MODIFIED ATMOSPHERE PACKAGING

Food distribution has undergone two major revolutions in the last century, canning and freezing. These gave consumers easy availability to most type of produce. However, energy crisis, ecological awareness and demand for healthy and fresh food has created a need for a technology that allows distribution of fresh produce around the year. It uses minimum processing and little energy and maximizes nutrition and flavour. Modified Atmosphere Packaging (MAP) theoretically, offers a possibility of meeting these requirements.

This new packaging concept is rapidly growing in the food packaging market. It improves the product quality, freshness and increases the shelf-life of the product as well as provides convenience to the consumer and adds value to the product. It is mainly used to extend the shelf-life of fresh produce and perishable products.

MAP enables the fresh produce or perishable product to be packaged when it is fresh and then maintains it in that condition, thereby, reducing distribution costs and enhancing flavours and nutrition value for the consumer. Horticultural produce respires even after harvesting. However, the biological processes, which cause deterioration get accelerated. This affects the nutritional value, flavour, texture and appearance. In adverse climatic conditions such deterioration happens very quickly. MAP slows the ongoing life processes not by changing the product but by adjusting its environment. Under the influence of MAP, the product is held in a state similar to that of animal hibernation. MAP maintains this state for a long period of time, during which deterioration is effectively stopped.

In a modified atmosphere package, the product is exposed inside the pack to the normal atmospheric gases (oxygen, nitrogen, carbon dioxide and water vapour) but in concentrations which are different from those in the ambient air. **The packaging consists of polymeric film pouch or plastic container with a specified gas permeability.**

Gases used in MAP

In MAP, the pack is flushed with a gas or a combination of gases. The common gases used are oxygen, nitrogen and carbon dioxide. Traces of carbon monoxide, nitrous oxide, ozone, argon, ethanol vapour and sulphur dioxide are also used. Minimum oxygen levels are used to pack food under MA because oxygen reacts with the foodstuff resulting in the oxidative breakdown of food into their constitutive parts. Oxygen also combines easily with fats and oils causing rancidity. Nitrogen is an inert gas. It has no anti-microbial activity and acts as a cushion, thereby preventing pack collapse. Since it displaces oxygen from the pack, oxidative rancidity is delayed. Carbon dioxide is responsible for the bacteriostatic and fungistatic effect in MA packaged food. It retards the growth of moulds and aerobic bacteria. The inhibitory effect of carbon dioxide to micro-organisms is increased as the temperature is lowered because of increased solubility.

Modified atmosphere can be created either passively by the product or intentionally by active packaging. **In passive modification, the respiring product is placed in a polymeric package and sealed hermetically.** Only the respiration of the product and the gas permeability of the film influence the change in gaseous composition of the environment surrounding the product. If the product's respiration characteristics are properly matched to the films permeability values, then a beneficial modified atmosphere can be passively created within a package. In case of active modification, two basic techniques are employed to replace air in MAP i.e. Gas flushing and Compensated Vacuum.

Gas Flushing

In this, the air is replaced by passing a stream of gas. The air gets diluted and the pack is sealed. The oxygen level in gas-flushed packs is up to 2 - 5%.

Compensated Vacuum

Here, vacuum is first applied to remove the air and then the desired gas or gas mixture is incorporated. Since it involves an extra step, this process is slower, but the residual oxygen is much less.

Active Packaging

Sometimes, certain additives are incorporated into the polymeric packaging film or within packaging containers to modify the headspace atmosphere and to extend shelf-life. This is referred to as Active Packaging. The concept of active packaging has been developed to rectify the deficiencies in passive packaging. For e.g. when a film is a good barrier to moisture, but not to oxygen, the film can still be used along with an oxygen scavenger to exclude oxygen from the pack. Similarly, carbon dioxide absorbents/emitters, enthanol emitters and ethylene absorbents can be used to control oxygen levels inside the MA pack. The appropriate absorbent materials are placed alongside with the food. By their activity, they modify the headspace of the package and thereby contribute to extend the shelf-life of the contents.

Thus, the Modified Atmosphere Package system is a dynamic one where respiration of the packaged product and gas permeation through the packaging film takes place simultaneously. During respiration, the packaged product takes oxygen from the package atmosphere and the carbon dioxide produced by the product is given away to the package atmosphere. This results in the depletion of oxygen and accumulation of carbon dioxide within the package. Consequently, the composition of the package air changes. Initially, (i.e. soon after sealing of the package) the composition of package air remains nearly same as that of ambient air. As the concentration of oxygen in the package air reduces, that of carbon dioxide increases, the oxygen and carbon dioxide concentration gradients between package atmosphere and ambient atmosphere begin to develop. This decrease in respiration and increase in gas permeation continues till an equilibrium is reached. At equilibrium, the rate of oxygen permeating (ingress) becomes equal to the rate of oxygen consumption (respiration) and the rate of carbon dioxide permeating (egress) becomes equal to the rate of carbon dioxide evolution (respiration). Thus, oxygen consumed during respiration is replaced simultaneously by the ingress of oxygen. Likewise, an equal amount of carbon dioxide that is evolved by the packaged produce permeates out of the package. As a result, the air composition remains constant. This state is known as equilibrium or steady state. The attainment of the Equilibrium State depends on proper designing of MA package.

Storage Temperature

Temperature is one of the most important factors in extending the shelf-life of perishable food. Except for bakery products and some dried products, modified atmosphere packaged products are stored at 0–5°C. Optimum storage temperature must be established for every product. Permeability of polymeric packaging films is also a function of temperature and it generally increases with the increase in temperature.

Advantages & Disadvantages of MAP Technology

The benefits of MAP technology to the manufacturer, retailer as well as consumer far outweigh the drawbacks.

Advantages

- Increased shelf-life allowing lesser frequency of loading of retail display shelves.
- Improved presentation – clear view of the product and all round visibility.
- Hygienic stackable pack, sealed and free from product drip and odour.
- Potential shelf-life increases by 50 to 400%.
- Reduction in production and storage costs due to better utilisation of labour, space and equipment.

Disadvantages

- Capital cost of gas packaging machinery
- Cost of gases and packaging materials
- Increased pack volume increases transport costs and retail display space
- Potential growth of food borne pathogens due to non-maintenance of required storage temperature by retailers and consumers.

Packaging Materials

In a modified atmosphere pack, changes start to take place immediately after packing the fresh produce as a result of the respiration of the packaged produce. The gases of the contained atmosphere and the external ambient atmosphere try to equilibrate by permeation through the package walls at a rate dependant upon the differential pressures between the gases of the headspace and those of the ambient atmosphere. It is in this context that the barrier to gases and water vapour provided by the packaging material must be considered. Thus, the success of the modified atmosphere pack depends upon the barrier material used.

The function of the MA package, is to exclude oxygen and moisture from the packaged food and thereby slow down oxidative rancidity (baked goods, pasta), retard growth of spoilage micro-organisms (meat, pasta, baked goods) and maintain colour (red meat). In other packages, the aim is to prevent egress of carbon dioxide to retard growth of micro-organisms (meat, baked goods and pasta). These packages require the use of gas barrier materials, which allow very little permeation of gases. Modified atmosphere packs for fresh produce must also allow entry of oxygen to maintain the aerobic metabolism of the product. In addition, some carbon dioxide must exit from the package to avoid build up of injurious levels of the gas. **These packages are made of plastic films with relatively high gas permeability.**

In MAP, the food is packed in an atmosphere other than air to suppress microbiological, chemical and physical changes, hence it is necessary to consider the following:

Nature of the Product

Fresh produce consists of living tissue, which will continue to respire even after harvesting. Oxygen may be required for the reactions, which are accompanied by the production of carbon dioxide and water, and in some cases, microbial growth may also occur. Some chemical reactions may take place, which cause changes in texture and colour of the product. Water activity, pH and storage temperature of the food exerts a strong influence on these reactions. Hence, it is necessary to consider the type and nature of the product, before choosing the packaging material.

Disposition of Metabolic Products

Part of the metabolities i.e. carbon dioxide, water vapour and volatile compounds are absorbed by the product, while some are lost to the outside atmosphere through the packaging material. The absorbed metabolities change characteristics of the product such as $a_{w,}$ pH, colour texture which may improve or shorten the storage life of the product. Reduction of pH will make the product less suitable for growth of some organisms while an increase in a_w will stimulate microbial growth and chemical reactions. The net result of all these changes depends on the type of food product, its initial conditions and the headspace atmosphere.

Permeability of the Packaging Material

The permeability of the packaging material determines the atmospheric conditions in the headspace and ultimately the shelf-life of the product. If an atmosphere higher in carbon dioxide and / or lower in oxygen is required, the material should be impermeable to the gases. Vegetables and fruits require a certain amount of oxygen in the headspace for maintenance of quality, therefore, packaging material for these products should be quite permeable to the oxygen, to allow atmospheric oxygen to replenish the gas in the package. Transparency of packaging material to light is also important.

The choice of packaging material is an extremely important part of the MAP operation. The materials must be cost effective, have low water vapour transmission rate, high gas barrier, mechanical strength to withstand machine handling and subsequent storage and distribution of the finished pack as well as have the capability of giving high integrity seals to ensure retention of gas within the pack until opened by consumer. Also, once a gas atmosphere is applied, the level and proportion of headspace gas/gases is controlled only by judicious selection of packaging material with specified permeability characteristics.

The wide range of materials used for MAP is:

- **Glass and Metal Containers**

  These are excellent barriers to gases but are not suitable for MAP because the quality of food processed and packed in these containers is not enhanced by gas introduction.

- **Semi-rigid and Plastic Containers**

  A combination of low cost semi-rigid containers and flexible lidding material with suitable permeability can be used for products needing physical protection during shipment and marketing.

- **Flexible Packaging Materials**
  Flexible plastic packaging materials comprise of nearly 90% of the materials used in MAP with paper, paperboard, aluminium foil, metal and glass containers accounting for the remainder. This is largely due to the changing consumer demand where convenience, quality, safety and impact on the environment are of prime considerations. **These materials provide a range of permeability to gases and water vapour together with the necessary package integrity, needed for MAP** (see Table 1).

TABLE 1

Permeability of Plastic Films to Gases (at 30°C) and Water Vapour (at 25°C, 90% R.H)

Material	**Permeability (mlm^{-2} MPa^{-1} per day)**			
	N_2	O_2	CO_2	H_2O
PE (0.922)	120	300	2,300	5,300
PE (0.954 – 0.960)	18	71	230	860
PP (0.910)	-	150	610	4,500
PVC	2.7	8.0	67	10,000
PVdC	0.07	0.35	1.90	94
PS	19	73	590	80,000
PA (Nylon 6)	0.67	2.50	10	47,000
PET (MylarM)	0.33	1.47	10	8,700

The major factors to be taken into account while selecting the packaging materials are:

- The type of package (i.e. rigid or semi-rigid lidded tray or flexible pouch)
- The barrier properties needed (i.e. permeabilities of individual gases and gas ratios when more than one gas is used)
- The physical properties of machinability and strength
- Integrity of closure (heat sealing), fogging of the film as a result of product respiration, and
- Printability

The correct atmosphere at the start will last long only if the permeability of the barrier material does not allow any rapid changes to occur. The transmission rate of the films used should be proportional to the surface area of the package and inversely proportional to the film thickness. It is necessary to measure the transmission rate of the films as well as check the presence of residual oxygen within the pack because residual oxygen is not fully eliminated by gas flushing. Therefore, dependent on the rate of transmission, residual oxygen modifies the original gas mix. The storage conditions also affect the performance of a MA pack. The storage temperature affects the rate of product respiration and the rate of film permeability. Sometimes, high barrier materials are essential, yet with some products that respire, it is important that high barrier films are not used as undesirable, hazardous anaerobic organisms may grow. Thus, while choosing a film for a particular pack, a wide range of factors need to be taken into account. Along with the barrier properties of a particular film, a modified atmosphere pack must also be machineable, capable of withstanding transport and handling, look attractive and carry a message and be cost effective.

Many of the films used in MAP, singly do not offer all the properties required for a modified atmosphere pack. To provide packaging films with a wide range of physical properties, many of these individual films are combined through processes like lamination and co-extrusion. There are several groupings in MAP films.

Polyethylene is most commonly used to provide a hermetic seal and also as a medium of control for characteristics like anti-fogging abilities, peelability and ability to seal through a degree of contamination. The different materials used are:

Polyolefins

- **Low Density Polyethylene:** This is an extremely versatile material and accounts for the biggest proportion of plastic materials used for packaging. This is an inert film with low permeability for water vapour but high gas permeability. Ethylene Vinyl Acetate, a co-polymer of ethylene and vinyl acetate has superior sealing qualities. Blended polyethylene can be used with different additives to make a peelable seal, which is strong and gives an adequate barrier. When used with other films for lidding, base webs, preformed trays, bulk packaging or horizontal / vertical form-fill-seal webs, low-density polyethylene can be laminated, extrusion coated or co-extruded.
- **Linear Low-Density Polyethylene (LLDPE):** Linear low density polyethylene has better impact strength, tear resistance, higher tensile strength & elongation, greater resistance to environmental stress cracking and better puncture resistance. Thus, LLDPE can meet certain special requirements but at some financial and technical cost. Variation on a basic LDPE film remains by far the most common film used for MAP.
- **High Density Polyethylene:** This film has a higher softening point than LDPE and provides superior barrier properties. It is not suitable as a sealant layer and hence is not used in thermoformable base webs but used as one of the layers in the lidding material in co-extruded form. It has better gas-barrier properties than LLDPE but poor clarity.
- **Polypropylene (PP) and Oriented Polypropylene (OPP):** PP is chemically similar to polyethylene and can be extruded or co-extruded to provide as the sealant layer. OPP provides high moisture vapour barrier and gas barrier, seven to ten times that of polyethylene. It also has excellent grease resistance. OPP coated with polyvinylidene (PVdC) in low gauge form provides high barrier to moisture vapour.
- **Co-extruded Oriented Polypropylene (COPP):** This film is mostly used for vertical form-fill-seal packs. This can be a blown film or a cast and drawn film via a stentered system. It has a good moisture vapour barrier and the gas barrier properties can be improved by coating it with PVdC. COPP can be laminated as a part of the lidding material. It can be produced by co-extrusion with the basic properties or it can be perforated mechanically to provide a reduced resistance to gas flow on respiring products.

  This is the only commercially available film when gas flow is desired in the modified atmosphere pack. It is mainly used as breathable packages for fresh produce.
- **Inomers:** The first commercially available inomer was the polymer of ethylene, Surlyn A. It is similar in properties to polyethylene but has many advantages; for example, it develops a high tack and can seal through a level of surface contamination. Inomers can be extrusion coated but they are not cost effective.

Vinyl Polymers

- **Ethylene Vinyl Acetate Co-polymer (EVA):** EVA is a polymer with high flexibility in sheet form and has higher permeability to water vapour and gases (in comparison to LDPE). In both, lidding and base films, it is mainly used as a component of the sealant layer.
- **Poly Vinyl Chloride (PVC):** It is most widely used as the thermoformable base for MA packs. PVC provides good gas barrier and a moderate barrier to moisture vapour. It has excellent oil and grease resistance. Both the barrier properties and strength characteristics vary with thickness. PVC film is manufactured in a different way than the 'blown' or 'stentered' techniques used for other MAP films, it is milled and calendered.
- **Polyvinylidene Chloride (PVdC) Co-polymer:** This co-polymer of vinylidene chloride with vinyl chloride is used in MAP as a gas-barrier coating for lidding films and in film form as a sandwiched barrier layer. It has outstanding barrier properties with low permeability to water vapour and gases. It is mainly used as a coating on polyester and OPP for lidding films.
- **Ethylene Vinyl Alcohol (EVOH):** This is a moisture sensitive, very high gas-barrier material, which is sandwiched between the main formable and sealant layer to provide protection. It is expensive and hence it is used at the lowest gauge that provides adequate barrier properties for the intended laminate.

Styrene Polymers

- **Polystyrene:** This is a clear thermoplastic material with a high tensile strength but a poor barrier to moisture vapour and gases. Polystyrene alone is brittle, but it can be blended (sytrene-butadiene or styrene polybutadiene) to get required properties. This affects the clarity though.
- **High-impact Polystyrene:** This is an opaque, thermoformable, moderately low gas-barrier material and is used as a component of a laminate or co-extrusion.

Polyamides

The commonly used material is Nylon-6. In MAP, this film is either laminated or extrusion coated with polyethylene and is used as lidding material producing physically the strongest material.

Polyesters: Polyethylene Terephthalate (PET)

PET is used in various forms in MAP, as a low gauge oriented film of high clarity as lidding material and in crystalline or amorphous form as in-line preformed or thermoformed trays. As a lidding material, it is used as 12μ polyester / 3μ PVdC.

Other Polymers

The other films used for thermoforming are polycarbonate and Acrylonitrite Butadieine Styrene (ABS).

No single polymer offers all the properties required for MAP. In addition to barrier properties, properties like machinability / sealability must also be taken into account. One inherent requirement for all MAP packs is the ability to retain the desired atmosphere as long as possible. This is achieved first by choosing a film or films to provide the required gas and moisture vapour permeability characteristics and second by ensuring seal integrity of the packs. To achieve the above film characteristics the different plastic films are either laminated or co-extruded. Table 2 provides a list of common specifications.

TABLE 2

Typical Specifications

Thermoform **Base web** 200µ UPVC/70µ LDPE 400µ UPVC/100µ LDPE 650µ UPVC/100µ LDPE 400µ APET/100µ LDPE 300µ Barex/100µ LDPE In addition to these, some specifications based on polystyrene/ EVOH/LDPE and smaller percentages of APET/EVOH/PE	**Lidding laminate** 15µ polyester-PVdC/60µ LDPE/ antifog coating 12µ polyester-PVdC/ co-extruded polyethylene 15µ oriented PA (nylon)/ 60µ LDPE 21µ coated co-extruded PP/50µ LDPE
Tray lidding Preformed trays APET, CPET, UPVC or HDPE based specifications	**Lidding lamination** 15µ polyester-PVdC/60µ LDPE/ antifog coating 12µ polyester-PVdC/ co-extruded polyethylene 15µ oriented PA (nylon)/ 60µ LDPE 21µ coated co-extruded PP/50µ LDPE
Horizontal form-fill-seal	**Flexible Materials** 15µ polyester-PVdC/60µ LDPE/antifog coating 12µ polyester/ 38µ LDPE 30µ co-extruded PP 15µ/co-extruded PP/30µ LDPE 28µ coated co-extruded PP
Vertical form-fill-seal	**As horizontal form-fill-seal** 15µ polyester-PVdC/60µ LDPE/antifog coating 12µ polyester/ 38µ LDPE 30µ co-extruded PP 15µ/co-extruded PP/30µ LDPE 28µ coated co-extruded PP
Bulk gas packs	**Flexible Materials** LDPE/PA (nylon)/LDPE PA (nylon)/ EVHOH/MDPE LDPE/EVOH/LDPE

Note: The potential list is extensive, but this is an indication of the range of specifications currently in use.

Studies Conducted at IIP

Shelf-life studies of some meat and meat products, poultry and poultry products were carried out at the Institute for development of consumer packaging systems using the MAP Technology. The following products were considered for developing consumer packs:

- Chilled goat meat
- Chilled beef
- Whole dressed chicken
- Pig meat - Ham

The packaging materials selected were:

1) 10μ PET / 45μ HD – LD - Co-extruded
2) LDPE – BA – Nylon – BA – LLDPE – 100μ

The types of packages exposed were:

1) Ordinary pack
2) Vacuum pack
3) Gas packaging (MAP) using following gas mixtures
   a) 80% O_2 + 20% CO_2 (gas I)
   b) 70% O_2 + 20% CO_2 + 10% N_2 (gas II)
   c) 50% N_2 + 50% CO_2 (gas III)
   d) 100% CO_2 (gas IV)

The consumer packages were exposed to refrigerated temperature of 0°C to 4°C.

Gas mixtures I & II were used for packing chilled goat meat and chilled beef while gas mixtures III & IV were used for packing whole dressed chicken. Gas mixture IV was used for packaging ham samples. The shelf-life of the meat and meat products in the different types of pack is given in the Table 3.

TABLE 3

Shelf-life of the Meat and Meat Products in Different Types of Packs (in days)

Material	Chilled Goat			Chilled Beef			Whole Dressed Chicken			Ham		
	Ordinary Pack	Vacuum Pack	Gas I & GasII	Ordinary Pack	Vacuum Pack	Gas I & Gas II	Ordinary Pack	Vacuum Pack	Gas III & Gas IV	Ordinary Pack	Vacuum Pack	Gas IV
10μ PET/45μ HD - LD Co - extruded	2	3	3	2	5	4	4	9	9	11	28	35
LDPE - BA - NYLON - BA - LLDPE-100μ	2	3	3	2	6	4	5	9	10	12	28	35

The results indicate that in case of gas packaging (MAP), there is a delay in the induction of initial spoilage changes as compared to ordinarily packed samples.

Conclusion

MAP has revolutionised fresh food packaging, enabling retailers to market fresh foods that are prepared and packed in central preparation units, rather than prepared back store. The technique has also extended shelf-life, allowing products to survive both the distribution time to store, as well as the display time in the store.

Plastics with their unique and diverse combination of properties are ideal material to meet the growing demands of innovation and performance in MAP, in a sustainable manner.

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