
Technological Options of Packaging to Control Food Quality

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1. Introduction

The shelf life of perishable foods as meat, poultry, fish, fruit, vegetables and fresh cereal-based products is limited by various factors that generally bring to changes in odor, flavor, color and texture until to their complete unacceptability. Packaging is the main tool to prevent product deterioration and prolong its shelf life. The package protects the food against physical, chemical and biological damage. It also acts as a physical barrier to oxygen, moisture, volatile chemical compounds and microorganisms that are detrimental to food. The package has to be considered as an integral part of the preservation system because it provides a barrier between the food and the external environment. It is usually a composite item meeting several different needs [1]. What we call the preservation role is a fundamental requirement of food packaging, since it is directly related to the safety of the consumer. Package performance depends on numerous variables, such as the initial food quality, the processing operations, the size, the shape and appearance of package, the distribution method and the disposal of packages. Generally speaking, the properties which determine their adequacy to meet performance requirements can be grouped into the following categories: mechanical, thermal, optical and mass transport properties. Mass transport phenomena are of great importance to food packaging with plastics, since a polymeric matrix is permeable to moisture, oxygen, carbon dioxide, nitrogen and other low molecular weight compounds. Glass and metal packaging materials are not permeable to low molecular weight compounds, whereas paper-based materials are too permeable. Hence, these last types of materials do not provide an opportunity for the designer to optimize the barrier properties for various applications. The polymers can provide a wide range (by three or four orders of

magnitude) of permeability for different applications, thus justifying studies aimed to ensure adequate barrier protection. Therefore, in situations where food deteriorations are driven by either gas or moisture permeation to the ambient environment, an accurate choice of packaging mass transport properties may bring about an increase to product shelf life. Each category food has its specificity in quality attributes, storage conditions, expected shelf life and packaging tools applied. Together with transport properties of film, another valid packaging option to maintain product quality is represented by the proper selection of headspace conditions. Vacuum packaging and modified atmosphere packaging (MAP) are two widely used strategies for food preservation [2]. The first strategy means a complete lack of gas in the package whereas, under MAP, headspace environment may change during storage but there is no additional manipulation of the internal environment. Packaging under these conditions can protect products against deteriorative effects, which may include discoloration, off-flavor and off-odor development, nutrient loss, texture changes, pathogenicity, and other measurable factors. With the increasing demand for fresh and natural products without addition of dangerous chemicals, MAP or vacuum seem to be ideal methods of preservation for many foods, being simple and cheap to be applied. The few disadvantages are related to need of equipments and proper packaging materials and, in the specific case of MAP, to the limitation on retail for the increased pack volume of bags.

Today the efforts to improve the performances of packaging with clear effects on food quality can be directed towards two many working areas, green polymers and active packaging. The performance expected from bio-plastic materials used in food packaging application is containing the food and protecting it from the environment while maintaining food quality. It is obvious that to perform these functions is important to control and modify their mechanical and barrier properties, that consequently depend on the structure of the polymeric packaging material. In addition, it is important to study the change that can occur on the characteristics of the bioplastics during the time of interaction with the food. Studies of the literature show up that only a limited amount of biopolymers are used for food packaging application [3, 4]. Unlike the usual wrap, films, labels and laminates came from fossil fuel resources, the use of biodegradable polymers represents a real step in the right direction to preserve us from environmental pollution. This kind of packaging materials needs more research, more added value like the introduction of smart and intelligent molecules able to give information about the properties of the food inside the package and nutritional values. It is necessary to make researches on this kind of material to enhance barrier properties, to ensure food properties integrity, to incorporate intelligent labeling, to give to the consumer the possibility to have more detailed product information than the current system [5, 6].

Active packaging is the most relevant innovative idea applied for consumer satisfaction. It has been defined as a system in which the product, the package and the environment interact in a positive way to extend shelf life of product or to achieve some characteristics that cannot be obtained otherwise [7]. In many present-day active packaging technologies the active agent is placed in the package with the food, in a small sachet, pad or device manufactured from a permeable material which allows the active compound to achieve its purpose but prevents direct contact with the food product, protecting the food from con-

tamination or degradation. Active packaging developments are now focusing on incorporating the agents into the polymeric matrices which constitute the package walls; the resulting materials act by releasing substances which have a positive effect on the food or by retaining undesired substances from the food or the internal atmosphere of the package. The migration of a substance may be achieved by direct contact between food and packaging material or through gas phase diffusion from packaging layer to food surface. Although the former is the packaging situation usually meets, the latter solution has exerted interesting effects due to simple and wide applications. Among the migratory agent categories, a further division would be made between controlled and uncontrolled release systems. Even though uncontrolled delivery packages intended for food applications are more abundant, controlled release systems are of industrial relevance due to their aptitude to prevent sensorial or toxicological problems or inefficiency of the system, caused by a too high or a too low concentration of delivered substance [8]. The active packaging technology provides several advantages compared to direct addition of active compounds, such as lower amounts of active substances required, localisation of the activity to the surface, migration from film to food matrix and elimination of additional steps within a standard process intended to introduce the active compounds at the industrial processing level such as mixing, immersion, or spraying. New regulations, the Commission Regulation (EC) No 450/2009 (EC, May 2009), and the Question Number EFSA-Q-2005-041 (EFSA, July 2009), together with Regulation 1935/2004 (EC, October 2004) make active packaging possible within the European Union [9].

The current work aims to overview the main technological options of packaging to control food quality. In particular, the attention will be focused on the use of proper headspace conditions and applied active packaging systems. Case studies are given for main food categories, such as dairy products, meat, fish, fruit and vegetables.

2. Headspace conditions

Vacuum, gas flushing or controlled permeability of the pack are valid techniques to control biochemical, enzymatic and microbial degradations so as to avoid or decrease the main degradations that might occur in food. This allows the preservation of fresh state of the food product without temperature or chemical treatments used by competitive preservation techniques, such as canning, freezing, dehydration and other processes. MAP is the replacement of air in a pack with a single gas or mixtures of gases; the proportion of each component is fixed when the mixture is introduced. No control is exerted over the initial composition, and the gas composition is likely to change with time owing to the diffusion of gases into and out of the product, the permeation of gases into and out of the pack, and the effects of the product and microbial metabolism [10]. MAP was first recorded in 1927 as an extension of shelf life of apples by storing them in atmosphere with reduced oxygen and increased carbon dioxide concentrations. In 1930s it was used to transport fruit in the holds of ships. Increasing the carbon dioxide concentration surrounding beef carcasses transported long distances an increase in shelf life by up to 100% was shown [11]. Marks and Spenser intro-

duced MAP for meat in 1979; the success of this product led, two years later, to the introduction of MAP for bacon, fish, sliced cooked meats and cooked shellfish. MAP techniques are now used on a wide range of fresh or chilled foods, including raw and cooked meats and poultry, fish, fresh pasta, fruit and vegetables and more recently coffee, tea and bakery products. The advantage of MAP for the consumer are:

- increased shelf life allowing less frequent loading of retail display shelves;
- reduction in retail waste;
- improved presentation-clear view of product and all round visibility;
- hygienic stackable pack, sealed and free from product drip and odor;
- easy separation of sliced products;
- little or no need of chemical preservatives;
- increased distribution area and reduced transport costs due to less frequent deliveries;
- centralized packaging and portion control;
- reduction in production and storage costs due to better utilization of labor, space and equipment.

The disadvantages of MAP are:

- capital cost of gas packaging machinery;
- cost of gases and packaging materials;
- cost of analytical equipment to ensure that correct gas mixtures are used;
- cost of quality assurance systems to prevent distribution of leakers;
- increase of pack volume which will adversely affect transport costs and retail display space;
- benefits of MAP are lost once the pack is opened or leaks.

MAP does not increase significantly the shelf life of every type of food since some products that undergo processes such as smoking, curing, etc., already have extended shelf lives because of pre-packaging treatments. In these cases MAP may improve other quality aspects such as color stability or slice separation. The safety and the stability of foods depend on microorganisms initially present, being unable to overcome various adverse factors, both extrinsic and intrinsic to the food. Modification of the atmosphere surrounding the food may provide one condition to inhibit microbial growth. In table 1 there is a description of the principal degradations that take part in a common food product and the role of MAP in contrasting these factors. The combination of chilled temperatures and MAP generally results in a more effective and safer storage regime and longer shelf life [12]. Atmospheres within the product are influenced by the type of material used in the package and the initial gas mixture used. Some materials allow diffusion of gases in and/or out of the package during stor-

age while if the film is fully permeable, the atmosphere inside the pack becomes the same as the air outside. In semi-permeable films, the atmosphere in the pack rise to a gas equilibrium. Packs for MAP are made from one or more polymers: polyvinylchloride (PVC), polyethylene terephthalate (PET), polyethylene (PE), and polypropylene (PP), depending on the characteristics desired for the final use. There are many factors which must be taken into account:

- barrier properties: permeability to various gases and water vapor transmission rate;
- machine capability: capacity of trouble-free operation (resistance to tearing, possibility to be heat-formed)
- sealing reliability: ability to seal to itself and to container;
- anti-fog properties: good product visibility;
- special characteristics: possibility of heating without removing product from the packaging and easy-peel seals for convenient opening.

	Spoilage	Rancidity	Enzymatic browning
Effects on products	change in smell, taste, texture, appearance, toxicity	less nutritional value, rancid taste	browning of vegetables
Type of products	vegetables, bakery cooked products	products containing vitamins and fats	vegetables
Role of MAP	gas mixture mainly constituted by CO ₂	N ₂ or other neutral gas replacement of air	N ₂ or other neutral gas replacement of air

Table 1. Main degradation factors and roles of MAP

The main gases used in MAP are: oxygen, nitrogen and carbon dioxide. These three gases are used in different combination according to the product and the needs of manufacturer and consumer. The choice for a particular combination is influenced by the microbiological flora and the sensitivity of the product to gases and color stability requirements. The basic concept of MAP of fresh foods is the replacement of the air surrounding the food in the package with a mixture of atmospheric gases different in proportion from that of air. Oxygen is the most important gas being used by both aerobic spoilage microorganisms and plant tissues and taking part in some enzymatic reactions responsible for food deterioration. For these reasons, under MAP, oxygen is either excluded or set as low as possible. This gas is generally set at low levels to reduce oxidative deterioration of foods, particularly in high fat product. Oxygen generally stimulates growth of aerobic bacteria, inhibiting growth of anaerobic bacteria, although there is a wide variation in the sensitivity of anaerobes to this gas. The exceptions occur when oxygen is needed for fruit and

vegetable respiration, color retention as in the case of red meat or to avoid anaerobic conditions in white fish [13]. One of the main function of oxygen is the maintenance of myoglobin in its oxygenated form, oxymyoglobin because this is the form responsible for the bright red color, which most consumers associate to fresh meat. Carbon dioxide is both water and lipid soluble and although is not bactericide or fungicide, it has a bacteriostatic and fungistatic properties. The effect on microorganisms consists in the extension of the lag phase and a decrease of growth rate. The effectiveness of this gas is influenced by its original and final concentrations, the storage temperature, the partial pressure of carbon dioxide, the initial bacterial population, the microbial growth phase, the growth medium used, the acidity, the water activity and the type of product being packaged [10, 14-16]. Yeasts which produce carbon dioxide during growth are stimulated by high levels of carbon dioxide and thus for some products where they are potentially a major cause of spoilage, MAP may not be an advisable option. Also *Clostridium perfringens* and *botulinum* are not affected by the presence of carbon dioxide and their growth is encouraged by anaerobic conditions. In general, carbon dioxide is most effective in foods where the normal spoilage microorganisms consist of aerobic and gram negative psychrotropic bacteria [17]. For maximum antimicrobial effect, the storage temperature of the product should be kept as low as possible, because the solubility of carbon dioxide decreases dramatically with increasing temperature, thus improper temperature could eliminate the beneficial effects of carbon dioxide. The absorption of carbon dioxide is dependent on the moisture and fat content of the product. If product absorbs excess carbon dioxide the total volume inside the package will be reduced, giving a vacuum package look known as pack collapse. Excess carbon dioxide absorption in combination with package collapse can also reduce water holding capacity of meats, resulting in unsightly drip. Genigeorgis [18] suggested that the antimicrobial activity of carbon dioxide was a result of the gas being absorbed onto the surface of the product forming carbonic acid, subsequent ionization of the carbonic acid and a reduction in pH. Other theories have been summarized:

- alteration of cell membrane function including effects on nutrient uptake and absorption;
- direct inhibition of enzyme systems or decreases in rate of enzyme reactions;
- penetration of membranes resulting in changes of intracellular pH;
- direct changes to physic-chemical properties of proteins.

Nitrogen is an inert gas which has been used as a packaging filler for many years to prevent pack collapse because of its low solubility in water and lipid. In MAP products, especially fresh meat packed in high concentrations of carbon dioxide, pack collapse occurs because of the solubility of carbon dioxide in meat tissue. Nitrogen is also used to replace oxygen in MAP products, to prevent rancidity and inhibit growth of aerobic organisms. The gas combination depends on product characteristics. Table 2 reports a comparison between storage in MAP and in air for different products. Some relevant case-studies that highlight the benefits and limits of MAP for main food categories are reported hereinafter.

PRODUCT	Temperature	Shelf life under MAP	Shelf life in AIR
Toast bread	Room	2-3 months	10 days
Cake	Room	40-60 days	- ^a
Croissant, milk bread	Room	6 weeks	Several days
Pizza	4-5°C	30 days	Several days
Hamburger, hot dog rolls	4-5°C	30 days	1 week
Cakes with cream	Room	25-30 days	-
Emmenthal	2-4°C	4-5 weeks	A few days
Bovine mozzarella	2-4°C	6-8 days	3 days
Robiola, Crescenza	2-4°C	3-4 weeks	1 week
Cheese slices	2-4°C	2-3 months	2-3 months
Gorgonzola	2-4°C	30 days	10 days
Parmesan in pieces	2-4°C	40-60 days	-

^a - means that air was never used to store product.

Table 2. Examples of food shelf life under MAP and air

The properties of meat that are important in determining shelf life include water binding capacity, color, microbial quality, lipid stability and palatability. The variables that influence the shelf life of packaged fresh meat are: product, package and headspace, packaging equipment, storage temperature, and additives. Plastic film properties, shrinkage, strength, oxygen transmission, moisture transmission, and anti-fog agents are important for meat package materials [19]. Fresh meat packaging is only minimally permeable to moisture to prevent desiccation, while gas permeability varies with the applications. MAP (commonly 70-80% O₂ and 20-30% CO₂) and vacuum packaging are widely used methods for packaging meat. Packaging under high oxygen concentration, however, may cause an increase in the lipid and protein oxidation. These reactions affect the functional, sensory and nutritional quality of meat products. Lipid oxidation leads to discoloration, increase drip-loss, off-odors and production of toxic compounds. In addition, these modifications can negatively affect the sensory quality of meat products in terms of texture, tenderness and color [20]. Protein oxidation can also result in the loss of enzyme activity and protein solubility, as well as in the formation of protein complexes and non enzymatic browning products. In a recent study [21], the effects of MAP (70% O₂ and 30% CO₂) and vacuum skin packaging on protein oxidation and texture of pork were investigated. Packaging under MAP containing high level of O₂ resulted in protein cross-linking, which reduced tenderness and juiciness of pork. Rowe et al. [20] proposed that the oxidation of muscle proteins may have a negative effect on beef tenderness that was attributed to an inactivation of μ -calpain with a subsequent decrease in proteolysis. Zakrys et al. [22] compared the effects of high levels of oxygen (80% O₂ 20% CO₂) with vacuum packaging and showed that high O₂ levels lead to high myosin inter-

molecular cross-links, low free thiol groups and high carbonyl content, demonstrating that a significant level of protein oxidation occurred. This protein oxidation was found to have a negative effect on meat tenderness. Results from this study suggested that high oxygen induced changes in myosin and intermolecular cross-linking, increased disulphide bond formation, protein oxidation and drip loss compared to vacuum packaged. Color of meat is a very important quality attribute that influences consumer acceptance of meat. The surface color of meat depends on the quantity of myoglobin present, on its chemical state and also on the chemical and physical conditions of other components. Meat showing a bright red color is assumed to be fresh, while oxidation of heme iron to form methamyoglobin produces the brown color which consumers find undesirable. An interesting study conducted by Mastromatteo et al. [23] evaluated the combination of different MAPs (from 20% to 40% of CO₂ ; from 5% to 20% of O₂ and from 75% to 40% of N₂) with natural essential oils on shelf life of reduced pork back fat content sausages. They found that lemon and thymol recorded the highest sensory score while all the investigated MAPs showed an antimicrobial effect; moreover, low carbon dioxide concentrations caused low color variations during storage. The combination of MAP and thymol was able to further improve the shelf life of meat, in fact the microbial threshold was never reached. A shelf life of more than 5 days for thymol-MAP samples was obtained, respect to the other investigated samples (2 days). To sum up, integration of meat characteristics with available packaging materials, equipment into current cold chain logistical and information systems have resulted in a sufficiently high state of complexity that has caused uncertainty and confusion among industry, regulatory agency, and consumer segments [13]. Meat and packaging industry must continue to work on systems that will ensure safe and palatable products. The review of Belcher [24] well summarized packaging developments that are resulting from numerous trends taking place in the meat industry and in the retail sector. Moreover, alternative non-thermal preservation technologies such as high hydrostatic pressure, super chilling, natural biopreservatives and active packaging have been proposed because they are also effective against spores. To increase their efficacy, a combination of several preservation technologies under the so-called hurdle concept has to be investigated [25].

As regard fresh-cut fruits and vegetables, process increases respiration rate and causes major tissue disruption as enzymes and substrates normally sequestered within the vacuole. Processing also increases wound-induced ethylene, water activity and surface area per unit volume, which, may accelerate water loss and enhance microbial growth since sugars also become readily available. These physiological changes may be accompanied by flavor loss, cut surface discoloration, color loss, increased rate of vitamin loss, shrinkage and shorter shelf life. MAP is largely used for minimally processed fruit and vegetables. It relies on the modification of the atmosphere inside the package in order to extend the food shelf life by reducing the respiration of the product and consequently its degradation rate. The effect of MAP on quality of many fresh-cut products has been studied and successful applications include mushroom [26], apples [27], tomato [28], butterhead lettuce [29], potato [30], or kiwifruit [31]. These products are metabolically active for long periods after harvesting due to both endogenous activity, such as respiration, and external factors such as physical injury, microbial flora, water loss and storage temperature. Respiration may result in anaerobiosis,

being quickly established if the produce is sealed in an impermeable film with low initial O₂ concentration. Subsequently anaerobic respiration of the produce will be initiated at very low O₂ concentrations, resulting in the accumulation of ethanol, acetaldehyde and organic acids and deterioration of organoleptic properties. Rate of respiration is influenced by the initial gas concentration so that, for example, reducing the oxygen to 2% and increasing the carbon dioxide concentration to 5%, results in more than 10-fold reduction of respiration rate in vegetables such as broccoli [32]. The maintenance of color is important and in red peppers, MAP has been shown to increase carotenoid retention and reduce browning [33]. The combination of storage time and temperature has been shown to be important in extending the shelf life of fruit in terms of texture, weight loss, pH and other nutritional changes. Temperature is also a factor in determining respiration rates of fruits. In freshly harvested beansprouts for example, which not only have a high respiration rate but also are characterized by high initial microbial populations, Varoquaux et al. [34], observed a 10-fold increase in respiration rate at 16.5 °C. In the case of fruit and vegetables with high respiration rates, there is an optimum initial atmosphere concentration to ensure minimal growth of aerobic spoilage bacteria together with an optimal film permeability to delay the development of anaerobic respiration and necrosis of vegetable. One of the obvious ways in which produce may be assessed for freshness is in terms of wilting and shriveling which are due to loss of moisture. Fruits and vegetables lose moisture when the relative humidity in the packaging is less than 80-95% of saturation and reduction in quality occurs if 3-6% of the produce moisture is lost [35]. Most films used for MAP of fruit and vegetables are relatively good water vapor barriers and are able to maintain a high relative humidity inside the pack. The relative humidity within a pack is influenced by the rate at which the product loses water vapor and by vapor transmission rate of the packaging film. Successful applications include broccoli florets, cauliflower florets, carrots, peeled garlic [36]. LDPE was found a good alternative to PVC for wrapping these vegetables. Comparative evaluation of the effect of storage temperature fluctuation on MAP of selected fruit and vegetables like mushrooms and mature green tomatoes was also studied by Tano et al. [37]. The quality of the products stored under temperature fluctuating regime was severely affected as indicated by extensive browning, loss of firmness, weight loss increase, ethanol level in plant tissue and infection, due to physiological damage and excessive condensation, compared to products stored at constant temperature. It was clear that temperature fluctuation can seriously compromise the benefits of MAP and safety of the product. Temperature is the most effective environmental factor in the prevention of fruit ripening. Both ripening and ethylene production rates increase with increase in temperature. To delay fruit ripening, temperature should be held as close to 0 °C as possible. The use of MAP as a supplement to proper temperature maintenance in the effort to delay ripening is effective for all fruits. Reducing oxygen concentration below 8% and/or elevating Carbon dioxide concentration above 1% retards fruit ripening. Successful applications include broccoli slaw, coleslaw, dry slaw, casserole mix, and mixed salads. Degradation of cut vegetables in terms of appearance was delayed by N₂ gas packaging and vegetables remained acceptable at temperature below 5 °C after 5 days. MAP may have the effect of increasing shelf life of some vegetables in terms of sensory properties but does not reduce growth of some microorganisms such as *L. monocytogenes*

and *Salmonella* Enterica. Therefore, the use of appropriate pre-harvest and postharvest sanitation practices to prevent contamination remains the most important measure for ensuring the microbiological safety of ready-to-eat fresh-cut products.

Shelf life of milk and milk-based products is limited because of their high water content and favorable pH for microbial growth [38-40]. The rapid spoilage adversely affects flavor and texture along with visual color changes of refrigerated raw and pasteurized milk, cottage cheese and other similar products. The responsible microorganisms include psychrotropic Gram negative bacteria, yeasts and moulds. These organisms produce extracellular protease and lipase activity, which reduce the functionality of milk proteins and fat and often produce undesirable aromas. Gram positive bacteria particularly those producing lactic and acetic acids, can spoil dairy foods, but the number of organisms required are generally higher than for Gram-negative bacteria, and the changes can be less noticeable. It has been reported that the product shelf life increases by low oxygen atmospheres because of the reduction in aerobic microorganisms. The antimicrobial effect of Carbon dioxide occurs near 10% level, and further increase in carbon dioxide affects growth of *Pseudomonas* and *Moraxella*. The largest inhibition by carbon dioxide occurs with Gram negative psychrotrophs bacteria [41]. The protective role of carbon dioxide is also important for mould proliferation; its function in creating an anaerobic environment with the displacement of existing molecular oxygen, its extra and intracellular pH decreasing effect and its destroying effect on the cell membrane make carbon dioxide an inhibitory substance towards microorganisms. The antimicrobial effect of carbon dioxide is dependent on many factors, including the partial pressure, application time, concentration of gas, temperature of the medium [42], volume of headspace, acidity, water activity of the medium and type of organism present [43]. The applied composition for packaging of dairy products can vary from 10% to 100% carbon dioxide, balanced with N₂ as inert gas filler, to prevent package collapse as a result of carbon dioxide solubilization in the cheese. MAP has been applied to the packaging of cheese. The packaging of each type of cheese needs to be considered separately. Another fact to be considered is that some cheeses are carbon dioxide producers, while other not. It is important that the levels of carbon dioxide are controlled because for certain cheese high levels of carbon dioxide have been found to impart off-flavor [44-46]. Cheese stored under carbon dioxide contained high concentrations of aldehydes and fatty acids and lower concentrations of alcohols and esters than cheeses stored under nitrogen. Hard and semi-soft cheeses, such as cheddar, are commonly packed in 100% carbon dioxide or mixtures of carbon dioxide and nitrogen. Soft cheese have also a limited shelf life. An alternative to conventional packaging is to use MAP. Carbon dioxide acts both directly on moulds and indirectly by displacing oxygen. Vacuum packaging does not remove all of the oxygen and thus, moulds and yeasts can still occur [47]. The gas mixture typically used is 70% N₂ and 30% CO₂ to inhibit mould growth, to keep the package from collapsing and to prevent shred matting. Alves et al. [48] reported that atmospheres $\geq 50\%$ carbon dioxide were more effective than air or 100% nitrogen in improving shelf life of sliced mozzarella cheese. High carbon dioxide atmospheres have been shown to inhibit growth of lactic and mesophilic bacteria [49]. Piergiovanni et al. [50] compared Taleggio cheese packaged under four modified atmospheres and stored at 6 °C to conventional paper wrapping and found that samples packaged in MAP had satisfac-

tory quality. Gammariello et al. [51] evaluated the shelf life of Stracciatella cheese packaged in four different gas mixtures at 8 °C and showed that MAP 50:50 and 95:5 (O₂:CO₂) prolonged the sensorial acceptability limit by delayed growth of spoilage bacteria, without affecting the dairy microflora. Del Nobile et al. [52] suggest that MAP of Ricotta with 95% carbon dioxide inhibits microbial growth without effects on lactic acid bacteria, probably due to their facultative anaerobic nature, and also maintains the natural color of Ricotta.

MAP found wide application also for fresh fish. Fish such as herring and haddock benefits from being packaged under MAP since this reduces the production of peroxides which affect fish sensory characteristics and hence shelf-life [53]. However, high levels of carbon dioxide may result in carbon dioxide dissolution into the fish flesh, causing deformation or collapse of the packaging and also affecting the product color. The resulting drop in pH of the tissue may cause a decrease in the flesh's water holding capacity and drip may occur, reducing shelf-life. Fresh hake stored in up to 60% carbon dioxide exerted a shelf life significantly longer than those stored in air. MAP inhibits bacterial growth, reduces the formation of total volatile bases and trimethylamine and delays alterations in protein functionality [54]. In cooked fish such as smoked blue cod and smoked atlantic and silver salmon, a high concentration of carbon dioxide increases shelf life without showing drip or muscle exudate observed in fresh fish. carbon dioxide extends fish shelf life due to the inhibition of Gram negative and lactic acid bacteria. carbon dioxide concentrations in all MAP fishery products should be carefully monitored, especially when stored for long periods of time, because carbon dioxide does not inhibit *C. botulinum* and the effect of temperature abuse may increase the risk of botulism in those products which contain spores of non-proteolytic *C. botulinum* [55, 56].

3. Active packaging

Active packaging has been classified as a subset of smart packaging and referred to as the incorporation of certain additives into packaging film or within packaging containers with the aim of maintaining and extending product shelf life [57-59]. Another definition states that packaging may be termed active when it performs some desired role in food preservation other than providing an inert barrier to external conditions [60]. Hence, active packaging includes components of packaging systems that are capable of scavenging oxygen; absorbing carbon dioxide, moisture, ethylene and/or flavor/odor taints; releasing carbon dioxide, ethanol, antioxidants and/or other preservatives; and/or maintaining temperature control and/or compensating for temperature changes (Table 3). In the food and beverage market, growth of active packaging concepts is being driven by the growing use of packaged food, increasing demand for ready-prepared foods such as microwave meals, and increasing use of smaller package sizes. Although many active packaging technologies are still developmental, there are commercial successes, particularly in oxygen scavengers. Oxygen scavengers are easily oxidizable substances included in the packaging system to remove oxygen by means of a chemical reaction. The substance is

usually contained in sachets made of a material highly permeable to air but it can also be included in bottle closures or in the plastic film matrix. Different studies show that the use of scavengers led to faster reduction and to lower levels of residual oxygen, as compared to nitrogen flushing. The most common substances used are iron powder and ascorbic acid. Scavengers also differ in the reaction speed, from immediate action (0.5 to 1 day) to slow action (4 to 6 days), on the application, particularly the moisture content of the food, and on the function, i.e., oxygen scavenging only or dual function, such as absorbing or generating carbon dioxide, besides removing the oxygen. The scientific literature contains a number of references which examine the influence of oxygen scavenger sachets on fresh beef discoloration. Gill and McGinnis [61] performed an oxygen absorption kinetics study with a commercial oxygen scavenger (FreshPax™ 200R) and reported that discoloration could be prevented in ground beef if large numbers of scavengers were used in each pack to bring residual oxygen to <10 ppm within 2 h at a storage temperature of -1.5 °C. The inclusion of oxygen scavengers (Ageless® SS200) in master packs flushed with 50% carbon dioxide and 50% nitrogen significantly improved color stability of *M. longissimus dorsi* and *M. psoas major*, relative to controls [62]. In addition to fresh beef oxygen scavenging technology has also been applied to pork [63] and pork products, where, Martinez, Djenane, Cilla, Beltràn, and Roncalès [64] reported that fresh pork sausages stored in 20% CO₂ and 80% N₂ plus an oxygen scavenger (Ageless® FX-40) for up to 20 days at 2 ± 1 °C reduced psychrotrophic aerobic counts and extended shelf life in terms of color and lipid stability. An alternative to sachets involves the incorporation of the oxygen scavenger into the packaging structure itself. This UV light-activated oxygen scavenging film, which structurally is composed of an oxygen scavenger layer extruded into a multilayer film, can reduce headspace oxygen levels from 1% to ppm levels in 4–10 days, compared to oxygen scavenging sachets. The OS2000™ scavenging films found applications in a wide variety of food products including dried or smoked meat products and processed meats [65]. Berenzon and Saguy [66] evaluated the applicability of oxygen absorbers for extending shelf life of military ration crackers packaged in hermetically sealed tin cans and stored at 15, 25 and 35 °C for up to 52 weeks. Sensory evaluations suggested that crackers stored without oxygen absorbers developed oxidative rancid odors after 24 weeks at 25 and 35 °C. Independently of storage temperatures, no oxidative rancid odors were observed after 44 weeks with oxygen absorbers. Opposed to the currently available chemical oxygen scavengers, systems based upon natural and biological components could have advantages towards consumer perception and sustainability [67]. A model system for a new oxygen scavenging poly(ethylene terephthalate) (PET) bottle is proposed using an endospore-forming bacteria genus [68]. Incorporated spores could actively consume oxygen for minimum 15 days, after an activation period of 1–2 days at 30 °C under high humidity conditions. Although the system shows some clear opportunities, such as being a biological based system and its capability of solving polymer compatibility and recyclability issues, towards the current chemical systems, further investigations are necessary to determine a possible interaction between spores and food product.

Active packaging	Action mechanisms	Food applications
Oxygen scavengers	Slowed food metabolism, reduced oxidative rancidity, inhibited undesirable oxidation of labile pigments and vitamins, controlled enzymatic discoloration, inhibited growth of aerobic microorganisms.	Bread, cakes, cooked rice, biscuits, pizza, pasta, cheese, cured meats and fish, coffee, snack foods, dried foods and beverages.
Carbon dioxide scavengers/emitters	Slowed respiration rate, inhibited microbial growth.	Coffee, fresh meats and fish, nuts and other snack food products and sponge cakes.
Ethylene scavengers	Slowed respiration rate, thus slowed softening and ripening	Fruit, vegetables and other horticultural products.
Preservative releasers	Antimicrobial and antioxidant effect.	Cereals, meats, fish, bread, cheese, snack foods, fruit and vegetables.
Ethanol emitters	Effective against mould, can also inhibit the growth of yeasts and bacteria.	Pizza crusts, cakes, bread, biscuits, fish and bakery products.
Moisture absorbers	Inhibited microbial growth and moisture related degradation of texture and flavor.	Fish, meats, snack, cereals, dried foods, sandwiches, fruit and vegetables.
Flavor/odor absorbers	Malodorous constituents causing off-flavors are absorbed.	Fruit juices, fried snack foods, fish, cereals, poultry, dairy products and fruit.
Temperature control	Able to maintain chilled temperature.	Ready meals, meats, fish, poultry and beverages.
Temperature compensating	Gas permeability responding to temperature changes to avoid anoxic conditions.	Fruit, vegetables and other horticultural products.

Table 3. Examples of active packaging systems

Another important example of scavenger is the packaging with ethylene scavenger property. Ethylene has long been recognized as a problem in post-harvest handling of horticultural products because it is responsible for a wide variety of undesirable effects: it accelerates the respiration of fruits and vegetables, as well as softening and ripening, and it is responsible for a number of specific post-harvest disorders. The removal of this gas from storage chambers and packages of fruits and vegetables is, therefore, of the utmost importance, and it is done as a regular practice in the case of chambers, although is only more recently done in the case of removal from a single package. Ethylene is a very reactive compound that can be altered in many ways, such as chemical cleavage and modification, absorption, adsorption, etc. This creates a diversity of opportunities for commercial applications for the removal of ethylene [69]. Most substances designed to remove ethylene from package are delivered either as sachets that go inside the package or are integrated into the packaging material, usually a plastic polymer film. The most commonly used are based in potassium permanganate, activated carbon and activated earth. Meyer & Terry [70] studied the effect of 1-methylcyclo-

propene (1-MCP) and a newly developed palladium (Pd)-promoted ethylene scavenger (e + [®]Ethylene Remover) on changes in firmness, color, fatty acids and sugar content of early and late season avocado (*Persea americana Mill.*), cv. Hass, during storage at 5 °C and subsequent ripening at 20 °C. Results have shown that the [®]Ethylene Remover is effective at delaying ripening of avocado at low temperature, similarly to 1-MCP; however, subsequent ripening was not impaired. Similarly, but to a lesser extent and concomitant with trends in firmness retention and color changes, [®]Ethylene Remover led to greater maintenance of mannoheptulose and perseitol than that of controls. Initial findings have demonstrated for the first time that the presence of a palladium-based scavenger was effective at removing ethylene to below physiologically active levels for preclimacteric green bananas and green avocado fruits. Reduced carbon dioxide production and control of color change from green to yellow was observed for the preclimacteric bananas. Results suggested that the normal and expected climacteric respiratory rise has been disrupted. Therefore, for the first time an ethylene scavenger has been shown to be capable of extending shelf life even when the climacteric respiratory rise has already been initiated [71].

In order to suppress spoilage and remove offensive odors in fresh products carbon dioxide absorbers are used. On the other hand, carbon dioxide emitters are useful in modified atmosphere packaging, because carbon dioxide suppresses the bacteria that cause spoilage. Both carbon dioxide generators and absorbers are available in sachet format [72].

Ethanol emitters are particularly effective in extending the shelf life of high water activity baked products. The use of ethanol generating sachets or strips avoids the ethanol spraying directly onto the product surface prior to packaging [60]. The ethanol is absorbed or encapsulated in a carrier material enclosed in sachets of selective permeability to ethanol to allow for ethanol accumulation in the headspace. The level of ethanol in the packaging headspace depends obviously on the sachet size and on product water activity.

Fragrances incorporated in packaging also found commercial use in food, personal care, pharmaceutical, and nutraceutical packaging. In food packaging, fragrances are being used as a marketing tool to create consumer awareness and to enhance brand image. Because cyclodextrins are able to form inclusion complexes with various compounds, they present a potential interest as agents to retain or scavenge substances such as odors, bitter compounds, lactose, cholesterol, etc., or to add aromas, colors, or functional ingredients whose release could enhance the quality of the packaged product and extend its shelf life [73-75].

Control of moisture is also important for food preservation. In most cases, the packaging material itself is responsible for the control of moisture transfer between the internal and external environment, providing an adequate barrier. There are situations however, where a greater control is needed to avoid the build-up of liquid water inside the package, therefore requiring liquid water control or humidity buffering as in the case of transpiration of fresh produce, melting of ice in fish transportation, temperature fluctuation in high water activity food packages and drip of tissue fluid from cut meats and produce [60]. To this aim, absorbent pads or sheets, anti-fog additives in the polymer film, humectant between two layers of a highly water vapor permeable film or sachets of inorganic desiccant salts, are generally used to accomplish liquid removal or humidity buffering.

Antioxidant food packaging films were produced by incorporation of ascorbic acid, ferulic acid, quercetin, and green tea extract into an ethylene vinyl alcohol copolymer matrix. The efficiency of the films developed was determined by real packaging applications of brined sardines. The evolution of the peroxide index and the malondialdehyde content showed that, in general, the films improved sardine stability. Films with green tea extract offered the best protection against lipid oxidation [76]. A natural citrus extract was also sprayed onto the surface of polyethylene terephthalate trays to delay lipid oxidation of cooked turkey meat slices, stored at 4 °C over 4 days [9]. The high surface roughness, demonstrated by optical profilometry, and the high level of solubility of the antioxidant in water allowed a good effectiveness of the citrus extract coating. Patties made of minced chicken breast and thigh packed in standard vacuum-packaging or in antioxidant active packaging containing rosemary extract were subjected to high pressure treatment (800 MPa, 10 min, 5 °C) and subsequently stored at 5 °C. The active packaging was able to delay surface lipid oxidation up to 25 days. The migration of α -tocopherol from a multilayer active packaging made up of high density polyethylene, ethylene vinyl alcohol and a layer of low density polyethylene containing the antioxidant, was studied. The antioxidant delivering system delayed the lipid oxidation of whole milk powder and it was more effective at temperatures higher than 20 °C [77].

The most investigated active systems are the packaging with antimicrobial properties, even if there has been little commercial activity in North America or Europe. Japan has historically been a leader in antimicrobial use. To date the literature counts various research works and review papers dealing with advances in antimicrobial packaging. Generally speaking most of them are focused on *in vitro* test and can be subdivided in various categories: (i) there are studies aimed to develop new active systems with recently exposed natural compounds; (ii) studies finalized to underline the release kinetic of the active agents from the matrix to the food, with the intent to realize controlled release systems; (iii) studies aimed to develop bio-based active systems and (iv) works that use the nanotechnology approach. Among the abundant list of research articles and reviews available in the scientific literature on this topic, some recent works have been selected. Kanatt et al. [78] studied active films of chitosan and polyvinyl alcohol containing aqueous mint extract/pomegranate peel extract. Ramos et al. [79] studied antimicrobial active films based on polypropylene (PP) and containing thymol and carvacrol at three different concentrations. Trans-2-hexenal was encapsulated into β -cyclodextrins and incorporated into a poly(L-lactic acid) matrix by extrusion and casting [75]. A newly synthesized polyester (poly-butylene adipate) containing covalently bound quaternary phosphonium groups was developed by Anthierens et al. [80]. The resulting polyester showed great antimicrobial activity through direct contact without any migration of active groups. Among the bio-based active systems, various bio-active packaging were developed to control insect pest in granary weevils [81, 82]. The efficacy of edible films produced from whey protein isolate and glycerol, including incorporation of lactic acid, propionic acid, chitooligosaccharides and natamycin was assessed by Ramos et al. [83]. Suppakul et al. [84] studied the diffusion of linalool and methylchavicol from thin antimicrobial low-density polyethylene-based films. Cellulose acetate-based mono and multilayer films including potassium sorbate were prepared using dry phase inversion technique [85].

Monolayer films, prepared using powdered cellulose and poly(vinyl) alcohol were coated with cellulose membrane to obtain multilayer films and sorbic acid was incorporated as antimicrobial agent [86]. Cerisuelo et al. [87] studied by a mathematical model the release of carvacrol from an ethylene-vinyl alcohol coating on a polypropylene film while Del Nobile et al. [88] studied the release of thymol from zein-based films. Bierhalz et al. [89] studied release behavior in water and diffusion coefficients of single and composite films based on alginate and pectin containing natamycin. Organic/inorganic compounds, essential oils, bacteria originated antibacterial proteins, enzymes and fruit extracts have shown great potential in inhibiting microbial growth in food stuff. However, the development of new resistant strains of bacteria to current antibiotics has led to the search for new bactericides that can effectively reduce the harmful effects of microorganisms. With the emergence of nanotechnology, the search for effective biocidal agents has focused on the development of nanostructures of coinage metals like silver, copper, zinc and gold [90]. ZnO nanoparticles loaded starch-coated polyethylene film were developed by Tankhiwale and Bajpai [91]. Montmorillonite nanoclay and rosemary essential oil were incorporated into chitosan film to improve its physical and mechanical properties as well as antimicrobial and antioxidant behavior [92]. Silver nanoparticles (AgNPs) have been abundantly exploited for technological applications as bactericidal agents. Recently, AgNPs were incorporated with success into biobased materials [93] and into a hydroxy-propyl methylcellulose matrix [94]. Although numerous antimicrobial systems continue to be investigated in food simulating models, real applications are limited by technical, aesthetic and regulatory barriers. To this regards, a few recent examples can be cited. Microencapsulated beta-cyclodextrin and trans-cinnamaldehyde complex was incorporated into a multilayered edible coating made of chitosan and pectin to coat fresh-cut papaya that was then packaged in Ziploc trays with Ziploc lids for 15 days. The layer-by-layer assembly with incorporation of microencapsulated antimicrobial was effective in extending shelf life and quality of fruit [95]. The antimicrobial proteins lysozyme and lactoferrin were incorporated into paper containing carboxymethyl cellulose [96]. The antimicrobial activity on common food contaminants was also retained in the released protein, and a synergism between the two proteins was evident in tests carried out with paper containing both proteins. Lysozyme was most effective in preventing microbial growth when the system was applied to thin meat slices laid on paper sheets containing either or both antimicrobial proteins. Cellulose/silver nanocomposites were investigated to decrease the microbial loads in minimally processed foods and meat [97]. The active systems were synthesized by means of reduction by UV/heat of silver nitrate adsorbed on fluff pulp cellulose fibres. Minimally processed fruits and meat products were packaged in trays containing commercial absorbent pads or silver loaded absorbers and in contact with silver loaded absorbers, spoilage counts were significantly reduced. Active packaging based on silver nanoparticles, obtained by allowing silver ions from nitrate solutions to replace the Na⁺ of natural montmorillonite and then reduced by a thermal treatment, were applied to fruit salad [98] and fresh dairy products [99, 100]. The striking feature of these works is the interesting antimicrobial effects, without compromising sensory properties. The antimicrobial effectiveness is usually complicated by several factors, including temperature, moisture levels, chemistry of the antimicrobial agent and release mechanism. Moreover, it is necessary to

consider odor or color change that an antimicrobial could provoke in the packaged product. The cost-benefit ratio of antimicrobials is also a limiting factor for commercial growth and rates of return in the food industry are small. All these considerations explain the limited diffusion of active systems, although several antimicrobials have been successful in the laboratory. Applications with good potential are value added products such as pre-sliced and prepared foods.

4. Final considerations

Packaging design is clearly a fundamental part of a new launch product. Considering the importance of packaging in determining product shelf life, the correct approach allows considering on the same level of importance the product development and its packaging system. The key to successful packaging is selection of materials and designs that best balance the competing needs of product characteristics, marketing considerations including distribution and consumer needs, environmental and waste management issues, and cost. Food packaging technologies also require integration with other processing and preservation activities such as freezing, irradiation, pulsed electric fields, high pressure processing, and pulsed light. Globalization, packaging life cycles, and requirement for strict safety measures are increasing the pressure to produce new packaging systems able to transport food items and that also allow the traceability along the food distribution chain. Due to the diversity of product characteristics and basic food packaging demands and applications, any packaging technologies offering to deliver more product and quality control in an economic and diverse manner would be favorably welcomed. To meet tomorrow's concerns, there continues to be a large amount of research to evaluate areas such as active packaging, traceability, sustainable resources and antimicrobial packaging. Advances in these areas will continue to give us a safe and sustainable food supply. The use of modified atmosphere technique can extend shelf life. Its use does not eliminate the need for proper control of storage conditions, especially temperature, nor for the adequate training handlers at sensory characteristics and shelf life of many food products, inhibiting the growth of pathogenic bacteria. MAP will continue to be used in the future, most probably with several different MAP formats in use around the world. Mechanistic, logistical, and perception obstacles will require effort and ingenuity to overcome existing package and system difficulties and promote implementation of new processing and packaging technologies. Moreover, the concept of combining antimicrobial/antioxidant agents within the package to control the deterioration and growth of microorganisms in food, will have a strong impact on both shelf life prolongation and food safety. Although the evidence suggests that active packaging is a promising technology, its potential cannot be fully realized unless major technical problems are overcome. More research related to the control of the migration of the active agents at rates suitable for different real food systems is still needed. Recognition of the benefits of active packaging technologies by the food industry, development of economically viable packaging systems and increased consumer acceptance opens new frontiers for active packaging technology.

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