TECHNICAL BULLETIN:
BARRIER PACKING

1 Introduction

Multilayer structures with polyethylene in the majority proportion continue to capture numerous applications in the food sector, due to the high protection they provide to the product (due to its mechanical resistance), in addition to its excellent appearance and low cost. The appropriate packaging selection criteria is defined by the food to be contained; Thus, for example, dry foods such as cereals, pasta and cookies require a high moisture barrier, while fruits and vegetables require an adequate balance of oxygen and carbon dioxide to continue their respiratory cycle once packed.

In recent years, the use of Modified Atmosphere Packaging (MAP) has seen rapid growth in the food packaging segment. This technology consists of modifying the respiration of the packaged product by controlling the levels of oxygen and carbon dioxide inside the package, maintaining the quality of the product and extending its shelf life. Additionally, MAPs preserve the characteristic moisture of fruits and vegetables, preserving their freshness and good appearance for a long period of time. The selection of the appropriate materials plays a fundamental role when designing a MAP, in addition to other factors such as:

- Balance of O2, CO2 and water vapor appropriate to the type of food to contain.
- High brightness and clarity, which allow the consumer to observe the freshness of the product through structure.
- Excellent seal and resistance to penetration, to maintain the modified atmosphere design inside the package.

The first of these factors is crucial to guarantee the freshness of food for as long as possible. The reason is that these foods are still alive and need certain levels of oxygen and moisture to continue their metabolism, maintaining their characteristic flavor and appearance from the time the product is packaged until its final consumption.

2 Collection of basic information for the design of the appropriate packaging

The composition of the atmosphere inside the package depends on the interaction of a number of factors including the characteristic permeability of the package, respiration of the product and the environment; That is why the packaging design requirements must respond to the needs of each food to be contained and to the environmental conditions to which the product will be exposed. Each food has specific requirements, different from each other.

Some considerations to take into account are[1]:

- Nature of the food to be packed.
- Product storage temperature.
- Gasket surface area.
- Approximate weight of the product to be packed.
- Minimum packing thickness.
- Respiration rate of the product to be packed and the required CO2/O2 coefficient.

The proper combination of the variables described above is the key to successful performance of a MAP. Table 1 illustrates how appropriate packaging increases the shelf life of some products.

Table 1. Estimated shelf life for some products[2].

Producto	Empacado al aire (días)	MAP (días)
Beef	4	12
Pork	4	9
Chiken	6	18
Cooked foods	7	28
Fish	2	10
Bread	7	21
Cooffee	3	548

3 Optimal storage conditions [1]

Oxygen levels: in many cases, the shelf life of products can be extended with low storage temperatures, at oxygen concentrations between 2 and 5%. However, other products require higher concentrations of oxygen (5 to 7%) to extend their shelf life; very low oxygen levels retard respiration, but there is a risk of early decomposition of the product.

Carbon Dioxide Levels: Optimum carbon dioxide levels in packaging typically range from 1-20%, as high concentrations of CO_2 can be beneficial or detrimental depending on the type of product. In packaging for strawberries, for example, carbon dioxide acts as a fungicide, preserving fungal growth on the fruit; on the contrary, in lettuce packaging, a CO_2 concentration above 2.5% can cause brown spots on the product, which is unattractive to the consumer.

Relative Humidity: Fresh produce generally requires high levels of humidity to maintain freshness and prevent weight loss. The recommended relative humidity for most vegetables should be between 98 and 100%, while for some fruits the required relative humidity should be around 90%. A high level of humidity promotes the growth of fungi in some foods, while a low level can cause rapid dehydration of the product.

Table 2 lists the recommended storage conditions for some products. Nitrogen is usually used as an inert gas to displace oxygen and carbon dioxide in MAPs, when the application required.

Table 2. Recommended storage conditions for some products[2].

	Temperature (°C)	O_2 (%)	CO_2 (%)
Foods that not breathe			
Sliced meat	0-2	0	80
Red meat	0-2	30	30
Fish	0-2	30	40
Chicken	0-2	0	30
Frozen meals (cooked)	0-2	0	20
Cheese	0-2	0	0
Pasta	0-5	0	60
Bakery products	20-22	0	100
Foods that breathe			
Lettuce	0-5	2 - 5	0 - 22
Apple	0-5	2 - 3	1 - 2
Broccoli	0-5	1 - 2	5 - 7
Strawberry	0-5	10	15 - 20
Mushroom	0-5	21	10 - 15
Tomato	8 - 12	3 - 5	0
Banan	12 - 15	2 - 5	2 - 5
Avocado	5 -13	2 - 5	3 - 10

4 Equations for the design of MAPs

The development of MAPs has been carried out after numerous studies of the behavior of fresh foods in environments with low oxygen levels. The goal of MAPs is to create a balanced atmosphere with the lowest level of oxygen and the highest level of carbon dioxide possible without harming the product. This atmosphere can be achieved through a harmonic interrelation of a set of variables, which in equilibrium state can be expressed as follows[3]:

$$\mathbf{P_{O2} = RR_{CO2}*t*W/\ [A*(CO_{2atm}-\ CO_{2emp})]}$$

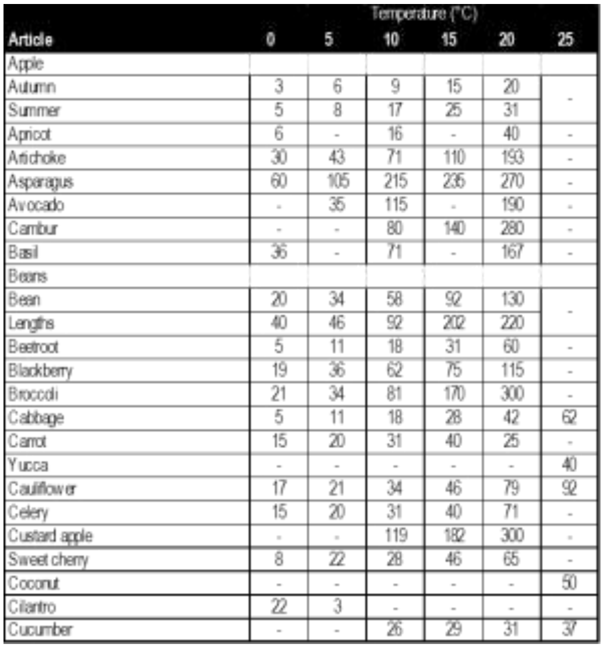
$$\mathbf{P_{CO2} = RR_{CO2}*t*W/\ [A*(CO_{2emp}-\ CO_{2atm})]}$$

Where:
P_{O2}: film oxygen permeability ($ml*mil/m^2*h*atm$).
P_{CO2}: carbon dioxide permeability of the film ($ml*mil/m^2*h*atm$).
RR_{O2}: respiration rate as oxygen consumption of food (ml/kg*h).
RR_{CO2}: rate of respiration as production of carbon dioxide from food (ml/kg*h).
t: film thickness (mil).
W: weight of food (kg).

A: gasket surface area (m^2).
(O_{2atm} - O_{2emp}): oxygen gradient between the outside and inside of the package.
(CO_{2emp} - CO_{2atm}): carbon dioxide gradient between the inside and outside of the package.

This formula is very useful for estimating how changes in each of the variables implicit in it affect the permeability requirements of the packing. Table 3 lists the respiration rates of some fruits and vegetables at different storage temperatures.

Tabla 3. Approximate respiration rates (in $mgCO_2*Kg´*h´$) for some fruits and vegetables.



	Temperature (°C)					
Article	**0**	**5**	**10**	**15**	**20**	**25**
Apple						
Autumn	3	6	9	15	20	-
Summer	5	8	17	25	31	
Apricot	6	-	16	-	40	-
Artichoke	30	43	71	110	193	-
Asparagus	60	105	215	236	270	-
Avocado	-	35	115	-	190	-
Cambur	-	-	80	140	280	-
Basil	36	-	71	-	167	-
Beans						
Bean	20	34	58	92	130	-
Lengths	40	46	92	202	220	
Beetroot	5	11	18	31	60	-
Blackberry	19	36	62	75	115	-
Broccoli	21	34	81	170	300	-
Cabbage	5	11	18	28	42	62
Carrot	15	20	31	40	25	-
Yucca	-	-	-	-	-	40
Cauliflower	17	21	34	46	79	92
Celery	15	20	31	40	71	-
Custard apple	-	-	119	182	300	-
Sweet cherry	8	22	28	46	65	-
Coconut	-	-	-	-	-	50
Cilantro	22	3	-	-	-	-
Cucumber	-	-	26	29	31	37

To convert to $mlCO_2*kg^{-1}*h^{-1}$ divide by 2 to 0 °C,by 1.9 a 10 °C and for 1.8 to 20 °C.

The permeability requirements for a given package are achieved with the combination of two or more materials in a multilayer structure (coextrusion or lamination), in order to minimize costs and achieve the performance desired in the rest of the properties required by the application. In many cases, the use of engineering materials, such as EVOH, PA (Nylon), PVDC, etc., is required, although, due to their cost, their use in the total structure is minimized. MAP films cannot be economically achieved by monolayer extrusion.

The total permeability of the multilayer structure can be calculated based on the contributions of each layer, as follows[5]:

$$1/P = [(t_1/P_1) + (t_2/P_2)\ldots + (t_n/P_n)]$$

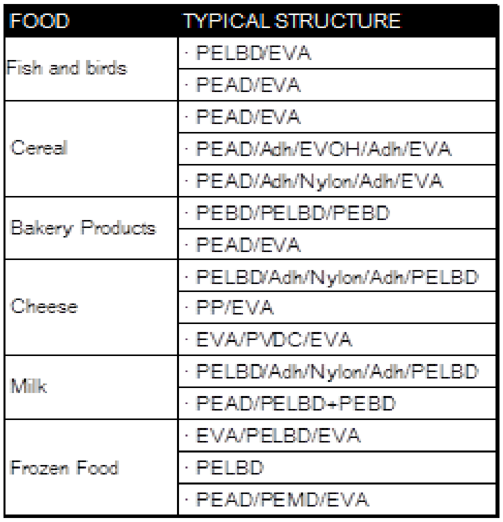
P: total permeability of the coextruded structure.

P_i: permeability of the layer of the structure multilayer (i=1,2,…n).

t_i: layer thickness of the multilayer structure (i=1,2,…n).

As a reference, Table 4 shows several typical structures used in non-respiring foods, and Table 5 reports permeability values of some materials commonly used in this type of application.

Table 4. Typical structures used in some non-respiring foods5. (Adh indicates adhesive)



FOOD	TYPICAL STRUCTURE
Fish and birds	· PELBD/EVA
	· PEAD/EVA
Cereal	· PEAD/EVA
	· PEAD/Adh/EVOH/Adh/EVA
	· PEAD/Adh/Nylon/Adh/EVA
Bakery Products	· PEBD/PELBD/PEBD
	· PEAD/EVA
Cheese	· PELBD/Adh/Nylon/Adh/PELBD
	· PP/EVA
	· EVA/PVDC/EVA
Milk	· PELBD/Adh/Nylon/Adh/PELBD
	· PEAD/PELBD+PEBD
Frozen Food	· EVA/PELBD/EVA
	· PELBD
	· PEAD/PEMD/EVA

Table 5. Barrier properties of some materials[6].

Material	OTR (cc*mm/m^2/d@23°C,0% RH)	WTR (G*mm/m^2/d@37.8°C,90% RH)
PEBD	163	0.40 - 0.48
PELBD	170	0.32 - 0.48
PEAD	58	0.16 - 0.32
PP	58	0.28
PA6	1.00	4.00 - 8.00
PA66	1.00	4.00 - 8.00
EVOH	0.008	0.80 - 1.80
PVDC	0.058	0.04
PS	136	2.80 - 4.00
Surlyn	78 - 194	0.40 – 3.60

Similarly, in Table 6 it is possible to observe the typical ranges of permeability in packaging intended to store fruits and vegetables.

Table 6. Typical ranges of permeability of packaging for foods that breathe[7].

Property	Typical Range	Function
OTR (cc*mil/100in^2*d)	300-1200	Allow product to breathe
CO_2TR (cc*mil/100in^2*d)	1000-5200	Allow product to breathe
WVTR (g*mil/100in^2*d)	<2.5	Prevent product dehydration

5 Oxygen Scavengers [8]

Oxygen scavengers are additives that act by consuming the oxygen present in the packaging through a classic oxidation reaction. An oxidizable plastic (commonly PET or PA) is used for the reaction, which is catalyzed by a transition metal, usually cobalt. The reaction of these additives is triggered by moisture moving through the polymer matrix.

Oxygen scavengers are called active systems because the reaction begins immediately after they come into contact with moisture and oxygen; once active, they exert their action until there is not enough catalyst to maintain the oxidation reaction.

Oxygen scavengers are highly effective mainly during the first part of their life cycle, consuming both the oxygen that enters the packaging and that which is generated by the packaged product. Under ideal storage conditions, properly additivated packaging can easily maintain oxygen levels around 1 ppm for six months on the shelf.

6 Processing Effects on Film Permeability

In semi-crystallized polymers, the passage of gases occurs mainly through the amorphous zone of the polymeric matrix; for this reason, polymers with a higher degree of crystallization have a lower permeability than those with a lower crystal content. However, it has been shown that the processing conditions can significantly influence the permeability properties of the films, regardless of the degree of crystallization of the material used. Thus, a tubular film with a better MD/TD balance of its molecules will present greater opposition to the passage of gases than a film totally oriented in MD; This principle 9 is described in various studies as a "pattern of tortuosity" (See Figure 1).

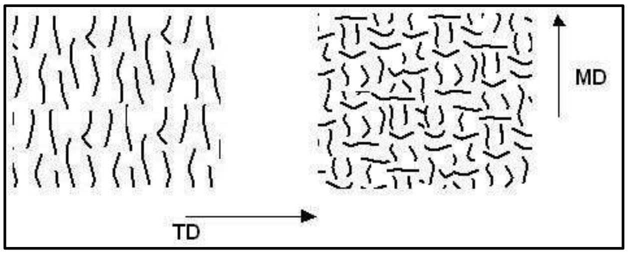


Figure 1. Concept of the tortuous pattern.

There are numerous very sophisticated analytical methods that allow us to measure how oriented the crystalline structure of the polymer is in a certain direction of the structure. However, a very simple technique to measure film balance is the determination of the MD/TD tear strength coefficient.

Figure 2 illustrates the effect of the MD/TD balance (measured through tear strength) on the permeability properties of an HDPE, where it is observed that the films with the best balance (tortuous pattern) present a lower permeability.

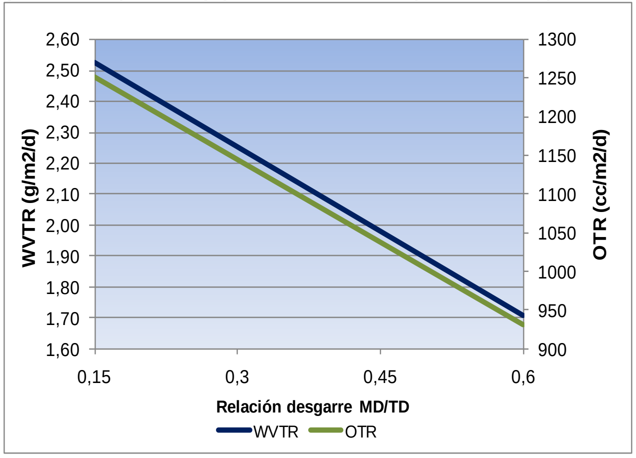


Figure 2. Effect of the MD/TD balance on the permeability to oxygen and water vapor.

Among the variables that affect the MD/TD balance and, consequently, the permeability of tubular films is:

- Blow ratio (BUR).
- Nozzle opening (gap)
- Cooling line height (ALE).
- Flow
- Thickness

As Figure 3 shows, the balance produced by the increase in BUR and the decrease in the gap has a positive effect by reducing the water vapor permeability of the tubular films. Similarly, a high cooling line contributes to the formation of larger crystals, which in turn prevents the passage of gases through the film (Figure 4).

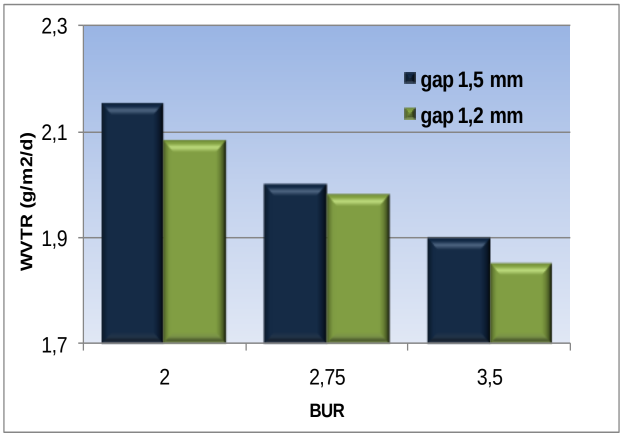


Figure 3. Effect of the BUR and the opening of the nozzle (gap) in water vapor permeability [9].

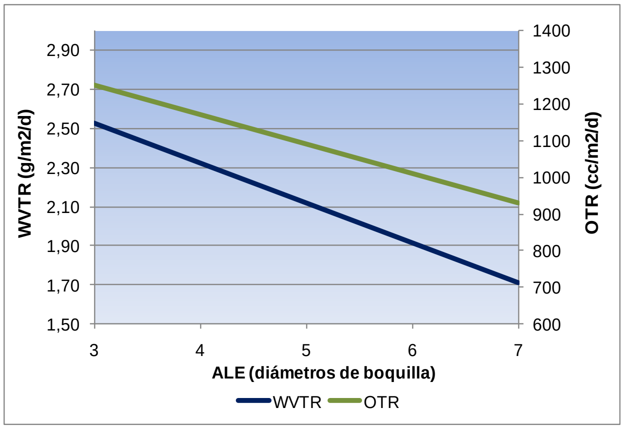


Figure 4. Effect of ALE on permeability to oxygen and water vapor.

7 Bibliographic references

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