed and when gas impermeable films were used. The ability of ethanol to act as a vapor phase inhibitor was confirmed by the finding that similar increases in mold-free shelf life were obtained when the same amount of ethanol was sprayed over all surfaces of the product prior to packaging and sealing and when ethanol was merely added to the base of the same size bag before adding the product and sealing. Extensions in mold-free shelf life varied according to the type of product, tightness of the package, gas permeability of the packaging material and seal integrity. Treatment with 0.5% by product weight of food grade ethanol (95%) was found, under optimum conditions, to at least double mold-free shelf life, while treatment with 1.0% was found to at least triple shelf life. Ethanol was found to retard the rate of staling of both bread and cake in addition to inhibiting mold growth. The flavor of ethanol could be detected by sensory panels in cake treated with 1.0% but not 0.5% ethanol by product weight (Seiler, 1998).

Another way of adding ethanol (besides the injection or deposition of a small amount into the package immediately prior to sealing) is to use sachets of paper-EVA copolymer containing powdered silica gel (35% w/w) onto which food grade ethanol (55% w/w) has been absorbed. Vanilla can be added to mask the smell of ethanol. These sachets are available commercially and can be placed inside the package prior to sealing. They allow the slow release of alcohol vapor, which exerts the preservative effect. The extension in shelf life has been shown by the supplier of the sachets to depend on the ethanol permeability of the packaging material, the integrity of the seals, the $a_{\rm w}$ of the food and the type of microorganisms present. Data on the permeability of plastic films to ethanol is scant; the permeability coefficient for ethanol through LDPE has been reported as $2.8 \times 10^{-4} \, {\rm g} \, {\rm cm}$ m⁻² day ⁻¹ kPa⁻¹.

Ethanol vapor generators have been shown to be effective in controlling at least 10 species of molds, including *Aspergillus* and *Penicillium* species; 15 species of bacteria including *Staphylococcus*, *Salmonella* and *E. coli* spp; and 3 species of spoilage yeast (Smith et al., 2004). For products with a_w s of less than 0.90, long increases in mold-free shelf life can be obtained using 0.34%–0.69% of ethanol by weight of the product. For higher a_w products, up to 4% ethanol by weight may be required.

20.5.1.3.3 Oxygen Absorbers

It is very difficult to reduce the O_2 content to a very low level in packages of bakery products. The porous interiors of these products tend to trap O_2 in such a way that it does not readily interchange with gas which is flowing through the package as occurs in a simple flushing operation carried out as part of MAP. Repeated vacuumizing followed by release of vacuum with an anaerobic gas system would probably solve this problem but would also lead to collapse of products such as bread and rolls. One approach to overcome this problem is to place an O_2 -absorbent material inside the package after it has been flushed with N_2 or CO_2 . Sachets containing iron powder which rapidly react with O_2 have been evaluated for this purpose.

In tests reported by Seiler (1998), slices of bread and Madeira cake which had been artificially inoculated with molds were placed in bags of O_2 impermeable film with an O_2 -absorbent sachet and heat sealed; no mold growth appeared even after prolonged storage at 27° C. In further tests in which films with higher O_2 permeability and leaking seals were used, the extensions in mold-free shelf life were greatly reduced. Permeability of the film was found to be more important than leakage sites in the seals. It was concluded from these tests that the use of O_2 -absorbing sachets can result in commercially worthwhile increases in shelf life of baked products, provided that the packaging material used is sufficiently impermeable to O_2 and the packages are well sealed.

The effect of an ethanol emitter (EE) or ethanol emitter combined with an O_2 absorber (EE + OA) on the shelf life extension of sliced bread packaged in high barrier SiO_x -coated PET-LDPE pouches stored for 30 days at 20°C was investigated by Latou et al. (2010). Bread with (WP) and without (WOP) preservatives served as controls. Aroma quality deterioration during storage was due to the loss of volatile compounds and the formation of "off-flavors" from lipid oxidation. Neither the EE nor the EE + OA had an adverse effect on the initial odor, taste and texture of bread. Based on sensory (texture) and microbiological data, shelf life was ~4 days for samples WOP; 6 days for samples WP; 24 days for samples containing the EE and at least 30 days for samples containing the EE + OA.

20.5.2 BISCUITS, COOKIES AND CRACKERS

20.5.2.1 Manufacture

The three basic ingredients used to manufacture products in this category are wheat flour, fat and sugar which are combined in different combinations, together with salt and other ingredients in lesser quantities, to produce a wide range of products. The mixing process achieves two purposes: intermingling of ingredients, and certain chemical and physical changes which depend on the type of product being produced.

Doughs fall into two categories: hard and short. Hard doughs (crackers and "tea and coffee" biscuits) have low fat, high water and receive a single-stage mix. Short doughs (pastry products, short-bread and American-style cookies) have high fat, low water and usually high sugar levels, and are usually mixed in two stages. Baking is usually carried out in tunnel ovens where the formed dough pieces are conveyed through a series of heated sections. From the oven, the product is taken onto a series of conveyors where it cools and loses the last traces of moisture. After cooling, some products are directly packaged but many types require additional processing to add non-baked enrichments such as cream and chocolate (Manley, 2011).

20.5.2.2 Indices of Failure

Three indices of failure are usually associated with biscuits: loss of crispness, development of rancidity and development of fat bloom. The possible role that packaging may play in controlling the rate of deterioration is now discussed for each index.

20.5.2.2.1 Loss of Crispness

Freshly baked biscuits usually have moisture contents within the range 1%-5% and $a_{\rm w}$ s from 0.1 to 0.3. If biscuits are completely sealed in a material with a very low WVTR, then the small amount of moisture in the atmosphere inside the package will rapidly come into equilibrium with that in the biscuits and no further change will take place. However, if the packaging material has a medium WVTR or if the package seals are not perfect, moisture from the ambient air will enter the package and ultimately lead to a loss of crispness.

The critical $a_{\rm w}$ at which biscuits, cookies and crackers lose their crispness depends on their formulation but it is typically ~0.5 \pm 0.2. Given the large volume of such products manufactured each year, there are surprisingly few published moisture sorption isotherms (MSIs). Palou et al. (1997) reported the MSIs for three cookies and two corn snacks at 25°C, 35°C and 45°C; McMinn et al. (2007) reported the MSIs for oatmeal biscuits at 5°C, 20°C, 40°C and 60°C; Cervenka et al. (2008) reported the MSIs for gingerbread over the temperature range 20°C–30°C; and Al-Muhtaseb et al. (2010) reported MSIs for Madeira cake over the temperature range 5°C–60°C.

Figure 20.2 presents the MSIs at 20°C for crackers and cookies. At any particular $a_{\rm w}$, the cracker had a higher EMC or sorbed water than the cookie, which was not surprising as the latter contained 10 times as much fat as was in the cracker (Kim et al., 1999).

Although it is possible to produce cream fillings that contain no moisture, some products such as Amaretti cookies are multidomain systems characterized by a soft internal almond paste ($a_w \sim 0.74$; moisture content $\sim 13\%-14\%$) and a crunchy external crust ($a_w \approx 0.40$; moisture content $\sim 5\%-6\%$).

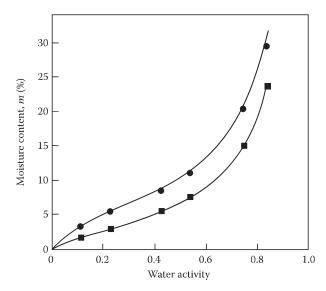


FIGURE 20.2 Moisture sorption isotherm at 20°C for a cracker (●) and cookie (■). (Redrawn from Kim, S.S. et al., *J. Food Sci.*, 64, 300, 1999.)

This leads to a severe hardening of the internal almond paste and a softening of the crust due to the redistribution of water, severely limiting the shelf life to only a few days (Farris and Piergiovanni, 2008). Arimi et al. (2010) monitored the loss of crispness in Crackerbread biscuit with increasing a_w ; the critical water activity (a_c) at 25°C ranged between 0.51 and 0.59.

Obviously, it is useful to know the initial and critical moisture contents or $a_{\rm w}$ s of biscuits so that a satisfactory package can be selected that will give the desired shelf life in a particular environment. The following example (Robertson, 2011) demonstrates how this can be done.

Example 20.1

McMinn et al. (2007) reported the moisture sorption data for oatmeal biscuits and the resulting MSI at 40°C is shown in Figure 20.3. For the purposes of this example, it is assumed that the biscuits had an initial moisture content m_i of 1.0% (0.010 g H₂O per g of dry solids) and a critical moisture content m_c of 3.6% due to loss of crispness. The equilibrium moisture content m_c at 40°C corresponding to 90% RH is 11.5% and the pseudo-equilibrium moisture content m_c obtained by linearizing the straight line portion of the isotherm is 5.0%; the slope of the straight line (*b*) is 0.055 g H₂O g solids⁻¹ unit a_w^{-1} .

Calculate the shelf life of the biscuits if they are packed in either a $26\,\mu m$ two side acrylic coated OPP film or a $50\,\mu m$ one side acrylic coated, one side PVdC copolymer coated white opaque OPP. The weight of biscuits in the rectangular package is $250\,g$ and the dimensions of the package are $8\times 16\times 4\,cm$. The packed product is to be distributed under tropical conditions ($38\,^{\circ}$ C and $90\,^{\circ}$ RH).

Surface area of the rectangular packs = $448 \text{ cm}^2 = 0.0448 \text{ m}^2$

Weight of dry solids in the package = $250 \times 99\% = 247.5$ g

Vapor pressure of pure water at 38°C = 4.969 cm Hg

Using data from the plastic film supplier, the WVTR of the two films at 38°C and 90°RH are as follows:

$$26 \, \mu \text{m OPP} = 5.0 \, \text{g m}^{-2} \, \text{day}^{-1}$$

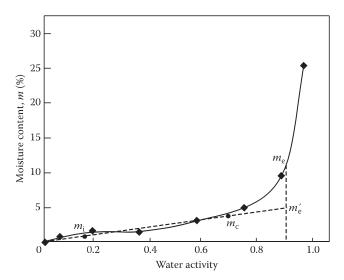


FIGURE 20.3 Moisture sorption isotherm at 40°C for oatmeal biscuits with a superimposed straight line of slope b. Initial (m_i) , critical (m_c) and equilibrium (m_e) moisture contents are indicated together with the pseudo-equilibrium (m'_e) moisture content used for package shelf life calculations. (Plotted using data from McMinn, W.A.M. et al., J. Food Eng., 79, 481, 2007.)

$$50 \, \mu m \, OPP = 3.4 \, g \, m^{-2} \, day^{-1}$$

The WVTRs must be converted into water vapor permeances P/X by dividing by the driving force for water vapor transfer:

Driving force at 38° C and 90° RH = $4.969 \times 0.90 = 4.472$ cm Hg

For 26 mm OPP film:

$$\frac{P}{X} = \frac{5.0 \text{ g}}{\text{m}^2 \text{ day}} \times \frac{1}{4.472 \text{ (cm Hg)}}$$
$$= 1.118 \text{ gm}^{-2} \text{ day}^{-1} (\text{cm Hg})^{-1}$$

For 50 µm OPP film,

$$\frac{P}{x} = 0.760 \text{ gm}^{-2} \text{ day}^{-1} (\text{cm Hg})^{-1}$$

Substituting into Equation 12.10 for biscuits packed in $26\,\mu m$ OPP film:

$$ln\frac{0.05 - 0.010}{0.05 - 0.036} = 1.118 \cdot \frac{0.0448}{247.5} \cdot \frac{4.969}{0.055} \cdot \theta_s$$

Solving for shelf life θ_s :

$$\theta_s = \frac{[\ln 2.857]}{0.01828} = \frac{1.0498}{0.01828} = 57 \text{ days}$$

If the biscuits were packed in the 50 mm OPP film instead:

$$\theta_s = 84 \text{ days}$$

If a longer shelf life were required (say 200 days), then Equation 12.10 could be recalculated for another film with a lower permeance. As noted earlier, the calculated shelf life will be longer than what would actually be achieved in practice because the pseudo-equilibrium moisture content $m'_{\rm e}$ used in the calculations is significantly less than the real equilibrium moisture content which is the driving force for water vapor transport. Because of the simplifying assumptions made in the previous calculations, the calculated shelf lives should be verified by actual shelf life testing.

20.5.2.2.2 Rancidity

The development of oxidative rancidity in biscuits is not normally a problem, even when the biscuits are stored under light as the packaging material typically contains a white pigment. Lu and Xu (2009) reported on the effect of light-barrier properties of packaging films on the photo-oxidation and shelf life of commercial cookies containing 23.5% fat. Cookies were packed in three different films: 125 mm transparent BON-LDPE, 170 mm semi-transparent PET-BON-LDPE and 45 mm opaque BOPP-metCPP. They were stored at 40°C under UV light with an intensity of 51x (the same intensity as from fluorescent lights in supermarkets). The shelf life (determined as the time to reach a critical peroxide value [PV] of 19.7 meq kg⁻¹) was 37 days for BON-LDPE, 52 days for PET-BON-LDPE and 76 days for BOPP-metCPP. However, there were large differences in the OTRs of the three films (the OTR of the best was 25 times that of the poorest) which would have had a significant influence on shelf life, in addition to the effect of the different light transmission properties of the three films which varied by a factor of 12. Where fat oxidation is a problem, anti-oxidants may be added to the biscuits or they could be packed in a reduced O₂ or MA.

A shelf life prediction model of lipid-containing bakery products (biscuits with 20% fat) was developed by Calligaris et al. (2007). PV was chosen as a representative index of the quality depletion of biscuits during their shelf life, as changes in PV were linearly related to consumer acceptability. The evolution of peroxides was predicted by a modified Arrhenius equation accounting for changes in the physical state of biscuit fat. Knowledge of the relationship between peroxides and sensory acceptability, together with the temperature dependence of peroxide formation, allowed the development of a mathematical model to simply and quickly calculate the shelf life of biscuits. However, as Talbot (2011) has pointed out, peroxides measured by the PV test are, in themselves, generally tasteless and it is only when they are broken down further into aldehydes, ketones, etc., that off-flavors develop.

20.5.2.2.3 Fat Bloom

Fat bloom is a gray discoloration which can occur on the surface of biscuits during storage. Its identity is easily confirmed by gently warming the product when the discoloration will disappear. The formation of bloom is accelerated by cyclic variations in temperature during storage of the products and is associated with the use of certain fats and fat blends. This mode of deterioration is unlikely to be affected by different packaging materials.

20.5.2.3 Packaging

The traditional material used for the packaging of biscuits has been RCF coated with either LDPE or PVdC copolymer and often with a layer of glassine in direct contact with the product if it contained fat. However, this combination of material has been largely replaced by OPP, either as plain or, more commonly, pearlized OPP film, coextruded OPP film or acrylic-coated on both sides. Plain OPP films are economical but generally require a heat seal coating to improve sealability. Coextruded OPP films provide superior seal strength. If a superior O₂ barrier is required, then acrylic-coated OPP is used, and one side is sometimes coated with PVdC copolymer rather than acrylic. In addition, acrylic and PVdC copolymer-coated OPP films provide a superior flavor and aroma barrier compared with that of uncoated OPP.

Mechanical protection is generally provided either by placing the product in a protective rigid container such as a paperboard carton of appropriate caliper or by packing the product tightly

together, the choice depending on a number of factors. If the product is particularly moisture sensitive, the carton will need to be overwrapped with a film which can provide a good barrier to water vapor. A further option is to place the biscuits inside a tray (typically made from thermoformed PVC or HIPS but now more commonly PET) and then overwrap the tray with a film that provides suitable protection from water vapor and O_2 .

20.6 SNACK FOODS

Dictionary definitions of a snack include "a slight or casual or hurried meal, a small portion of food or drink, or a very light meal" and "a food not meant to be eaten as a main meal of the day, but consumed to get a brief supply of energy for the body or consumed between meals purely for the enjoyment of its taste." Until the 1970s, commercial snack foods were basically potato chips or crisps, nuts, cookies and confectionery. Snack foods now include a very wide range of products, including potato and corn chips, alkali-cooked corn tortilla chips, pretzels, popcorn, extruded puffed and baked/fried products, half-products, meat snacks and rice-based snacks (Lusas and Rooney, 2001).

The snack food industry today relies more and more on extrusion cooking processes. A major distinction can be made between direct expanded snack foods and the expanded pellet forms. The former are usually very light structures, which emerge from the cooker/extruder and require only adjustment to moisture content before enrobing and flavoring, whereas the latter are typically compact and dense and require rather specialized drying before expanding. This is achieved by means of a number of techniques including frying in oil, rotating in sand or salt roasters, microwave heating or fluid bed toasters.

20.6.1 FRIED SNACK FOODS

20.6.1.1 Manufacture

Fried snack foods can consist of many different ingredients. Although the most popular have been based on potatoes and nuts, large quantities are also made from cereal ingredients, with the most widely used cereal being corn. Nuts are consumed on their own, with dried fruits or used as components in various foods such as muesli, snack bars and chocolate confectionery. The most commonly consumed nuts include almonds, Brazil nuts, cashew nuts, chestnuts, coconut, hazelnuts, macadamia, peanuts, pecans, pine nuts, pistachio nuts, sunflower seeds and walnuts. There has been increasing interest in the nutritional components of nuts, particularly phytochemicals including carotenoids, phenolic acids and phytosterols, and polyphenolic compounds such as flavonoids, proanthocyanidins and stilbenes (Bolling et al., 2011).

Common to all these snacks is fat which is used as a processing agent to dehydrate the product (as in the case of potato chips) or puff it (as in the case of some extruded products) and develop characteristic flavors. As a consequence, the end of shelf life of many fried snack foods is closely related to the development of rancidity by the fat.

The manufacture of potato chips (also referred to as crisps in some countries) is quite straightforward. After washing, peeling and trimming, potatoes are thinly sliced, washed to remove adhering starch granules, blanched and then dried before passing on a conveyor through hot oil in which they are rapidly dehydrated and cooked. Excess oil is drained or centrifuged off and the chips cooled, salted, flavored (usually by powder adhesion to the residual fat on the chips) and packaged. During the processing of potatoes to chips, the moisture content of the potato is reduced from about 79%–5%, and of the final 95% of dry matter in chips, 35%–40% is fat.

20.6.1.2 Indices of Failure

There are two major indices of failure of fried snack foods: development of fat rancidity and loss of crispness.

20.6.1.2.1 Rancidity

All fats are subject to deterioration by oxidative and hydrolytic rancidity which leads to the formation of objectionable odors and flavors. Hydrolytic rancidity is responsible for the development of "soapy" flavors and for facilitating deterioration by direct oxidation. Oxidative rancidity results in food spoilage associated with fat deterioration, that is, the presence of pungent or acrid odors, and this is the more important of the two mechanisms with respect to food acceptability (Labuza, 1982).

The susceptibility of fried snack foods to oxidative rancidity depends on the type of fat used and the number of unsaturated bonds in the fatty acid moiety. Oxidation of oils is mainly responsible for volatile compound changes in potato chips during storage. To minimize the development of rancidity, the product must be protected from O_2 , light and trace quantities of metal ions. The addition of phenolic-type antioxidants such as BHA, BHT and TBHQ is very helpful but is not always permitted by legislation.

Several approaches for improving the storage stability of potato chips are available. Since the bulk density of chips is typically $0.056\,\mathrm{g}$ mL⁻¹, they have a very large headspace volume per unit weight of product. If the product is packed at atmospheric O_2 concentration, then the headspace O_2 is sufficient to cause O_2 uptake in excess of $3\,\mathrm{mL}$ O_2 (STP) g⁻¹. Consequently, inert gas packaging results in a very significant increase in the shelf life of potato chips, provided that the headspace O_2 concentrations attained are below 1% and the package permeability to O_2 is very low. The package should be designed to avoid light penetration.

Lee and Pangloli (in press) fried potato chips in mid-oleic sunflower oil and stored them in closed glass jars at ambient temperature (\sim 22°C) either in the dark or under fluorescent light (16.1–18.31x) for 6 weeks. Lightness and yellowness of chips decreased with storage time, and PVs were influenced by storage conditions and time. The results indicated that potato chips fried in mid-oleic sunflower oil might retain the desirable fried flavor during 6 weeks storage in a sealed container in the dark, which is not an option for products sold through supermarkets unless the package is a very good light barrier.

Bellomo et al. (2009) packaged pistachio kernels in pouches containing either PA or EVOH as an O₂ barrier layer, with and without O₂ scavengers, and stored them at 10°C, 25°C and 37°C for 14 months. The oil showed a slight increase in acidity and PV, irrespective of storage temperature.

20.6.1.2.2 Loss of Crispness

Crispness is a salient textural characteristic for fried snack foods, and its loss due to absorption of moisture is a major cause of snack food rejection by consumers. Water affects the texture of snack foods by plasticizing and softening the starch/protein matrix, which alters the mechanical strength of the product. Although several investigators have discussed a moisture content limit at which the textural quality of a snack food product becomes organoleptically unacceptable (typically 3%-3.5%), moisture content limits are strongly dependent on the method used for moisture determination. A more reliable approach to establishing moisture conditions for textural acceptance is as a function of $a_{\rm w}$. The critical $a_{\rm w}$ for potato chips and corn is in the range of 0.40-0.50. The initial $a_{\rm w}$ for potato chips has been reported as 0.076, which corresponds to a moisture content of $0.65\,{\rm g}$ H₂O per $100\,{\rm g}$ solids, well below the monolayer value of $2.9\,{\rm g}$ H₂O per $100\,{\rm g}$ solids (Katz and Labuza, 1981). The critical $a_{\rm w}$ s for puffed corn curl and extruded rice snacks have been reported as 0.36 and 0.43, respectively (Min et al., 2010). The influence of different packaging materials and of gas flushing on the O_2 content of potato chip packages is shown in Figure 20.4.

20.6.1.3 Packaging

From the modes of deterioration discussed earlier, it is clear that a satisfactory package for fried snack foods would need to provide a good barrier to O_2 , light and moisture.

Fried snacks foods are typically packaged in multilayer structures, although spiral-wound, paperboard cans lined with aluminum foil or a barrier polymer and sealed under vacuum with an LDPEfoil end are used for some specialty products which also require mechanical protection. In addition,

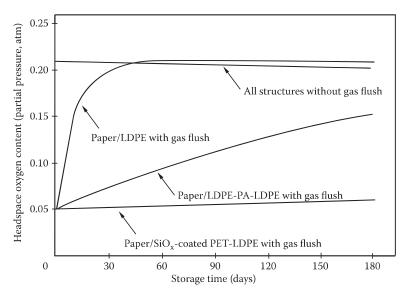


FIGURE 20.4 Influence of different packaging materials and of gas flushing on the O_2 content of potato chip packages at 25°C. (From Pfeiffer, C. et al., *Food Technol.*, 53(6), 52, 1999.)

the use of metal cans for fried nuts is popular for premium products, where the container is usually gas flushed with N_2 immediately prior to seaming.

Limited information is available on the effects of packaging materials on the stability of snack foods during ambient storage. Because these products are frequently displayed for sale under fluorescent lights, flexible packages are usually pigmented or (occasionally) placed inside paperboard cartons. The use of metallized films is widespread, and although they are reasonably efficient light barriers, they do permit some light to penetrate into the package.

Potato chips packaged in OPP-LDPE-PVC, HDPE-EVA copolymer plus a UV light-absorbing compound or HDPE-EVA copolymer plus a TiO₂ light barrier developed distinct oxidized flavors within 7 days when stored at 21°C, 55% RH and under 1100–25001x of continuous fluorescent light. Potato chips stored under the same conditions, but packaged in HDPE plus TiO₂ and a brown light-absorbing pigment construction or an aluminum foil-LDPE construction were stable throughout 10 weeks of storage (Kubiack et al., 1982). O₂-barrier film characteristics did not influence the oxidative stability of the air-packaged potato chips. The barrier properties of the various films used are presented in Table 20.4.

TABLE 20.4

Construction and Properties of Flexible Packaging Materials Used for Packaging of Potato Chips

Film Construction	WVTR ^a (mL m ⁻² day ⁻¹)	OTR ^b (mL m ⁻² day ⁻¹)
OPP-LDPE-OPP-PVdC copolymer	3.5	6
HDPE-HDPE + UVab-EVA	3.0	1500
$HDPE-HDPE + TiO_2-EVA$	3.0	1500
$HDPE + TiO_2 - HDPE + Br^c - HDPE$	3.0	1500
OPP-LDPE-Foil-LDPE-HDPE-EVA	0	0

Source: Kubiak, C.L. et al., J. Food Prot., 45, 801, 1982.

- ^a Measured at 37.8°C and 90% relative humidity.
- b Measured at 22.8°C and 0% relative humidity.
- ^c Brown-pigmented light barrier.

Walnut kernels retained acceptable quality for about 2 months in LDPE pouches under air, 4–5 months in PET-LDPE laminate under N_2 and at least 12 months in SiO_x-coated PET-LDPE pouches under N_2 at 20°C, with samples stored in the dark retaining slightly higher quality than those exposed to light (Mexis et al., 2009). The effect of parameters investigated followed the sequence: temperature > package O_2 barrier > lighting conditions.

The effects of storage temperature, packaging material OTR and variety on the oxidative stability of vacuum-packaged walnut kernels were studied over a 12 months storage period by Bakkalbaşı et al. (2012). The effect of storage temperature on lipid oxidation was greater than the effect of packaging material OTR. It was concluded that for vacuum-packed walnut kernels in PA-LDPE pouches (OTR 63 mL m⁻² day⁻¹ at 23°C), storage at 20°C protected against oxidation for 12 months.

Mexis et al. (2011) found that acceptable conditions for packaging and storage of nonirradiated and irradiated raw almonds for 12 months at 20° C with N_2 MA were with an O_2 absorber, irrespective of lighting conditions (dark and $825 \, \mathrm{lx}$), packaging material O_2 barrier (OTRs of 0.3 and $22 \, \mathrm{mL} \, \mathrm{m}^{-2} \, \mathrm{day}^{-1}$) and irradiation dose, although lower doses (1.0 kGy) gave better sensory results than higher doses (3.0 kGy).

An economical method for packaging peanuts and pecans for long term storage utilizes the CO₂ adsorption properties of these commodities and involves placing them in plastic pouches impervious to air and CO₂, flushing with CO₂ and then heat sealing the pouches. CO₂ is adsorbed into the pores of the commodities resulting in the formation of a vacuum inside the pouches. Both shelled, raw peanuts and shelled, roasted and blanched peanuts are protected from any significant deterioration of flavor and other quality factors for up to 12 months.

The formation of a collapsed, tight package a few weeks after vacuum-packaging of cereals, grains and nuts due to the adsorption of CO_2 is well documented. If these products are packaged in CO_2 in a plastic bag of low gas permeability and the bag is sealed, the package volume gradually decreases as CO_2 gas is absorbed and finally a skintight package is obtained.

20.6.2 EXTRUDED AND PUFFED SNACKS

20.6.2.1 Manufacture

Extrusion has provided a means of manufacturing new and novel products and has revolutionized many conventional snack manufacturing processes. The most popular and successful extruders used in the production of snack foods have been single-screw extruders, although twin-screw extruders are also used. The extruder must exercise a number of functions in a short time under controlled, continuous or steady-state operating conditions. These functions may include heating, cooling, conveying, feeding, compressing, reacting, mixing, melting, cooking, texturing and shaping (Huber, 2001).

The majority of extruded snacks on the market fall into the category of expanded snacks. They are usually light with a low bulk density and are seasoned with an array of flavors, oils and salt. A typical manufacturing process would consist of blending of the ingredients with water prior to being fed into the extruder. As the mix passes through the extruder, it is compressed, with the work performed on the mix during extrusion being transformed into heat. The combination of pressure and heat causes the mix to become very viscous, and as it passes through the extruder heads, the superheated moisture instantaneously vaporizes, resulting in puffing of the product.

The moisture content of the extruded product is normally between 8%–10% on a wet basis and it must be reduced to 1%–2% to give the desired product crispness. Additional drying at temperatures up to 150°C for 4–6 min is used. Sometimes, the product is subsequently fried in oil to remove moisture and develop a desirable flavor. The product is then cooled and any fines removed prior to coating with flavors. This is achieved by first spraying the product with vegetable oil and then dusting with a variety of dry flavors and/or seasonings. Alternatively, the oils, flavors and seasonings may be mixed together and applied to the extruded product as it is tumbled in a flavor-application reel.

Puffed snack foods such as popcorn were originally made by placing grains of corn onto very hot plates. This caused the moisture in the grains to suddenly expand into steam, thus causing the grain to be puffed and simultaneously cooked. This method was refined by heating the grain in a quick-release but hermetically sealed cylinder where the sudden release of pressure caused the grain to puff or expand. A similar principle is used in extrusion. The efficiency of the process has been improved so that many cereals can now be puffed up to four to eight times their original size; these expanded original-texture grains are used in many snack products.

20.6.2.2 Indices of Failure

The major index of failure for extruded and puffed snacks is loss of crispness. The critical $a_{\rm w}$ for puffed corn curl has been reported as 0.36 which corresponds to a moisture content of 4.2 g H₂O per 100 g solids (Katz and Labuza, 1981). The initial $a_{\rm w}$ of this product was 0.082 with a corresponding moisture content of 1.83 g H₂O per 100 g solids. For popcorn, initial and critical $a_{\rm w}$ s were 0.062 and 0.49, with corresponding moisture contents of 1.70 and 6.1 g H₂O per 100 g solids. The sensory crispness intensity of popcorn as a function of $a_{\rm w}$, with the critical $a_{\rm w}$ of 0.49 marked as $a_{\rm c}$, is shown in Figure 20.5.

The critical $a_{\rm w}$ for extruded rice snacks has been reported to be 0.43, which corresponds to 6.5% moisture content (Chauhan and Bains, 1990). A report on the effects of $a_{\rm w}$ on the textural characteristics of puffed rice cakes indicated that rice cake lost its crispness and became tough as the $a_{\rm w}$ increased above 0.44, a critical point with respect to texture (Hsieh et al., 1990). Rice cakes with $a_{\rm w}$ between 0.23 and 0.44 were crisp and low in hardness. Data such as this is essential before selection of a suitable packaging material can be made.

The development of stale and/or oxidized and rancid flavors and odors can also be a problem limiting the shelf life of certain extruded and puffed snacks.

20.6.2.3 Packaging

Many extruded and puffed snack foods are packaged in an identical material to that discussed earlier for fried snack foods. However, because the major index of failure is loss of crispness, a package that provides a good barrier to water vapor is the primary requirement. Some extruded and puffed

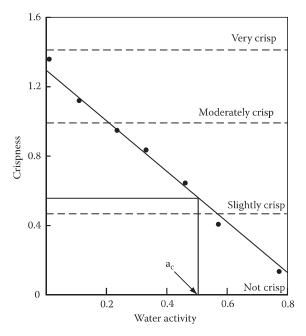


FIGURE 20.5 Sensory crispness intensity of popcorn as a function of water activity; the critical $a_{\rm w}$ of 0.49 is shown as $a_{\rm c}$. (From Katz, E.E. and Labuza T.P., *J. Food Sci.*, 46, 403, 1981.)

snacks are comparatively less sensitive to O_2 than fried snack foods and the O_2 barrier requirements of the packages are consequently less stringent.

20.6.3 FRUIT-BASED SNACKS

A large variety of dried fruits, usually with added nuts and honey, sugar or syrup, are used in the manufacture of this type of snack food. Their composition is infinitely variable, leading to the development of bars with a wide variety of flavors and textures. Generally, these products are in the intermediate moisture category and have $a_{\rm w}$ s in the range of 0.20–0.40. This is because of their relatively high sugar content (25%–30%) mainly in the form of glucose, sucrose and fructose from several ingredients such as corn syrup, glucose syrup, sweetened condensed (evaporated) skim milk, raw cane sugar and invert sugar syrup.

Also in this category are snacks based largely on flaked cereals such as oat flakes or wheatflakes or puffed cereals such as rice, to which dried fruits, nuts and carob chips are also added to produce variations in flavor and texture. Again, many of these snacks have a chewy texture and an $a_{\rm w}$ which places them in the intermediate moisture category. The fat content of these chewy bars can be as high as 24%.

Packaging materials for these fruit-based snacks must provide a barrier to water vapor ingress to avoid the development of stickiness as a result of moisture uptake by the sugar in the product. In very dry atmospheres, moisture loss could be a problem. Before the packaging requirements can be specified with any degree of precision, the MSI for this type of product would be required.

20.7 CONFECTIONERY

20.7.1 SUGAR CONFECTIONERY (CANDY)

20.7.1.1 Manufacture

The words "candy" and "confectionery" are often used interchangeably to mean a sweet sugar- or chocolate-based snack or dessert food. Strictly defined, the word *candy* refers to products containing sugar as the dominant component and does not include chocolate products. *Confection* is a more general term referring to any sweet product manufactured from sugar and other ingredients. Products falling within the latter definition will be discussed in this section.

Confectionery has four major basic ingredients: sucrose, glucose, fructose and water. These can be combined with flavorings and colorings to make confections such as fondants and boiled sweets. When milk solids, fat, proteins and modified starches are added as well, products such as jellies, pastilles, toffees and caramels can be produced. The primary difference between the various confectionery products is in the amounts and types of sugars and in the amount of water. In one group (which includes the hard candies and soft, chewy products), uncrystallized sugars are present in a very viscous solution, which is handled like a solid at room temperature. In the other group (which includes fondant crèmes and other crystallized or grained products), sucrose is present in crystalline form, usually as microscopic crystals dispersed in syrup.

Sugars impart the texture necessary to distinguish one confection from another and to provide a unique experience to the consumer. Whether found as crystal, glass or fluid solution, the key to making high quality candy is understanding and controlling the transitions of sugar (Hartel et al., 2011). During processing, sugars in confectionery formulations typically go through one or more phase transitions, depending on the nature of the product. Changes in phase behavior may also occur during storage, usually with a negative effect on shelf life. The physical state of the sweetener can have a critical influence on the attributes of the confection; that is, crystals affect both appearance and textural properties.

Hard candies (also known as *boiled sweets*) are made almost entirely of sugar, typically combinations of sucrose, glucose and fructose. The mixture of sugars is heated under vacuum to reduce

the moisture content to about 1%, after which flavors, colors and acid (normally citric) are mixed in, and the plastic mass formed into the desired shape. After cooling to set, the sweets are packaged as rapidly as possible, preferably while still warm.

Toffees and caramels are made by boiling sucrose, glucose syrup, condensed milk, vegetable fats and salt. Other ingredients may include cream, butter and various flavorings, although the inherent flavor is due to the Maillard nonenzymic browning reaction between reducing sugars and milk proteins (Jackson, 1995). After cooling to about 45°C–50°C, the toffee is cut and packaged. Because caramel is a dispersion of fat globules in a high solids, highly supersaturated, viscous sugar matrix that cannot crystallize, all the component sucrose molecules, rather than just those in the syrup phase, influence the a_w .

Confections such as fondant and fudge are composed of sucrose in the form of crystals suspended in a saturated sugar solution. A typical composition of base fondant is about 75% sucrose, 15% glucose and 10% water. The mixture is boiled at 120°C and cooled rapidly to about 50°C when it is subjected to violent agitation to cause rapid nucleation and crystallization. Fudge is basically a toffee or caramel with a high sugar content, which has been deliberately crystallized during processing. Typically, caramel is cooked to about 120°C, cooled to about 50°C and then fondant added to initiate crystallization; it is then cooled to allow crystallization to occur (Edwards, 2000).

The solid crystals in fondant and fudge have no effect on a_w , and the phases are stable provided that the system is protected from atmospheric moisture by suitable packaging materials. The a_w of the syrup phase is related to both its composition and to any water loss or gain that may have occurred; a_w s of 0.78 and 0.65 having been quoted for fondant and fudge, respectively (Nelson, 1995).

20.7.1.2 Indices of Failure

An important difference in the indices of failure between the various candies is that crystallized products tend to dry out under normal storage conditions, while uncrystallized products tend to pick up moisture from the atmosphere. The $a_{\rm w}$ s of various types of sugar confectionery is presented in Table 20.5. Although not the only mode of failure, moisture migration is arguably the major determinant of the end of acceptable shelf life for many confections (Ergun et al., 2010). Thus, shelf life testing in confections often evaluates changes in physicochemical properties related to moisture changes.

TABLE 20.5
Water Activities of Various Kinds of Confectionery

Type of Product	Average $a_{\rm w}$	Usual Limits
Boiled sweets	0.28	< 0.30
Toffee	0.47	< 0.48
Caramels	0.50	0.45-0.55
Nougat	0.55	0.50-0.60
Gums and pastilles	0.60	0.51-0.64
Liquorice	0.64	0.53-0.66
Fruit jellies	0.65	0.60-0.70
Fudge	0.65	0.60-0.70
Turkish delight	0.66	0.60-0.70
Marshmallow	0.72	0.63-0.73
Fondant	0.78	0.75-0.84

Source: Adapted from Nelson, C., Wrapping, packaging and shelf life evaluation, in: Sugar Confectionary Manufacture, 2nd edn., Jackson, E.B. (Ed.), Blackie Academic & Professional, London, U.K., pp. 353–367, 1995.

One of the major defects in hard candy confections is *graining*, or sugar recrystallization. Hard candies are a metastable sugar glass and graining during storage can occur for two reasons. First, if crystals are already present within the glassy matrix (formed during manufacturing), they will start to grow if the temperature increases above $T_{\rm g}$. This form of graining is called internal graining. Second, a hard candy can begin to grain when sufficient moisture is adsorbed by the surface to increase molecular mobility to the point where nucleation can occur. As moisture penetrates into the candy, a syrup layer forms at the surface with a reduced $T_{\rm g}$ due to the higher water content. This form of graining is called external graining. Continued graining occurs as the layer slowly proceeds into the center of the confection. In both internal and external graining, flavor molecules more readily diffuse out of the candy causing a decrease in flavor. Also, the rearrangement of color molecules causes a change in appearance and texture of the candy as graining proceeds (Hartel et al., 2011). If the candies are not individually wrapped, they may stick together as a result of external graining.

Fondants generally have an $a_{\rm w}$ that is higher than the humidity of the surrounding atmosphere and thus they tend to dry out. This results in increased crystallization. One significant change arising from the loss of moisture is a decrease in volume. If the fondant is coated with chocolate, then this volume decrease causes either collapse of the coating or an air space inside the coating. Both consequences are undesirable, and although a collapsed coating is more apparent, an air space can permit condensation of moisture which leads to a localized area of high $a_{\rm w}$ where microbial growth could occur.

Two types of flavor changes can occur in confectionery: loss of desired flavor components and development of off-flavors. Packaging has an important role to play in preventing loss of desirable flavors from the product and providing a barrier to the entry of O_2 which can oxidize flavors.

Many confections, notably the hard candies, are brightly colored and therefore color stability is important. The main cause of color fading during storage is bleaching by light. Use of a package which is a complete barrier to light is generally undesirable because the attractiveness of brightly colored confectionery is an important selling point. The use of synthetic, light-stable colors in hard candies is widespread.

20.7.1.3 Packaging

The type of packaging required to protect the confection from moisture uptake will depend on the $a_{\rm w}$ of the confection and the RH of the ambient atmosphere. The packaging type will also depend on whether or not the confection deteriorates by gain or loss of moisture under these conditions.

It has been customary to wrap boiled sweets, toffees and caramels individually, partly as a hygienic measure, partly to protect them from atmospheric moisture, partly to prevent them from sticking together and partly to avoid the intermingling of the flavors of assortments. Since the wrapping machines operate at very high speeds, the mechanical and electrostatic properties also govern to a high degree the choice of packaging materials to be used (Hooper, 1999). Both ends of the wrapper sleeve are twisted to effect a closure.

Fibrous materials are generally unsuitable since they promote adhesion of the wrapper to the sweet. Materials such as waxed paper, waxed glassine and waterproof, plasticized RCF have been used successfully for many years but the use of cast PP (which holds the twist better than RCF) is now widespread. Although these materials offer some barrier to water vapor, they provide little protection in this situation because the overlap is not sealed. Thus, an outer package that provides a barrier to moisture is required, and this is usually a heat sealed bag made from coated RCF or a polyolefin, although metal containers, glass jars and foil or metallized laminates are also used. In some situations, cartons made from paperboard are used. The board may be coated with LDPE, or the carton may have a plain or waxed glassine liner or one made from thin gauge HDPE.

20.7.2 CHOCOLATE

20.7.2.1 Manufacture

Chocolate is a suspension of finely ground, roasted cocoa beans or cocoa mass and sugar particles in cocoa butter (the lipid fraction of the cocoa mass). Milk chocolate is similar but with the addition of whole milk powder. Cocoa beans are roasted to develop flavor and then ground to liberate some fat. Other ingredients are mixed in and the particles further reduced in size to a maximum of about 30 µm. The final stage is *conching*—agitation under heat (75°C–80°C for plain and 50°C–60°C for milk chocolate) to remove water and unwanted volatile substances, improve flavor and texture and reduce viscosity. During this process, an enormous increase in surface area of the solid particles occurs, and the resulting chocolate mass becomes quite dry. The sugar particles are not easily wetted by the cocoa butter and, although small, are compacted into aggregates (Beckett, 2009).

Although cocoa butter can crystallize in a number of polymorphic forms, only one such form (β or form V) is stable. Chocolate is tempered by heating to 50°C to remove all crystal nuclei and then cooled gradually to about 27°C where crystallization commences. The temperature is then raised to 32°C when only a finely dispersed seed crystal of form V remains. The chocolate is then cooled at a controlled rate when stable crystals form and the surface of the chocolate takes on a good gloss (Bralsford and Le Fort, 1990).

20.7.2.2 Indices of Failure

The amount of liquid fat present in chocolate is significant, not only in determining the sensory (particularly textural) quality, but also in influencing the shelf life of chocolate products (Subramaniam, 2011). The melting characteristic of cocoa butter between 30°C and 35°C is responsible for the fast meltdown of chocolate in the mouth. The solid fat content of cocoa butter decreases from 76% at 25°C to 1% at 35°C and zero at 40°C, making chocolate very sensitive to temperature. If melting and subsequent solidification occur, then the surface texture becomes rough. If the temperature oscillates just below the melting point, then fat will move from the body of the chocolate to the surface, giving rise to a defect known as *fat bloom*: the shiny surface turns dull and, later on, a grayish-white layer starts to develop (Nöbel et al., 2009). Bloom can also arise as a result of using fats in chocolate that are incompatible with cocoa butter and from insufficient tempering during chocolate processing. Storing chocolate below 18°C will prevent bloom from occurring. Generally, there is little that can be done by packaging to prevent such defects occurring.

Sugar bloom is another defect that affects the appearance of chocolate. Although on cursory examination it appears similar to fat bloom, sugar bloom consists of a layer of sugar crystals on the surface. It is caused by exposing the surface of chocolate to air of high humidity and/or by the use of refined sugar having a high moisture content.

Oxidative and lipolytic rancidity are flavor defects, the former coming from oxidation of unsaturated fats and the latter from enzymic hydrolysis of short- and medium-chain triglycerides. Cocoa butter contains tocopherols (liposoluble vitamin E compounds), which act as antioxidants and therefore confer a natural protection against oxidation during storage.

Being high in fat, chocolate is very likely to absorb any foreign odors from the surrounding atmosphere unless adequately protected by suitable packaging materials.

Chocolate is sold in many forms where the product often contains not only chocolate but also other ingredients such as fruits, nuts and caramel which influence the likelihood of different storage defects occurring.

20.7.2.3 Packaging

Suitable packaging for chocolate must provide a good barrier to light, O_2 , water vapor and foreign odors (Mohas, 2010). The most common material used to package blocks of chocolate used to be unsealed aluminum foil of $0.009 \, \text{mm}$ thickness. At this thickness it exhibits "dead wrap" characteristics (i.e., it takes on the shape of the product around which it is placed). No sealing was possible

but folding and overlapping of the foil provided adequate protection when covered with a thin, printed paperboard sleeve. In warmer climates, a layer of waxed tissue paper was placed inside the foil to prevent fat staining of the outer package; it was also claimed to offer protection against odor penetration (Minifie, 1999).

It is now more common to package chocolate blocks in a laminate consisting of aluminum foil and LDPE, making it possible to heat seal the package. Such a package is a better water vapor and odor barrier than the foil and the foil-paper packages. Such packages sometimes contain a layer of paper, either between the foil and the LDPE or on the outside of the foil when the latter is laminated directly to the LDPE. In some packages, the foil is replaced by PVdC copolymer, the latter being applied as a thin coating on the LDPE.

Traditionally, almonds and peanuts have been used in confectionery products such as chocolate in the United States, while hazelnuts are more common in Europe. Recently, Mexis et al. (2010) showed that dark chocolate with hazelnuts packaged with an O_2 absorber in a barrier packaging material maintained its aroma, taste and nutritional quality substantially longer than other packaging methods. Chocolate was packaged in either PET-LDPE or SiO_x -coated PET-LDPE under vacuum or N_2 or with an O_2 absorber, and stored in the dark at 20° C for 12 months. "Commercial" control samples for comparison purposes consisted of chocolate packaged in aluminum foil in air while "model" control samples used for sensory evaluation consisted of chocolate packaged in glass jars and stored at -18° C. The chocolate with hazelnuts retained acceptable quality for \sim 8 months in commercial packages. For samples packaged in PET-LDPE, irrespective of the storage atmosphere, the shelf life was 8–9 months, and for samples packaged in SiO_x -coated PET-LDPE, the shelf life was 11 months, irrespective of storage atmosphere. Finally, for samples packaged with an O_2 absorber, the shelf life was at least 12 months irrespective of packaging material.

Chocolate-coated confectionery such as coated caramel bars are typically packaged in pearlized OPP which is cold sealed longitudinally and at each end; cold sealants avoid the risk of melting the chocolate during the sealing operation.

Packages of individual chocolates are frequently purchased for gifts and special occasions, and this is reflected in the sometimes very elaborate packaging which is used. Thermoformed PVC, HIPS or PET trays with individual cavities for each piece are common, with many of the individual chocolates being wrapped in colored, thin gauge, aluminum foil. Recently, trays made from thermoplastic starch have been used. The trays are placed inside paperboard boxes and overwrapped with RCF or polyolefin film. Sometimes, metal or glass containers are used, which provide an excellent barrier to moisture (Jones, 2009).

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