

10 Modified atmosphere packaging

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SECTION A MAP GASES, PACKAGING MATERIALS AND EQUIPMENT

10.A1 Introduction

The normal gaseous composition of air is nitrogen (N₂) 78.08% (volume per volume will be used throughout this chapter), oxygen (O₂) 20.96% and carbon dioxide (CO₂) 0.03%, together with variable concentrations of water vapour and traces of inert or noble gases. Many foods spoil rapidly in air due to moisture loss or uptake, reaction with oxygen and the growth of aerobic microorganisms, i.e. bacteria and moulds. Microbial growth results in changes in texture, colour, flavour and nutritional value of the food. These changes can render food unpalatable and potentially unsafe for human consumption. Storage of foods in a modified gaseous atmosphere can maintain quality and extend product shelf life, by slowing chemical and biochemical deteriorative reactions and by slowing (or in some instances preventing) the growth of spoilage organisms.

Modified atmosphere packaging (MAP) is defined as 'the packaging of a perishable product in an atmosphere which has been modified so that its composition is other than that of air' (Hintlian & Hotchkiss, 1986). Whereas controlled atmosphere storage (CAS) involves maintaining a fixed concentration of gases surrounding the product by careful monitoring and addition of gases, the gaseous composition of fresh MAP foods is constantly changing due to chemical reactions and microbial activity. Gas exchange between the pack headspace and the external environment may also occur as a result of permeation across the package material.

Packing foods in a modified atmosphere can offer extended shelf life and improved product presentation in a convenient container, making the product more attractive to the retail customer. However, MAP cannot improve the quality of a poor quality food product. It is therefore essential that the food is of the highest quality prior to packing in order to optimise the benefits of modifying the pack atmosphere. Good hygiene practices and temperature control throughout the chill-chain for perishable products are required to maintain the quality benefits and extended shelf life of MAP foods.

10.A1.1 *Historical development*

The first commercial applications of the use of modified gas atmospheres were for CAS of fruits and vegetables. Fresh carcass meat was exported from New Zealand and Australia under CAS in the early 1930s. Early developments were generally for storage and transportation of bulk foods. Scientific investigations on the effect of gases on extending the shelf life of foods were conducted in 1930 on fresh meat. Killefer (1930) reported a doubling of the shelf life of refrigerated pork and lamb when these meats were stored in an atmosphere of 100% CO₂. The earliest published research on poultry products was conducted in the 1930s. Fresh poultry was stored in an atmosphere of 100% CO₂ which was found to considerably extend shelf life.

Ogilvy and Ayres (1951) conducted studies on the effect of enriched CO₂ atmospheres on the shelf life of chicken portions. They reported an increasing effect on the shelf life as the CO₂ concentration of the storage atmosphere increased up to 25% CO₂.

Commercial retailing of fresh meat in MAP tray systems was introduced in the early 1970s. European meat processing and packaging developed during the 1980s with centralised production of MAP meat in consumer packs for distribution to retail outlets. In the past few years, there has been a considerable increase in the range of foods packed in modified atmospheres for retail sale including meat, poultry, fish, bacon, bread, cakes, crisps, cheese and salad vegetables. UK retail sales of products packed under MAP grew from approximately 2 billion packs in the mid 1990s to 2.8 billion packs in 1998. Carcass meat and cooked meat and meat products accounted for 29% and 15% of the total volume of MAP retail foods (Anon, 1999).

10.A2 **Gaseous environment**

10.A2.1 *Gases used in MAP*

The three main gases used in MAP are O₂, CO₂ and N₂. The choice of gas is totally dependent upon the food product being packed. Used singly or in combination, these gases are commonly used to balance safe shelf life extension with optimal organoleptic properties of the food. Noble or *inert* gases such as argon are in commercial use for products such as coffee and snack products, however, the literature on their application and benefits is limited. Experimental use of carbon monoxide (CO) and sulphur dioxide (SO₂) has also been reported.

10.A2.1.1 *Carbon dioxide*

Carbon dioxide (CO₂) is a colourless gas with a slight pungent odour at very high concentrations. It is an asphyxiant and slightly corrosive in the presence of

moisture. CO_2 dissolves readily in water (1.57 g kg^{-1} at 100 kPa, 20°C) to produce carbonic acid (H_2CO_3) that increases the acidity of the solution and reduces the pH. This gas is also soluble in lipids and some other organic compounds. The solubility of CO_2 increases with decreasing temperature. For this reason, the antimicrobial activity of CO_2 is markedly greater at temperatures below 10°C than at 15°C or higher. This has significant implications for MAP of foods, as will be discussed later. The high solubility of CO_2 can result in pack collapse due to the reduction of headspace volume. In some MAP applications, pack collapse is favoured, for example in flow wrapped cheese for retail sale.

10.A2.1.2 Oxygen

Oxygen (O_2) is a colourless, odourless gas that is highly reactive and supports combustion. It has a low solubility in water (0.040 g kg^{-1} at 100 kPa, 20°C). Oxygen promotes several types of deteriorative reactions in foods including fat oxidation, browning reactions and pigment oxidation. Most of the common spoilage bacteria and fungi require O_2 for growth. Therefore, to increase the shelf life of foods, the pack atmosphere should contain a low concentration of residual O_2 . It should be noted that in some foods a low concentration of O_2 can result in quality and safety problems (for example, unfavourable colour changes in red meat pigments, senescence in fruits and vegetables and growth of food poisoning bacteria), and this must be taken into account when selecting the gaseous composition for a packaged food.

10.A2.1.3 Nitrogen

Nitrogen (N_2) is a relatively un-reactive gas with no odour, taste or colour. It has a lower density than air, non-flammable and has a low solubility in water (0.018 g kg^{-1} at 100 kPa, 20°C) and other food constituents. Nitrogen does not support the growth of aerobic microbes and therefore inhibits the growth of aerobic spoilage but does not prevent the growth of anaerobic bacteria. The low solubility of N_2 in foods can be used to prevent pack collapse by including sufficient N_2 in the gas mix to balance the volume decrease due to CO_2 going into solution.

10.A2.1.4 Carbon monoxide

Carbon monoxide (CO) is a colourless, tasteless and odourless gas that is highly reactive and very flammable. It has a low solubility in water but is relatively soluble in some organic solvents. CO has been studied in the MAP of meat and has been licensed for use in the USA to prevent browning in packed lettuce. Commercial application has been limited because of its toxicity and the formation of potentially explosive mixtures with air.

10.A2.1.5 Noble gases

The noble gases are a family of elements characterised by their lack of reactivity and include helium (He), argon (Ar), xenon (Xe) and neon (Ne). These gases are being used in a number of food applications now, e.g. potato-based snack products. While from a scientific perspective it is difficult to see how the use of noble gases would offer any preservation advantages compared with N₂ they are nevertheless being used. This would suggest that there may be, as yet unpublished, advantages for their use.

10.A2.2 Effect of the gaseous environment on the activity of bacteria, yeasts and moulds

Foods can contain a wide range of microorganisms including bacteria and their spores, yeasts, moulds, protozoa and viruses. While the packaging technologist will generally be concerned with preventing the growth of bacteria, yeasts and moulds in foods, one should be aware that certain pathogenic microorganisms, while not growing in the food, may survive during the shelf life period and cause food poisoning or disease in consumers. This section is concerned with the major microbial groups that can be controlled or affected by MAP.

10.A2.2.1 Effect of oxygen

Bacteria, yeasts and moulds have different respiratory and metabolic needs and can be grouped according to their O₂ needs (Table 10.1).

Aerobes. They require O₂ for growth and include the ubiquitous Gram-negative spoilage bacteria belonging to the *Pseudomonas* genus. This grouping also includes certain pathogenic bacteria such as *Vibrio parahaemoly-*

Table 10.1 Oxygen requirements of some microorganisms of relevance in modified atmosphere packaging

Group	Spoilage organisms	Pathogens
Aerobes	<i>Micrococcus</i> sp. Moulds e.g. <i>Botrytis cinerea</i> <i>Pseudomonas</i> sp.	<i>Bacillus cereus</i> <i>Yersinia enterocolitica</i> <i>Vibrio parahaemolyticus</i> <i>Camplobacter jejuni</i>
Microaerophiles	<i>Lactobacillus</i> sp. <i>Bacillus</i> spp. <i>Enterobacteriaceae</i>	<i>Listeria monocytogenes</i> <i>Aeromonas hydrophilia</i> <i>Escherichia coli</i>
Facultative anaerobes	<i>Brocothrix thermosphacta</i> <i>Shewanella putrefaciens</i> Yeasts	<i>Salmonella</i> spp. <i>Staphylococcus</i> spp. <i>Vibrio</i> sp.
Anaerobes	<i>Clostridium sporogenes</i> <i>Clostridium tyrobutyricum</i>	<i>Clostridium perfringens</i> <i>Clostridium botulinum</i>

ticus. Note that some other *Vibrio* species are classified as facultative aerobes.

Microaerophiles. They grow under low concentrations of O₂. Thus, an environment low in O₂ may be selective for some important pathogens including *Campylobacter jejuni* and *Listeria monocytogenes*. Some microaerophilic bacteria, e.g. *Lactobacillus* species, may also require increased levels of CO₂ under low oxygen conditions for optimum growth.

Facultative anaerobes. They generally grow better in O₂ but are also able to grow without it. These include various important genera from the Enterobacteriaceae including pathogenic organisms such as *Escherichia coli*, *Salmonella* and *Shigella* species, *Staphylococcus aureus*, *Listeria monocytogenes*, *Brochothrix* species, *Vibrio* species, fermentative yeasts and some *Bacillus* species. *Aeromonas hydrophilia* is a new and emerging pathogen that appears to be particularly associated with fish and fish products. Many strains are psychrotrophic and some may grow between 3 and 5°C.

Anaerobes. They are inhibited or killed by the presence of O₂, e.g. the pathogenic bacterium *Clostridium botulinum*. The removal of O₂, for example in vacuum packaging, will restrict the growth of aerobic spoilage and pathogenic bacteria and therefore extend shelf life. However, as indicated above, there are other microorganisms including the pathogens *E. coli* and *A. hydrophilia* capable of growth under these conditions.

10.A2.2.2 Effect of carbon dioxide

The antibacterial properties of CO₂ have been known for some time (Valley & Rettger, 1927). More recent work has shown that CO₂ is effective against psychrotrophs (King & Nagel, 1975) and has potential for extending the shelf life of food stored at low temperatures.

There are several theories regarding the actual mechanism of CO₂ action. In general, CO₂ increases the lag phase and generation time of microorganisms, and this effect, as would be expected, is enhanced at lower temperatures. There appears to be an array of antimicrobial mechanisms including CO₂ lowering pH, inhibition of succinic oxidase at CO₂ concentrations greater than 10%, inhibition of certain decarboxylation enzymes and disruption of the cell membrane (Valley & Rettger, 1927; King & Nagel, 1975; Gill & Tan, 1979; Enfors & Molin, 1981). The area has also been reviewed by several workers including Daniels *et al.* (1985).

The sensitivity of selected spoilage and pathogenic bacteria to CO₂ is shown in Table 10.2. In general, the growth of Gram-negative bacteria is inhibited much more than that of Gram-positive bacteria. As indicated in Section 10.A2.1.1, the effects of CO₂ are markedly temperature dependent, and it is therefore imperative that the integrity of temperature control across the supply chain be

Table 10.2 Sensitivity of microorganisms relevant to modified atmosphere packaging to carbon dioxide

Inhibited by CO ₂	CO ₂ has little or no effect on growth	Growth is stimulated by CO ₂
<i>Pseudomonas</i> spp.	<i>Enterococcus</i> spp.	<i>Lactobacillus</i> spp.
<i>Aeromonas</i> spp.	<i>Brochothrix</i> spp.	<i>Clostridium botulinum</i> *
<i>Bacillus</i> spp.	<i>Lactobacillus</i> spp.	
Moulds including <i>Botrytis cinerea</i>	<i>Clostridium</i> spp.	
Enterobacteriaceae including <i>E. coli</i>	<i>Listeria monocytogenes</i>	
<i>Staphylococcus aureus</i>	<i>Aeromonas hydrophilia</i>	
<i>Yersinia enterocolitica</i>		

Effects will depend on the storage temperature and concentration of gas. For some microorganisms CO₂ concentrations close to 50% (v/v) and temperatures <10°C are required for significant effects. Growth inhibition may also be strain specific.

* Spore germination by *C. botulinum* may be enhanced in a CO₂ enriched environment (Eklund, 1982).

maintained in order to protect the health of the consumer. Of some concern is the observation that germination of spores of *C. botulinum* may be stimulated by CO₂ (Eklund, 1982).

CO₂, particularly at low temperatures, is soluble in water and lipids, and adjustment for adsorption is required. A high concentration of CO₂ can lead to defects, e.g. increased drip in fresh meats, and to container collapse. The latter can occur where CO₂ is the major gas present, and where the gas goes into solution in the water and lipid phases of the product. To counteract this effect, an insoluble gas such as nitrogen may be added to the gas mix. When CO₂ is required to control the bacterial and mould growth, a minimum of 20% is generally used. Optimal levels appear to be in the region of 20–30%. However, concentrations of 100% CO₂ may be used in bulk packs of meat and poultry.

10.A2.2.3 *Effect of nitrogen*

Nitrogen is a relatively un-reactive gas. It is used to displace air and, in particular, O₂ from MAP. Since air and consequently O₂ have been removed, growth of aerobic spoilage organisms is inhibited or stopped. It is also used to balance gas pressure inside packs, so as to prevent the collapse of packs containing high moisture and fat-containing foods, e.g. meat. Because of the solubility of CO₂ in water and fat, these foods tend to absorb CO₂ from the pack atmosphere.

10.A2.3 *Effect of the gaseous environment on the chemical, biochemical and physical properties of foods*

Food spoilage can also be caused by chemical and biochemical, including enzyme-catalysed, reactions in food. The packaging technologist should have

an awareness of these effects and understand the extent to which modified atmospheres can mitigate them.

Of the gases involved in MAP, O_2 , because of its reactivity, has been extensively studied. Because of the significance of O_2 , this section will largely be concerned with the influence of this gas. However, CO_2 , and to a lesser extent CO and ethylene (C_2H_4), have also been investigated. While reference to C_2H_4 is made in Section 10.B5 of this chapter, it is discussed in more detail in Chapter 9 of this book.

10.A2.3.1 Effect of oxygen

Apart from its effect on microorganisms, O_2 can promote oxidation of lipids, influence the colour of some food pigments, contribute to enzymic browning and promote off-flavours in some foods. It is important to note that the inclusion of O_2 in a modified atmosphere environment has the potential to have positive and or negative effects on product quality. The resultant effect is largely product dependent.

Lipid oxidation

Lipid or fat oxidation is often called oxidative rancidity and is promoted by O_2 . Oxidative rancidity is a major cause of food spoilage. The reaction of O_2 with unsaturated fatty acids in fat-containing foods is a major cause of deterioration of fats or fat-containing foods. Oxidation of unsaturated fat is referred to as autoxidation, since the rate of oxidation increases as the reaction proceeds. Hydroperoxides are the predominant initial reaction products of fatty acids with oxygen. Subsequent reactions control both the rate of reaction and the nature of the products formed. Some of these products, such as acids and aldehydes, are largely responsible for the off-flavour and off-odour characteristics of rancid foods. Removal of O_2 and its replacement with N_2 or CO_2 or mixtures thereof can inhibit the development of rancidity.

Pigment colour in meat

There are three major pigments in meat, oxymyoglobin, myoglobin and metmyoglobin. Consumers value the red colour (oxymyoglobin) of fresh meat as opposed to the purple colour of myoglobin. The colour cycle in fresh meat is reversible and dynamic, with the three pigments, oxymyoglobin (red), myoglobin (purple) and metmyoglobin (brown), being constantly formed and reformed. Brown metmyoglobin, the oxidised or ferric form of the pigment, cannot bind O_2 . The purple myoglobin, in the presence of O_2 , may be oxygenated to the bright red pigment oxymyoglobin, producing the familiar *bloom* of fresh meat, or it may be oxidised to metmyoglobin, producing the undesirable brown colour of less acceptable fresh meat. Whether the conversion of myoglobin to oxymyoglobin or metmyoglobin is favoured depends on O_2 concentration. Under low O_2 environments, the reduced myoglobin is oxidised

to the undesirable brown metmyoglobin pigment. Conversely, high O₂ environments favour the formation of oxymyoglobin.

The red colour of raw cured meat products is due to nitrosylmyoglobin, which is formed by the reaction of myoglobin with nitric oxide (NO). During heating, red nitrosylmyoglobin is converted to pink denatured nitrosohemochrome. The red/pink colours of raw and cooked cured meat products are unstable in air and in the light.

Oxygen and light cause the dissociation of NO from the cured meat pigments, resulting in brown/grey discoloration. Hence, MAP under low O₂ levels, and in opaque packages, greatly improves the desirable red/pink colour stability of cured meat products. The use of in-pack O₂ scavenging systems can reduce and maintain residual oxygen at a level that further extends the shelf life of cured meat products. The application of O₂ scavenging technology in food packaging is discussed in Chapter 9.

Photo-oxidation of chlorophyll

The green colour of chlorophyll changes to brown/grey when oxidised to pheophytin. This is undesirable, e.g. green pasta changing in colour to brown/grey. The photo-oxidation of chlorophyll and loss of desirable green colour can be significantly reduced by MAP under low O₂ levels and in opaque packages.

Oxidative off-flavours

Oxidative off-flavours and off-odours can be caused by numerous oxidative reactions in food and drink products. Oxidative warmed-over flavour is a characteristic off-flavour primarily associated with cooked meats and poultry. Commercially, this affects mainly the chilled ready meals and other cook-chill products. In cooked meats and poultry held at chilled storage temperatures, this stale, oxidised flavour may become apparent within a short time.

Meats, fish, poultry, liquid food, beverage and dairy products, for example, are highly susceptible to oxidative processes which can initiate a chain of reactions resulting in flavour impairment. This can occur relatively quickly. MAP under low O₂ levels can delay the onset of oxidative off-flavours.

10.A2.3.2 Effects of other MAP gases

Nitrogen is un-reactive and has no direct effect on the chemical and biochemical properties of foods. Because of the high solubility of CO₂ and its reaction with water to form carbonic acid, there is potential for some adverse effects on particular foods. These are probably due to the production of localised areas of low pH on or near the food surface. These effects if they do occur, and there is debate whether they occur in practice, may result in the loss of *bloom* in some meats for example. The mechanism is likely to be associated with pH-induced protein changes including denaturation and other changes in conformation,

resulting in atypical values for light absorption and reflection from the product surface. See also Section 10.B2 of this chapter.

Carbon monoxide can combine with myoglobin to form the bright red compound carboxymyoglobin that is similar in colour to oxymyoglobin. This compound is much more stable than oxymyoglobin and is one of the reasons why CO is toxic. CO also retards fat oxidation and the formation of metmyoglobin. For further discussion of meat pigments, refer to Section 10.B3 of this chapter. Currently, CO is not approved for use in MAP.

10.A2.4 Physical spoilage

Physical or physicochemical changes in food products can cause spoilage, thereby limiting the shelf life. For example, moisture loss in cut fresh vegetables causes wilting and reduction in textural crispness, moisture migration from the filling to the pastry of bakery products can cause a soggy/sticky consistency and syneresis of dairy products results in an undesirable and unsightly separated aqueous layer. Also, some food products are sensitive to chilled temperatures. For example, certain whole tropical fruits are susceptible to chilling injury when exposed to temperatures in the range 0–10°C. Chilling injury causes loss of quality through poor ripening, pitting of the epidermal cells, rotting and development of off-flavours. With the exception of preventing moisture loss and moisture uptake, MAP does not generally directly affect physical spoilage.

10.A3 Packaging materials

Selection of the most appropriate packaging materials is essential to maintain the quality and safety of MAP foods. Flexible and semi-rigid plastics and plastic laminates are the most common materials used for MAP foods. Plastic materials account for approximately one-third of the total materials demand for food packaging applications, and their use is forecast to grow.

Relative ease of forming, light weight, good clarity, heat sealing and strength are some of the properties of plastics that make them suitable as food packaging materials. Advances in polymer processing have enabled the development of plastics that are better suited to particular food packaging applications. However, no single plastic possesses the properties that make it suited to all food packaging applications.

Plastic packaging materials may consist of a monolayer formed from a single plastic, but most, if not all, MAP films are multilayer structures formed from several layers of different plastics. Using coextrusion, lamination or coating technologies, it is possible to combine different types of plastic to form films, sheets or rigid packs. By carefully selecting each component plastic, it is

possible to design a material which possesses the key properties of packaging importance to best match the requirements of the product/package system.

Plastics packaging for MAP applications is most commonly found in the form of flexible films for bags, pouches, pillow packs and top webs or as rigid and semi-rigid structures for base trays, dishes, cups and tubs. Commonly used plastic flexible laminates are produced from polyethylene (PE), polypropylene (PP), polyamide (nylons), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyvinylidene chloride (PVdC) and ethylene vinyl alcohol (EVOH). Rigid and semi-rigid structures are commonly produced from PP, PET, unplasticised PVC and expanded polystyrene.

10.A3.1 Main plastics used in MAP

The following section provides a brief overview of the commonly used plastics for MAP applications. More information on these including properties of packaging importance, definitions and terminology can be found in Chapter 7.

10.A3.1.1 Ethylene vinyl alcohol (EVOH)

Polyvinyl alcohol (PVOH) is an excellent gas barrier provided it is dry. In the presence of moisture, PVOH absorbs water, causing the plastic to swell and become plasticised. In this condition, the gas barrier properties of PVOH are greatly reduced. In order to provide greater polymer stability for commercial use, PVOH is copolymerised with ethylene to produce EVOH. The gas barrier properties of EVOH are less than those of PVOH when dry, but EVOH is less sensitive to the presence of moisture, and therefore, it is widely used as a gas barrier layer in MAP applications. This material has good processing properties and is therefore suitable for conversion into plastic films and structures. EVOH is always found laminated as a thin film, usually in the order of 5 μm thickness, sandwiched between hydrophobic polymers, e.g. PE or PP, that protect the polymer from moisture. EVOH also possesses high mechanical strength, high resistance to oils and organic solvents and high thermal stability.

10.A3.1.2 Polyethylenes (PE)

The polyethylenes are structurally the simplest group of synthetic polymers and the most commonly used plastic materials for packaging applications. There are several types of PE classified on the basis of density. All are composed of a carbon backbone with a degree of side chain branching which influences density. Low density polyethylene (LDPE) (density, 0.910–0.925 g cm^{-3}) is generally used in film form, whereas high density polyethylene (HDPE) (density, 0.940 g cm^{-3}) is commonly used for rigid and semi-rigid structures. PE are characterised as poor gas barriers, but their hydrophobic nature makes them very good barriers to water vapour. Therefore, by itself, PE cannot be

used as a packaging material in MAP applications that require a high barrier to gases. PE melts at a relatively low temperature ranging from approximately 100–120°C (dependent on density and crystallinity). A less branched variant called linear low density polyethylene (LLDPE) which offers good heat sealing properties is used as a sealant layer to impart heat sealing properties on base trays and lidding films.

Modified PE-based materials that contain interchain ionic bonding are called ionomers. These have enhanced heat sealing properties that enable them to seal more effectively through meat juices, fats and powders. Ionomers also form effective heat seals with aluminium. *Suryln* is Dupont's trade name for its range of ionomer materials. A copolymer of ethylene and vinyl acetate, ethylene vinylacetate (EVA), offers enhanced heat sealing properties over LDPE and is found as a heat seal layer in some MAP applications.

10.A3.1.3 Polyamides (PA)

Polyamides comprise the group of plastics commonly referred to as nylons which have widespread application in food packaging. Nylons generally have high tensile strength, good puncture and abrasion resistance and good gas barrier properties. Nylons are generally moisture sensitive (hydrophilic) and will absorb water from their environment. Moisture in the nylon structure interferes with interchain bonding and adversely affects their properties, including gas barrier. Under conditions of high relative humidity, the gas transmission rate of nylon films generally increases. However, there are commercial nylons that are less affected by moisture. Their relatively high strength and toughness make them ideal as vacuum pouches for fresh meat, where hard bone ends could puncture other plastic materials. In this application, nylon is generally laminated to PE which provides the heat sealing properties.

10.A3.1.4 Polyethylene terephthalate (PET)

Polyethylene terephthalate is the most common polyester used in food packaging applications. PET is a good gas and water vapour barrier, is strong, offers good clarity and is temperature resistant. Crystalline PET (CPET) has poorer optical properties but improved heat resistance melting at temperatures in excess of 270°C. Flexible PET film is used for barrier pouches and top webs as a lidding material for tray packs. CPET is used for dual ovenable pre-formed base trays where its high temperature resistance makes it an ideal container for microwave and convection oven cooking of food.

10.A3.1.5 Polypropylene (PP)

Polypropylene is a versatile polymer that has applications in flexible, rigid and semirigid packaging structures. MAP applications are generally for rigid base trays. PP is a good water vapour barrier but a poor gas barrier. Increasing the thickness of the material somewhat compensates for the high gas transmission

rate. PP melts at approximately 170°C. It can therefore be used as a container for microwaving low-fat food products. It should not be used for microwaving fatty foods, where temperatures in excess of its melting point could be reached. Foamed PP is used to provide the structural properties in laminates for MAP thermoformed base trays, where it is combined with an EVOH barrier and a PE heat sealing layer.

10.A3.1.6 *Polystyrene (PS)*

Pure polystyrene is a stiff, brittle material and has limited use in MAP applications. Expanded PS (EPS) which is formed from low density blown particles has been used for many years as a base tray for overwrapped fresh meat, fish and poultry products. Foamed PS has recently been used as a structural layer for pre-formed MAP base tray applications. The high gas permeability of foamed PS requires the material to be laminated to a plastic such as EVOH that provides the required gas barrier properties.

10.A3.1.7 *Polyvinyl chloride (PVC)*

Polyvinyl chloride has a relatively low softening temperature and good processing properties and is therefore an ideal material for producing thermoformed packaging structures. Although a poor gas barrier in its plasticised form, unplasticised PVC has improved gas and water vapour barrier properties which can at best be described as moderate. Oil and grease resistance are excellent, but PVC can be softened by certain organic solvents. It is a common structural material in MAP thermoformed base trays, where it is laminated to PE to provide the required heat sealing properties.

10.A3.1.8 *Polyvinylidene chloride (PVdC)*

Polyvinylidene chloride (a copolymer of vinyl chloride and vinylidene chloride) possesses excellent gas, water vapour and odour barrier properties, with good resistance to oil, grease and organic solvents. Unlike EVOH, the gas barrier properties of PVdC are not significantly affected by the presence of moisture. PVdC effectively heat seals to itself and to other materials. The high temperature resistance enables uses in packs for hot filling and sterilisation processes. Homopolymers and copolymers of PVdC are some of the best commercially available barriers for food packaging applications.

The above provides a brief introduction to the main plastic materials used in MAP applications. These and other plastics are covered in more detail in Chapter 7. It should be noted that certain desired properties can be enhanced by further processing the material. For example, coating a plastic with aluminium (metallisation) can improve the gas and vapour barrier properties and enhance the visual appearance of the material. PP is commonly metallised by passing the film through a *mist* of vapourised aluminium under vacuum. Similar treatments to improve gas and vapour barrier properties include

Table 10.3 Typical plastic-based packaging structures for MAP applications

Material	Application
UPVC/PE	Thermoformed base tray
PET/PE	Thermoformed base tray
XPP/EVOH/PE	Thermoformed base tray
PS/EVOH/PE	Thermoformed base tray
PET/EVOH/PE	Thermoformed base tray
PVdC coated PP/PE	Lidding film
PVdC coated PET/PE	Lidding film
PA/PE	Lidding film
PA/PE	Flow wrap film
PA/ionomer	Flow wrap film
PA/EVOH/PE	Flow wrap film
PET	Pre-formed base tray
PP	Pre-formed base tray
UPVC/PE	Pre-formed base tray

application of a silicon oxide (SiO_x) coating (also referred to as glass coating) to PET film and a diamond-like-carbon (DLC) coating to PET. The former has been used for MAP lidding film, with the advantages of providing excellent and stable barrier properties which are less influenced by the effects of temperature and humidity. To date, the main application of the latter has focused on non-MAP applications including a barrier coating on PET beverage bottles. Examples of MAP plastic structures are shown in Table 10.3.

10.A3.2 Selection of plastic packaging materials

Several factors must be considered when selecting package materials for MAP applications.

10.A3.2.1 Food contact approval

Packaging materials in contact with food must not transfer components from the packaging to the food product in amounts that could harm the consumer. In Europe, all food contact packaging must comply with EC Directives which are derived from the framework directive 89/109/EEC and which includes the plastics directive 90/128/EEC. Suppliers must provide evidence to demonstrate that migrant levels from plastics packaging into foods are below the recommended levels and that plastic packaging is safe in its intended use.

10.A3.2.2 Gas and vapour barrier properties

Packaging materials for MAP must have the required degree of gas and vapour barrier for the particular food application. Whereas some materials such as glass and metals (provided they are of sufficient thickness and possess no pores or other imperfections) are a total barrier to gases and vapours, plastic materials are permeable to varying degrees to gases and vapours. These molecules are

transported across a plastic package material by a mass transfer process called permeation. Permeation is defined as ‘the diffusional molecular exchange of gases, vapours or liquid permeants across a plastic material which is devoid of imperfections such as cracks and perforations’ (Hernandez, 1996). Essentially, the gas molecules sorb into one surface of the plastic, are transported through the material by a process of diffusion and desorb on the opposite surface. This process is shown diagrammatically in Figure 10.1.

The driving force for gas permeation through a polymer film is the difference in gas concentration between each side of the film. A concentration gradient drives a flow of permeant molecules from the high concentration side to the low concentration side of the film. In MAP, a gas concentration gradient exists between the pack headspace and the surrounding environment. In order to maintain the gas composition within the pack, the packaging material must be impermeable (a barrier) to gases.

Transmission rate is a measure of the gas or water vapour barrier of a packaging material. The transmission rate T is defined as the quantity Q of gas (or other permeant) passing through a material of area A in time t .

$$T = \frac{Q}{At}$$

Commonly used units for transmission rate are $\text{cm}^3 \text{m}^{-2} \text{day}^{-1}$ (for gases) and $\text{g m}^{-2} \text{day}^{-1}$ (for vapours including water vapour).

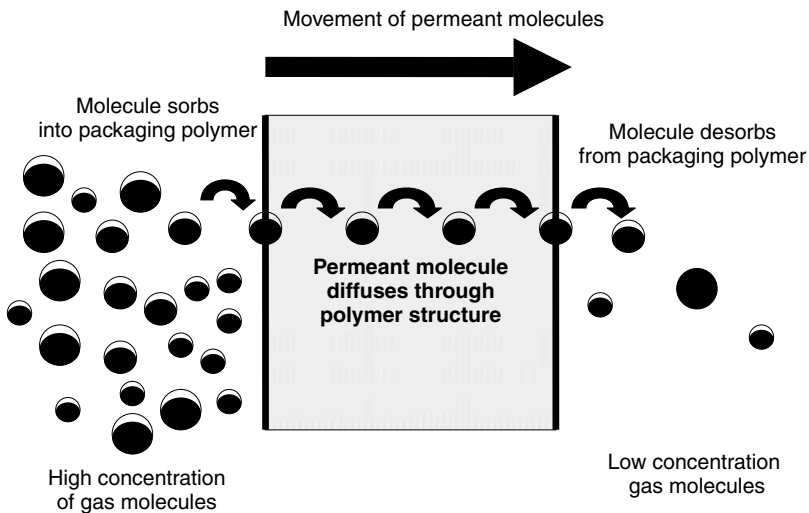


Figure 10.1 Permeability model for gases and vapours permeating through a plastic packaging film.

It is essential for packaging technologists to have details of the gas and vapour transmission rates for materials to be used for MAP. Such data should be available on the packaging specification. The lower the transmission rate value, the better the gas barrier properties of the material. Temperature has an effect on the permeability of gases and vapours and therefore should be quoted with transmission rate values on packaging specifications. Increasing temperature increases gas transmission rate across all common plastic packaging materials. The effect of temperature on the CO₂ transmission rate for a PET film is shown in Figure 10.2.

The driving force for gas transmission through a plastic film is the partial pressure difference of the gas between both sides of the material, and therefore, the gas concentration difference at the time of measurement should be quoted with the transmission rate value. Relative humidity (RH) is the driving force for water vapour transmission rate (WVTR), and therefore, WVTR values increase with increasing RH. Therefore, RH should always be quoted with WVTR values. RH can also influence the gas transmission rates of hydrophilic plastics and therefore should be quoted with gas transmission rate values (although generally gas transmission rates are measured at 0% RH). Gas transmission rates for some common food packaging plastics are summarised in Table 7.2.

Material thickness and gas concentration will affect the transmission rate. Therefore, the permeability coefficient, which compensates for material thickness and driving force, is used to compare gas barrier properties of different materials. The permeability coefficient P is defined as the quantity Q of gas under stated conditions permeating through a material of thickness l and area A , in time t , and under a partial pressure difference of Δp .

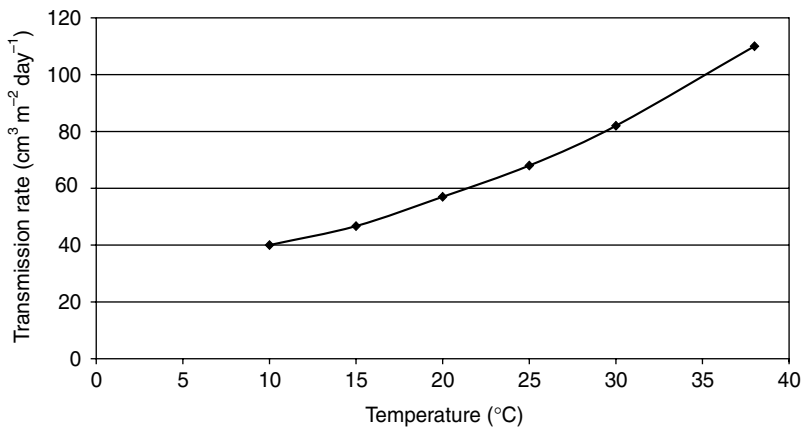


Figure 10.2 The effect of temperature on the transmission rate of CO₂ in 25 μ PET film measured at 0% RH and 100% CO₂.

$$P = \frac{QI}{At\Delta_p}$$

The SI units for P are $m^3 m^{-2} s^{-1} Pa^{-1}$.

The barrier properties are primarily dependent on the type of plastic, the permeant gas or vapour and its partial pressure difference across the material and the temperature. As a general rule, the permeability of a synthetic polymer to CO_2 is approximately three to five times higher than the permeability to O_2 . No single commercially available plastic provides a total barrier to gases and vapours, and therefore, the materials are selected on the basis of product type, desired shelf life, gas composition, availability and cost.

10.A3.2.3 Optical properties

Good optical properties, such as high gloss and transparency, are essential for bag, pouch and top web materials to satisfy consumer demand for a clear view of the product. To provide attractive appearance and shelf impact, some base tray materials are available in various colours. This also enhances the visual appeal of the product against the tray and helps consumers to identify product ranges and brands on the supermarket shelf. PET, PP and EPS trays are supplied in a range of colours. PVC trays are generally used in their natural form to provide a transparent pack.

10.A3.2.4 Antifogging properties

Condensation (fogging) of water vapour on the inner surface of food packs can occur when the temperature of the pack environment is reduced, resulting in a temperature differential between the pack contents and the packaging material. Fogging of the inner surface of lidding film is a result of light scattering by the small droplets of condensed moisture that leads to poor product visibility and an aesthetically displeasing appearance of the pack. This can be overcome by applying antifogging agents to the plastic heat sealing layer, either as an internal additive or as an external coating. These chemicals decrease the surface energy of the packaging film which enables moisture to spread as a thin film across the under surface of the pack rather than collecting as visible droplets. Antifogging agents include fatty acid esters. Most lidding materials are available with antifog properties, and commonly treated plastics include LDPE, LLDPE, EVA and PET.

10.A3.2.5 Mechanical properties

Resistance to tearing and puncture and good machine handling characteristics are important in optimising the packaging operation and maintaining pack integrity during forming and subsequent handling and distribution. A further important characteristic of laminates and co-extruded films and sheets is the ability of layers to bond effectively together during the packaging operation

and during subsequent storage and handling. Certain organic compounds may have an adverse effect on bond strength to the extent that weakened bonds can result in layers peeling apart.

10.A3.2.6 Heat sealing properties

Effective heat seals are essential for maintaining the desired gas composition within the pack. The ability to form effective heat seals through contamination such as meat juices, powders, fats and oils is an advantage in many applications. Heat seal quality is dependent on many factors including seal material, seal width and machine settings such as temperature, pressure and dwell time.

10.A4 Modified atmosphere packaging machines

The function of MAP machines is to retain the product on a thermoformed or pre-formed base tray, or within a flexible pouch or bag, modify the atmosphere, apply a top web if required, seal the pack and cut and remove waste trim to produce the final pack. Pack format, presentation and machine performance and versatility and pack costs are essential factors for the packer filler to consider before selecting a machine for a particular product application. The following section provides an overview of the types and operation of MAP machines.

10.A4.1 Chamber machines

For low production throughput, chamber machines are sufficient. These are generally used with pre-formed pouches, though tray machines are available. The filled pack is loaded into the machine, the chamber closes, a vacuum is pulled on the pack and back flushed with the modified atmosphere. Heated sealing bars seal the pack, the chamber opens, packs are removed and the cycle continues. These machines are generally labour intensive and cheap, with a simple operation but are relatively slow. Some chamber machines can handle large packages and are suitable for bulk packs.

10.A4.2 Snorkel machines

Snorkel machines operate without a chamber and use pre-formed bags or pouches. The bags are filled and positioned in the machine. The snorkel is introduced into the bag, draws a vacuum and introduces the modified atmosphere. The snorkels withdraw and the bag is heat sealed. Bag in-box bulk products and retail packs in large MAP master packs can be produced on these machines.

10.A4.3 *Form-fill-seal tray machines*

Form-fill-seal (FFS) machines form pouches from a continuous sheet of roll stock (flow wrap), or form flexible or semirigid tray systems comprising a thermoformed tray with a heat sealed lid. FFS machines may be orientated in a vertical plane or a horizontal plane. Flow wrapping machines are available in both vertical and horizontal formats. The type of format is dependent on the nature of the food product being packed. FFS machines using pre-formed trays or producing thermoformed trays are almost exclusively horizontal machines. This section focuses on horizontal form-fill-seal MAP machines which are used extensively in the food industry.

Thermoformed form-fill-seal tray machines use rollstock film for base web and lidding material. Base film is carried through the machine by clamps which attach onto the edge of the web and carry it through the forming, filling, evacuation, gas modification, sealing, cutting and discharge stages.

Base trays are produced by applying heat to the base roll stock, which when softened is immediately moulded into the desired shape and size. Forming of the heated, softened sheet can be achieved by applying a vacuum, air pressure, mechanical drawing or a combination of these processes. The softened heated film is normally drawn into the forming mould under the assistance of vacuum applied through evacuation holes located along the base edges and corners of the mould. This process produces a more defined and uniform tray shape. Where deep trays are required, a more uniform distribution of plastic can be achieved by prestretching the film using mechanical devices (plugs) which prevent excessive thinning of the container walls at the base edges and corners.

The tooling for the moulds represents a significant initial capital cost of thermoformed form-fill-seal tray machines. Moulds are generally fabricated from either steel or aluminium, the latter being cheaper but less durable than the former. Inserts, called filler plates, can be placed on the base of the die to decrease the forming depth and therefore produce shallow trays. Roll stock for base tray and lidding is supplied in reels of film wound on to a core of standard diameter (usually 3 or 6") which matches the film unwind system on the thermoforming machine. Reel diameters are usually supplied from 300 mm to 1000 mm, in increments of 50 mm.

Thermoformed trays are produced by one of the three following methods.

10.A4.3.1 *Negative forming*

Negative forming is suitable for flexible films but has limitations with rigid materials, unless the cavity shape is shallow with well-rounded corners. It comprises a two-stage cycle:

1. compressed air blows film up against a heating plate which softens the film
2. the softened film is blown down by compressed air through the heating plate into a mould (Fig. 10.3).

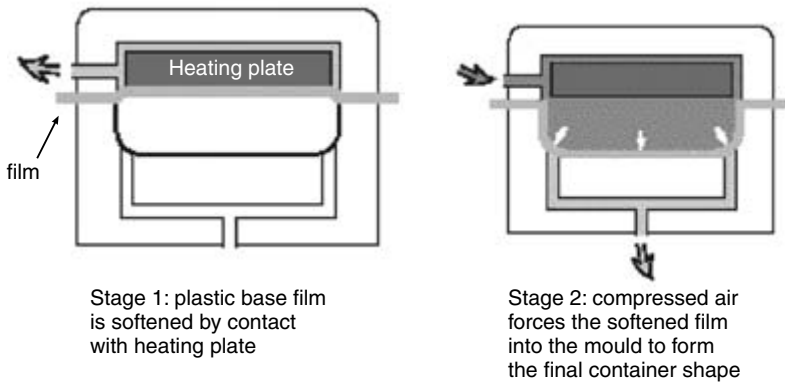


Figure 10.3 Thermoformed base tray produced by the negative forming method (courtesy of Multivac).

10.A4.3.2 Negative forming with plug assistance

Plug-assisted negative forming is used when deep or complex tray shapes are required. The plug prestretches the film to produce improved distribution of the softened plastic. This is essential to ensure tray corners have a sufficient thickness of material in order to prevent pinholes from forming or material becoming damaged during handling. This method can be used for flexible and rigid materials. It comprises a three-stage process:

1. film is softened between heated plates. Preheating can occur in one or several stages
2. plug descends and stretches the film
3. final shaping stage occurs by compressed air which pushes the film into the mould (Fig. 10.4).

10.A4.3.3 Positive forming with plug assistance

Plug-assisted positive forming is used for shaping rigid trays, where a more controlled distribution of film material is necessary to maintain the material thickness at the base and corners of the tray. It comprises three stages:

1. the film is heated between temperature-regulated plates
2. a vacuum produced at the base of the mould prestretches the film
3. the positive plug descends, and the film is blown up to it by compressed air. The plug forms the shape of the tray (Fig. 10.5).

Following the forming stage, the base tray advances to the filling station, where it is manually or automatically loaded with the food product. The pack then advances to the gassing station where the modified atmosphere is introduced and the top web heat sealed to the base tray. The sealed trays are labelled, coded and separated as necessary.

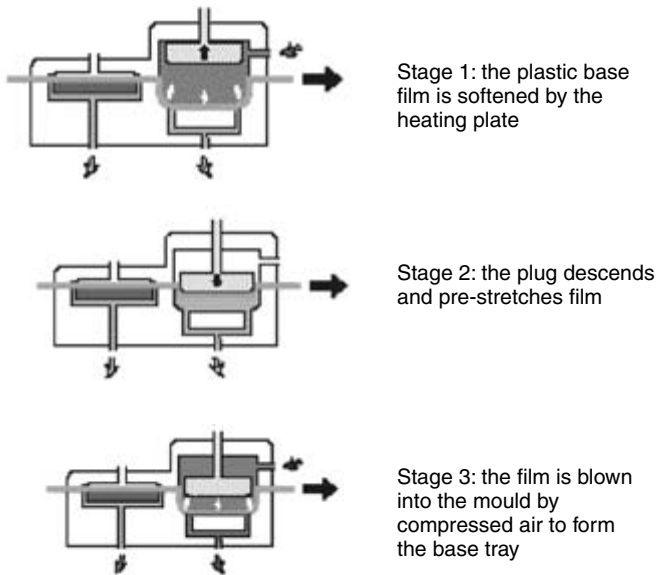


Figure 10.4 Thermoformed base tray produced by the plug assisted negative forming method (courtesy of Multivac).

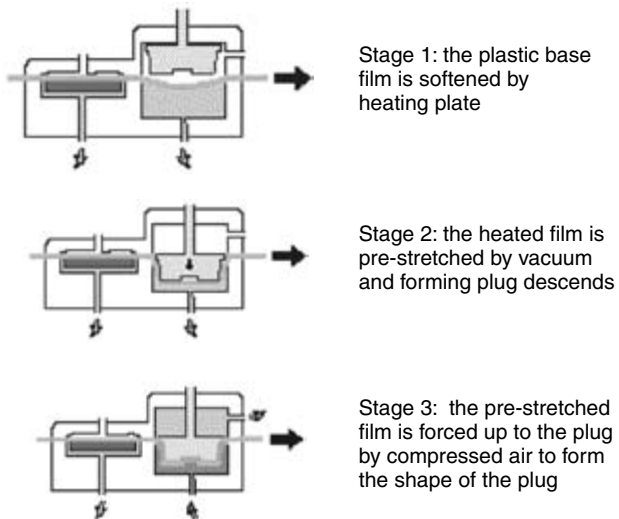


Figure 10.5 Thermoformed tray produced by plug assisted positive forming (courtesy of Multivac).

10.A4.4 Pre-formed trays

The alternative to thermoforming the base tray is to use pre-formed trays. These are loaded manually or automatically by a tray denester into the machine infeed and pass through the filling, gas flushing and sealing stages as would a thermoformed base tray. Examples of pre-formed trays are shown in Figure 10.6.

10.A4.4.1 Pre-formed trays versus thermoformed trays

Pre-formed trays have several advantages compared to thermoformed trays:

- Pre-formed trays offer more flexibility in tray design. A greater range of intricately shaped pre-formed trays are available than is currently possible to produce on thermoform machines.
- Pre-formed trays can offer enhanced appearance and presentation at point of sale.
- A greater range of tray materials can be used for pre-formed tray manufacture than would be possible with thermoform machines.
- Trays of the same shape but different colour or depth can be handled with no changeover.



Figure 10.6 Examples of plastic pre-formed trays for MAP foods.

- Greater flexibility in tray loading is possible with pre-formed trays. This operation can take place before packing and in an area separate from the packing operation.
- Generally, pre-formed trays require less downtime for changeover between different tray sizes compared to thermoform-fill-seal machines. A tooling set comprising the sealing die, frame carriages and cutting die has to be changed when a tray of different outer dimensions is used.

Thermoformed trays have the main advantage of lower packaging material costs. It is estimated that tray pack savings of between 30 and 50% are achievable mainly because costs of the thermoforming process are carried by the filler packer rather than the tray supplier. Transportation and storage costs will be higher for pre-formed trays compared to the roll stock equivalent for thermoformed trays.

10.A4.5 Modification of the pack atmosphere

MAP machines use mainly one of the two techniques to modify the pack atmosphere.

10.A4.5.1 Gas flushing

This method employs a continuous gas stream that flushes air out from the package prior to sealing. This method is less effective at flushing air out of the pack, and this results in residual oxygen levels of 2–5%. Gas flushing is therefore not suited for oxygen-sensitive food products. Generally, gas flushing machines have a simple and rapid operation and therefore a high packing rate.

10.A4.5.2 Compensated vacuum gas flushing

This method uses a two-stage process:

1. *The evacuation stage* – a vacuum is pulled on the pack to remove air. Generally, it is not possible to achieve a full vacuum, since reduced pressures will result in water to boil, at which point the vacuum cannot be improved. The vacuum achieved is generally between 5 and 10 Torr (1 Torr = 1 mmHg). As a general rule, the cooler and drier the food, the lower the achievable vacuum.
2. *Gas flushing stage* – the pack is flushed with the modified gas mix. The evacuation of air from the pack results in lower residual oxygen levels than that achieved by gas flushing, and therefore this method is better suited for packing oxygen-sensitive products.

The two-stage process employed by the compensated vacuum method results in a lower packaging rate than that possible with gas flushing.

10.A4.6 Sealing

An effective heat seal is critical to maintaining the quality and safety of the packaged product. Film factors (thickness and surface treatments) and plastic composition (resin type, molecular weight distribution and presence of additives) will determine the machine settings for the sealing operation. The correct combination of time, temperature and pressure of the seal bars is necessary to produce a good seal. Insufficient dwell time or temperature can result in ineffective seals that separate at the bond interface. Excessive dwell time or temperature can result in weakness adjacent to the seal area.

10.A4.7 Cutting

Packs are discharged as a continuous arrangement of filled and sealed packs from a thermoform-fill-seal machine, and therefore, the final operation is to separate into individual packs. This can be carried out by two methods – die cutting and longitudinal and transverse cutting.

Die cutting is achieved in one operation. A shaped blade is forced through the film which is clamped in place by a frame assembly. Transverse cutting separates packs into rows and is carried out by guillotines or punches which are driven through the film that is supported by anvils. This may be carried out in conjunction with longitudinal cutting where circular knives cut through the tray flanges parallel to the length of the film.

Regardless of the cutting method, it is important to ensure that an even flange remains around the lip of the tray in order to maximise the seal strength. Offset cutting could leave one side of the tray with a thin flange that may open during handling and distribution. Waste trim is either wound onto spindles at the machine discharge or removed by suction into collection bins.

Figures 10.7–10.11 show some of the above operations in a Multivac R230 thermoforming machine.

10.A4.8 Additional operations

Machines are generally integrated into production lines and combined with operations such as automatic filling, top web labelling, base web labelling, registration of printed top web, over printing and pack collation and case loading.

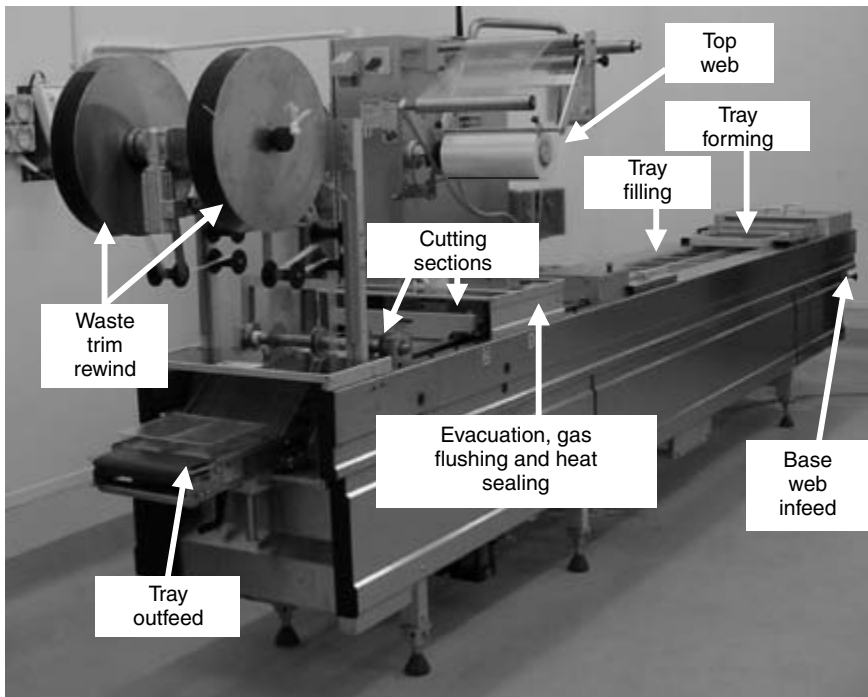


Figure 10.7 Multivac R230 thermoform fill seal machine.

10.A5 Quality assurance of MAP

Examples of instruments used in quality assurance of MAP are discussed in this section. These are provided by way of example and are not intended to be recommendations by the authors.

10.A5.1 Heat seal integrity

The majority of MAP form-fill-seal retail packs are heat sealed. The quality and safety of MAP food will be compromised if the seal integrity is lost during the required life of the pack. A breach of the heat seal will result in a rapid loss of the modified atmosphere in the pack. Therefore, the sealing operation constitutes a critical control point and must be monitored during production as part of the quality assurance procedure. It is of key importance that sealing bar temperature, pressure and dwell time are set according to machine manufacturer and packaging supplier specifications and conditions are monitored during machine operation.



Figure 10.8 Lower web unwind and infeed section on the Multivac R230.

Seal and pack integrity can be assessed by either destructive or nondestructive tests. Destructive tests are based on immersing packs in water and checking for escaping gas bubbles from around the seal. Other test methods measure seal strength by pressurising packs using compressed air until the seal fails. Non-destructive tests are based on measuring changes in pressure generated by packs under vacuum in sealed chambers. Some examples of seal integrity equipment are discussed below.

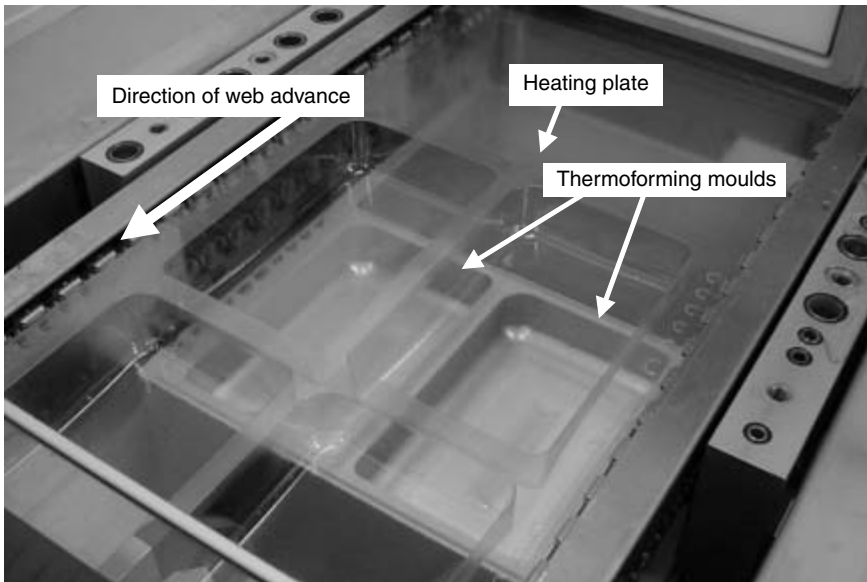


Figure 10.9 Base web thermoforming section on the Multivac R230.

10.A5.1.1 Nondestructive pack testing equipment

Ai Qualitech manufactures a range of vacuum leak testers (Q700 series) designed for the use in production or laboratory environments for MAP tray packs, pouches and pillow packs. When the vacuum is pulled, the pack expands, causing the top web to dome. A pressure sensor in contact with the top of the pack will detect pressure drop due to a leaking pack. Ease of use and objective and quantifiable measurement are possible benefits. The instrument can be supplied with pick and place equipment to enable online automatic operation. The instrument is capable of detecting holes of 10 μm or greater.

10.A5.1.2 Destructive pack testing equipment

An example of equipment which measures the heat seal strength of complete packs is LIPPKE 2500 SL Package Test System. The equipment can be used to measure seal rupture and also pack atmosphere leakage through pinholes or faulty seals. In the leak test mode, the pack is pressurised to a predetermined maximum and internal pack pressure monitored. Leaks are evident as a decrease in pack pressure. In the seal strength mode, a linear pressure increase is applied internally in the package. The pressure achieved at burst indicates the strength of the seal. Needle probe minimum penetration is 1 mm, which makes this instrument suitable for most types of pack.

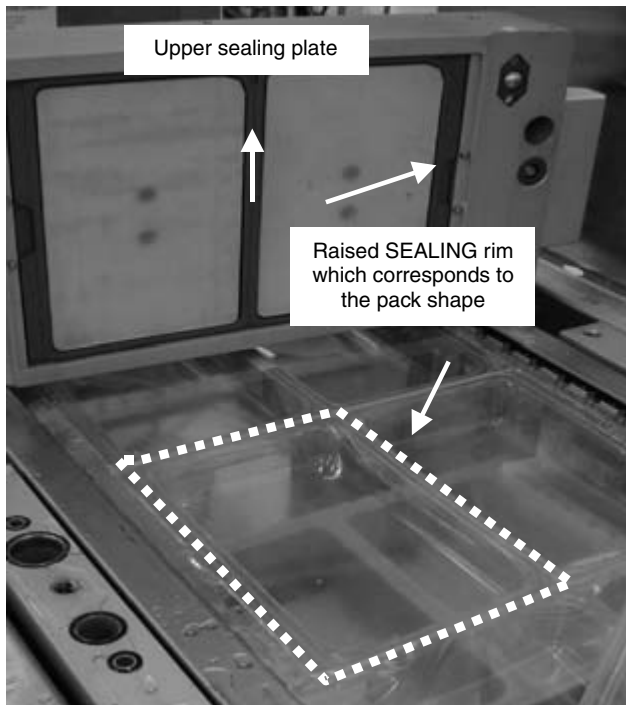


Figure 10.10 Top web heat sealing on the Multivac R230.

10.A5.2 *Measurement of transmission rate and permeability in packaging films*

Accurate determination of the oxygen, CO₂ and water vapour permeabilities of plastic-based film is important for MAP applications. Several methods exist for measuring transmission rate and permeability of gases and vapours across a packaging film. The most common test procedure is based on the isostatic method. In this method, both sides of the test film are maintained at the same total pressure but a constant partial pressure difference is maintained by passing test gas continuously on one side of the film while inert carrier gas continuously removes permeant from the other side of the film. This maintains a very low partial pressure of permeated test gas and establishes a constant gas concentration difference across the film. This is also referred to as the *concentration increase* method.

10.A5.2.1 *Water vapour transmission rate and measurement*

Water vapour transmission rate is defined as the time rate of water vapour flow, normal to the two surfaces, under steady-state conditions through unit

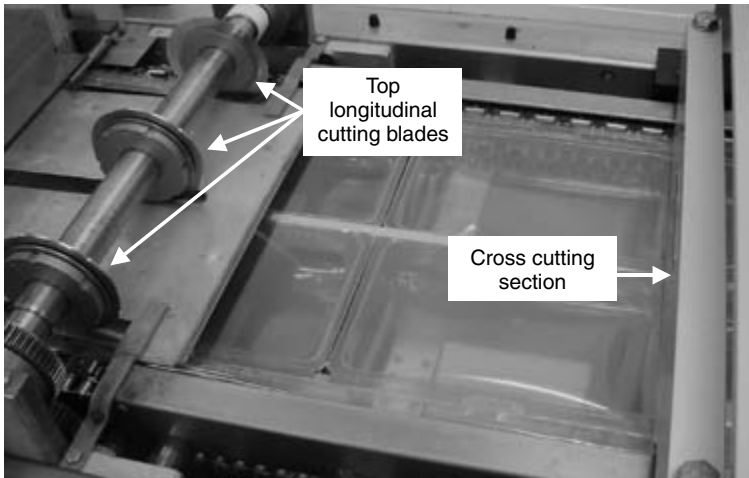


Figure 10.11 Cutting section on the Multivac R230.

area of a test film. There are several methods for measuring WVTR and water vapour permeability. Earlier methods were based on ASTM E96: Standard Test Methods for Water Vapor Transmission of Materials. This gravimetric procedure measured the weight increase by a desiccant sealed in an aluminium cup by the test film, with the apparatus being held in an environment of known and controlled temperature and RH. The weight increase of the dish occurs as a result of moisture uptake by the desiccant and is due to the water permeating through the test film from the surrounding environment into the sealed cup. The corresponding WVTR could be calculated from the weight increase. For high-barrier films, the test can take several days, if not weeks.

In 1990, ASTM introduced a test standard (ASTM F 1249: Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor) based on the isostatic method and employing solid-state electronics with pulse-modulated infrared sensors which can detect water vapour from 1 part per million. MOCON (Modern Controls Inc.) supply equipment to measure WVTR based on this standard. Test temperatures can be controlled from 10 to 40°C ($\pm 0.5^\circ\text{C}$) and RH from 35 to 90% RH ($\pm 3\%$). The instrument can test at 100% RH by inserting water-saturated sponges in the test cell.

Water vapour permeating across the test film is transported by dry N_2 gas to an infrared detection system intended for operation over a 5–50°C temperature range. The infrared photodetector produces a low-level electrical signal in response to the change in transmitted infrared radiation. The amplifier produces a filtered DC signal in direct proportion to the water vapour in the test cell and therefore proportional to the water vapour transmission of the test film. The WVTR of high-barrier materials can be determined within 2 days. Test measurements are reported in the units: $\text{g m}^2 \text{day}^{-1}$.

10.A5.2.2 Measurement of oxygen transmission rate

Oxygen transmission rate is defined as the time rate of gaseous oxygen flow, normal to the two film surfaces, under steady-state conditions through a unit area of a test film material.

MOCON Oxtran (Modern Controls, Inc.) measures the transmission rate of oxygen across flat films by a method based on the isostatic procedure. A coulometric sensor detects permeated oxygen and provides parts per billion sensitivity.

10.A5.2.3 Measurement of carbon dioxide transmission rate

The PERMATRAN C-IV, manufactured and marketed by MOCON (Modern Controls, Inc.), is an instrument for measuring the rate at which gaseous CO₂ diffuses through a flat film. Test films are clamped in a diffusion cell, and one half of the cell is flushed continuously with CO₂ gas. Permeated gas is carried to an infrared sensor where a response is generated proportional to the amount of CO₂ present. In cases where the test film offers a very low barrier to CO₂, the test film may be mounted on an aluminium foil mask to reduce the test surface area from 50 to 5 cm².

10.A5.3 Determination of headspace gas composition

10.A5.3.1 Oxygen determination

Oxygen promotes many food spoilage reactions as discussed in Section 10.A 2.3. Certain foods can be damaged by exposure to oxygen concentrations of 1–2%. The level of residual oxygen in the pack headspace is therefore of concern to food processors and forms part of the quality procedures for the manufacture and packing of oxygen-sensitive products. An example of the type of equipment which measures the concentration of headspace oxygen is the TORAY LC 750F Oxygen headspace analyser. This instrument determines residual oxygen by probing and sampling headspace gases in MAP packs and is suitable for production and laboratory use, with a response time of approximately 2 s.

10.A5.3.2 Carbon dioxide determination

Similar in operation to the TORAY LC 750F, the TORAY PG100 Carbon dioxide headspace analyser measures CO₂ in flexible, semi-rigid and rigid packages.

SECTION B MAIN FOOD TYPES

10.B1 Raw red meat

Microbial growth and oxidation of the red oxymyoglobin pigment are the main spoilage mechanisms that limit the shelf life of raw red meats. The packaging

technologist has to maintain the desirable red colour of the oxymyoglobin pigment, by having an appropriate O₂ concentration in the pack atmosphere, and at the same time minimise the growth of aerobic microorganisms. Highly pigmented red meats, such as venison and wild boar, require higher concentrations of O₂.

Aerobic spoilage bacteria, such as *Pseudomonas* species, normally constitute the major flora on red meats. Since these bacteria are inhibited by CO₂, it is possible to achieve both red colour stability and microbial inhibition by using gas mixtures containing 20–30% CO₂ and 70–80% O₂. These mixtures can extend the chilled shelf life of red meats from 2–4 days to 5–8 days. A gas/product ratio of 2:1 is recommended.

Red meats provide an ideal medium for the growth of a wide range of spoilage and food poisoning microorganisms including *E. coli*. Because raw red meats are cooked before consumption, the risk of food poisoning can be greatly reduced by proper cooking. The maintenance of recommended chilled temperatures and good hygiene and handling practices throughout the butchery, MAP, distribution and retailing chain is of critical importance in ensuring both the safety and extended shelf life of red meat products.

10.B2 Raw poultry

Microbial growth, particularly growth of *Pseudomonas* and *Achromobacter* species, is the major factor limiting the shelf life of raw poultry. These Gram-negative aerobic spoilage bacteria are effectively inhibited by CO₂. Consequently, the inclusion of CO₂ in MAP at a concentration in excess of 20% can significantly extend the shelf life of raw poultry products. CO₂ concentrations higher than 35% in the gas mixture of retail packs are not recommended because of the risks of pack collapse and excessive drip. Nitrogen is used as an inert filler gas, and a gas/product ratio of 2:1 is recommended. Since pack collapse is not a problem for bulk MAP master packs, gas atmospheres of 100% CO₂ are frequently used.

Since poultry meat provides a good medium for the growth of pathogenic microorganisms, including some that are not inhibited by CO₂, it is critical that recommended chilled temperatures and good hygiene and handling practices throughout the supply chain are adhered to and that products are properly cooked prior to consumption.

Early research into gas mixes for MAP of poultry meat reported discolouration of the meat at CO₂ concentrations higher than 25%. Even at 15%, the authors sometimes observed a loss of *bloom* (Ogilvy & Ayres, 1951). This research is at variance with the lack of problems reported from the commercial use of relatively high levels of CO₂ with meat products, with up to 100% in some products. Gas compositions of 25–50% CO₂ and 50–75% N₂ are used routinely.

It would appear that the problems that have been occasionally encountered with high levels of CO₂, e.g. development of greyish tinges on meat, may simply be due to high residual levels of O₂ rather than the concentration of CO₂ (Gill, 1990).

It is recommended that research into the optimal gas composition and package type and size should be conducted for individual food products. Furthermore, headspace gas composition will change during storage due to microbial respiration and gas exchange between the pack headspace and the environment. Therefore, processors should conduct trials to determine the extent to which gas composition changes through the shelf life of the product. The ratio of headspace pack volume to food product volume is also important, as is the types and thickness of the package material and the package design. Shelf life evaluations must reflect the conditions from manufacture to consumption of the product. It may also be necessary to consider the effect of pack opening on the subsequent shelf life of the product.

10.B3 Cooked, cured and processed meat products

The principal spoilage mechanisms that limit the shelf life of cooked, cured and processed meat products are microbial growth, colour change and oxidative rancidity. For cooked meat products, the heating process should kill vegetative bacterial cells, inactivate degradative enzymes and fix the colour. Consequently, spoilage of cooked meat products is primarily due to post-process contamination by microorganisms, as a result of poor hygiene and handling practices. The colour of cooked meats is susceptible to oxidation, and it is important to have only low levels of residual O₂ in packs. MAP using CO₂/N₂ mixes (gas compositions of 25–50% CO₂ and 50–75% N₂) along with a gas/product ratio of 2:1 is widely used to maximise the shelf life and inhibit the development of oxidative off-flavours and rancidity. Raw cured meat products, e.g. bacon, owe their characteristic pink reddish colour to nitrosylmyoglobin. This pigment is more stable than oxymyoglobin and is unaffected by high levels of CO₂ but is slowly converted to brown metmyoglobin in air. During cooking, nitrosylmyoglobin is converted to pink denatured nitrosoheme-chrome pigments that are unstable in air.

Processed meat products such as sausages, frankfurters and beef burgers generally contain sodium metabisulphite, which is an effective preservative against a wide range of spoilage microorganisms and pathogens. Cooked, cured and processed meat products containing high levels of unsaturated fat are liable to be spoiled by oxidative rancidity, but MAP with CO₂/N₂ mixtures is effective at inhibiting this undesirable reaction.

Potential food poisoning hazards are primarily due to microbial contamination or growth resulting from post-cooking, curing or processing contamination.

These can be minimised by using recommended chilled temperatures, good hygiene and handling practices. The low water activity (a_w) and addition of nitrite in cooked, cured and processed meat products inhibit the growth of many food poisoning bacteria, particularly *C. botulinum*. This inhibition may be compromised in products formulated with lower concentrations of chemical preservatives than those used in traditional foods. The potential effects of any changes in product formulation on the growth and survival of pathogens should always be considered. Cooked meats stored without any added preservatives will be at risk from growth of *C. botulinum* under anaerobic MAP conditions, particularly when held at elevated storage temperatures. It should be noted that many sliced, cooked, cured and processed meat products are vacuum packed for retail sale. However, the shelf life of such products in MAP is similar to that achieved in vacuum packs, and additionally, MAP allows for easier separation of meat slices.

10.B4 Fish and fish products

There has been a very significant increase in the sale of MAP fish products in Europe and particularly in the UK. Nevertheless, packaging technologists should be aware of a major concern limiting the development of MAP, namely *C. botulinum*. There is also debate about the cost benefits of MAP, since in some applications only relatively small increases in safe shelf life have been reported. Spoilage of fish results in the production of low molecular weight volatile compounds, therefore, packaging technologists need to consider the odour barrier properties of packaging films and select appropriate high-barrier materials for packaging strong flavoured fresh, smoked and brined fish and fish products.

Spoilage of fish and shellfish results from changes caused by three major mechanisms: (i) the breakdown of tissue by the fish's own enzymes (autolysis of cells), (ii) growth of microorganisms, and (iii) oxidative reactions. MAP can be used to control mechanisms (ii) and (iii) but has no direct effect on autolysis. Because autolysis is the major cause of spoilage of fish and shellfish stored at temperatures close to 0°C compared with the activities of bacteria, this may explain the reduction in benefits achieved from MAP of fish compared to other flesh products. MAP, while potentially inhibiting oxidative reactions, may be more effective at inhibiting microbial growth.

Oxidative reactions are much more important as shelf life limiters in fish compared with other flesh meat, because seafood has a higher content of polyunsaturated lipids. Storage temperature has a major effect on fat oxidation that occurs even at frozen temperatures. Note that salt addition can accelerate oxidative processes.

Generally, the major spoilage bacteria found on processed fish are aerobes including *Pseudomonas*, *Moraxella*, *Acinetobacter*, *Flavobacterium* and

Cytophaga species. There are several microorganisms that are of particular importance when dealing with MAP fish products, these include *C. botulinum*. Use of CO₂ can effectively inhibit the growth of some of these species, see Table 10.2. The aerobic spoilage organisms tend to be replaced by slower growing, and less odour producing, bacteria, particularly lactic acid bacteria such as lactobacilli, during storage.

Because fish and shellfish contain much lower concentrations of myoglobin, the oxidation status of this pigment is less important than that in other meats. Consequently, there is potential to use higher levels of CO₂, e.g. 40%. Because of the high moisture content and the lipid content of some species, N₂ is used to prevent pack collapse.

One of the concerns about MAP of fish is that removal of O₂ and its replacement by either N₂ or N₂/CO₂ results in anaerobic conditions that are conducive to the growth of protease-negative strains of *C. botulinum*. Because these bacteria can grow at temperatures as low as 3°C and do not significantly alter the sensory properties of the fish, there is the potential for food poisoning that can lead to fatalities. While there is no evidence that CO₂ promotes the growth of psychotropic strains of *C. botulinum*, there are, as discussed previously, some concerns about CO₂ promoting the germination of spores of this organism.

Considerable research has been undertaken to assess, and to control, the risks associated with the growth of *C. botulinum* in MAP of fish and other products. The Advisory Committee on the Microbiological Safety of Food (ACMSF) (Anon, 1992) have recommended controlling factors that should be used singly or in combination to prevent the growth of, and toxin production in prepared chilled food by, psychotropic *C. botulinum*. As far as MAP of raw fish products is concerned, risk can be effectively eliminated if storage temperature is held at 3°C or below and if the shelf life is limited to no more than 10 days.

Some fish processors include O₂ in their MAP to further reduce the risk of growth of clostridia. Gas mixtures of 30% O₂, 40% CO₂ and 30% N₂ are used for white non-processed fish, i.e. nonfatty fish. While this will increase the shelf life of some fish and fish products, it would not significantly enhance the shelf life of oily or fatty fish. High, 40%, CO₂ mixes along with 60% N₂ are generally used for smoked and fatty fish. Because of the risks already discussed, it would appear reasonable to aim for a target shelf life of 10–14 days at 3°C.

10.B5 Fruits and vegetables

Consumers now expect fresh fruit and vegetable produce throughout the year. MAP has the potential to extend the safe shelf life of many fruits and

vegetables. Packaging fresh and unprocessed fruits and vegetables poses many challenges for packaging technologists. As with all products, it is essential to work with the highest quality raw materials, and this is especially true for this product group, often referred to as *fresh produce*. The quality of fresh produce is markedly dependent on growing conditions, minimising bruising and other damage during harvesting and processing, adherence to good hygienic practices, controlling humidity to prevent desiccation while avoiding condensation to prevent mould growth, and maintaining optimum storage temperatures. Unlike other chilled perishable foods, fresh produce continues to respire after harvesting. The products of aerobic respiration include CO_2 and water vapour. In addition, respiring fruits and vegetables produce C_2H_4 that promotes ripening and softening of tissues. The latter if not controlled will limit shelf life.

Respiration is affected by the intrinsic properties of fresh produce as well as various extrinsic factors, including ambient temperature. It is accepted that the potential shelf life of packed produce is inversely proportional to respiration rate. Respiration rate increases by a factor of 3–4 for every 10°C increase in temperature. Hence, the goal of MAP for fruits and vegetables is to reduce respiration to extend shelf life while maintaining quality. Respiration can be reduced by lowering the temperature, lowering the O_2 concentration, increasing the CO_2 concentration and by the combined use of O_2 depletion and CO_2 enhancement of pack atmospheres. If the O_2 concentration is reduced beyond a critical concentration, which is dependent on the species and cultivar, then anaerobic respiration will be initiated. The products of anaerobic respiration include ethanol, acetaldehyde and organic acids. Anaerobic respiration, or anaerobiosis, is usually associated with undesirable odours and flavours and a marked deterioration in product quality. While increasing the CO_2 concentration will also inhibit respiration, high concentrations may cause damage in some species and cultivars.

Reducing O_2 concentrations below 5% will slow the respiration rate of many fruits and vegetables. Kader *et al.* (1989) have tabulated the minimum O_2 concentration tolerated by a range of fresh produce; while some cultivars of apples and pears can tolerate O_2 concentrations as low as 0.5%, potatoes undergo anaerobic respiration at around 5% O_2 . In general, O_2 concentrations below about 3% can induce anaerobic respiration in many species of fresh produce.

Elevated CO_2 can also inhibit respiration. If the gas concentration is too high, then anaerobic respiration is induced with consequent quality problems. CO_2 sensitivity is both species and cultivar dependant; strawberries are able to tolerate 15% CO_2 whereas celery is stressed by CO_2 concentrations above 2% (Kader *et al.*, 1989). The tolerance of strawberries to CO_2 can be used to inhibit the growth of the mould *Botrytis cinerea*.

The use of low concentrations of O_2 and elevated levels of CO_2 can have a synergistic effect on slowing down respiration and, indirectly, ripening. While

the mechanisms whereby MAP can extend the shelf life of fresh produce are not fully understood, it is known that the low O₂/high CO₂ conditions reduce the conversion of chlorophyll to pheophytin, decrease the sensitivity of plant tissue to C₂H₄, inhibit the synthesis of carotenoids, reduce oxidative browning and discolouration and inhibit the growth of microorganisms. These mechanisms are all temperature dependent. The effects of MAP on the physiology of fruits and vegetables have been the subject of extensive research by many groups and have been well reviewed, e.g. Kader (1986).

Packaging technologists should be aware of several major pathogens as far as MAP fresh produce is concerned, in particular *L. monocytogenes* and *C. botulinum*. As previously discussed, *L. monocytogenes* can grow under reduced O₂ levels and is not markedly inhibited by CO₂. This combined with its ability to grow at temperatures close to 0°C helps explain the concern.

The use of MAP atmospheres containing low concentrations of O₂ and elevated CO₂ concentrations may permit the growth of psychotropic protease-negative strains of *C. botulinum*. However, provided packs are stored at 3°C or below for not more than 10 days, there is unlikely to be a problem with clostridia. Temperature control is critical, since temperature abuse could lead to pack contents becoming toxic.

The environment in which fruits and vegetables are grown may harbour pathogens including *Salmonella* species, enterotoxigenic *E. coli* and viruses. While these microorganisms may not grow in MAP packs, particularly if the storage temperature is maintained around 3°C, they may survive throughout storage and could cause food poisoning through cross-contamination in the home or due to the consumption of raw or under-processed product. Hygienic preparation, sanitation in chilled-chlorinated water, rinsing and dewatering prior to MAP are now considered as essential treatments to fruits and vegetables prior to packaging to ensure low microbial counts and assure safety. Since there is a risk of anaerobic pathogens, such as *C. botulinum*, growing in MAP packs, a minimum level of O₂ (e.g. 2–3%) is usually recommended to ensure that potentially hazardous conditions are not created.

Equilibrium MAP (refer to Chapter 2) has been used for fresh produce. Essentially, this involves using knowledge of the permeability characteristics of particular packaging films, along with the respiration characteristics of the product to balance the gas transfer rates of O₂ and CO₂ through the package with the respiration rate of the particular product.

Increasingly, gas packing fresh produce along with CO₂/O₂/N₂ gas mixtures is being used. This approach may have benefit in reducing enzymic browning reactions before a passively generated equilibrium modified atmosphere has been established.

10.B6 Dairy products

MAP has the potential to increase the shelf life of a number of dairy products. These include fat-filled milk powders, cheeses and fat spreads. In general, these products spoil due to the development of oxidative rancidity in the case of powders and/or the growth of microorganisms, particularly yeasts and moulds, in the case of cheese.

Whole milk powder is particularly susceptible to the development of off-flavours due to fat oxidation. Commercially, the air is removed under vacuum and replaced with 100% N₂ or N₂/CO₂ mixes and the powder is hermetically sealed in metal cans. Due to the spray drying process, air tends to be absorbed inside the powder particles and will diffuse into the container over a period of ten days or so. This typically will raise the residual headspace O₂ content to 1–5% or higher (Evans, Mullan and Pearce, unpublished results). Because some markets require product with low levels of residual O₂ (<1%), some manufacturers re-pack the cans after ten days of storage. Obviously, this is both expensive and inconvenient. We have found that use of N₂/CO₂ mixes (Evans, Mullan and Pearce, unpublished results) can be helpful. Use of O₂ scavenging may also be useful. Refer to Chapter 9 for a more detailed discussion of O₂ scavengers.

English territorial cheeses, e.g. Cheddar, have traditionally been vacuum packed. Increasingly MAP is being used with high CO₂ concentration gas mixes. This has the advantage of obtaining a low residual O₂ content and a tight pack due to the CO₂ going into solution. It is important to balance this process using the correct N₂ level in the gas mix so as to avoid excessive pressure being put on the pack seal.

Use of N₂/CO₂ atmospheres has significant potential for extending the shelf life of cottage cheese. The cottage cheese is a high-moisture, low-fat product that is susceptible to a number of spoilage organisms including *Pseudomonas* spp. Use of gas mixtures containing 40% CO₂ balanced with 60% N₂ can increase the shelf life significantly.

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