



ADVANCES IN CLEAR HIGH-BARRIER PACKAGING MATERIALS

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The trend towards packaging products in clear materials continues to gain momentum. Product visibility is a powerful tool. It allows manufacturers to easily inspect the packaged product through the use of vision systems, metal detectors, and manual visual inspection. As any printing on the device is visible and does not need to be repeated on the package, labeling processes can be simplified and the potential for labeling mix-ups reduced. Patient safety is further enhanced because the end user is able to visually verify the identity and the size of the product before opening the package.

As medical devices and pharmaceutical products become more complex, the requirements placed on the packaging materials have increased. Fortunately, the material choices that we have today allow for a variety of approaches when packaging sensitive products. Passive barriers such as SiO_x, Al₂O₃, PVOH, PVdC, EVOH, PCTFE, and COCs provide many options when developing the ideal packaging material for a specific application. Performance can be further enhanced through the use of active packaging allowing even the most demanding products to be packaged in clear high-barrier materials. Clear high-barrier materials that meet both the performance and economics challenges of today's products are a reality.

THE STANDARD

When evaluating high barrier materials, aluminum foil is the benchmark by which we measure performance. Aluminum foil, if in perfect condition (no pinholes or imperfections), is impervious to moisture and gas regardless of the thickness of the foil. It is the ultimate barrier.

However, aluminum foil at thicknesses of less than one mil (0.001 inch or 25 microns) has pinholes. These pinholes are inherent to thin gauge foils and can be present in sufficient number to impact the barrier properties. As the gauge of aluminum foil decreases, the number of pinholes typically present increases. The impact pinholes have on the barrier properties of thin gauge aluminum foil is illustrated in Chart 1. This chart shows the water vapor transmission rate of aluminum foil as a function of foil thickness (as detailed in ASTM B479 Standard Specification for Annealed Aluminum and Aluminum-Alloy Foil for Flexible Barrier, Food Contact, and Other Applications).

When package clarity is desired, there are a number of clear high-barrier material options many of which have barrier properties that exceed that of the thin gauge aluminum foils. The appropriate choice is dependent upon many factors:

- Type of barrier needed for the application (Oxygen, water vapor, aroma, chemical, ultra-violet light, and/or microbial barriers are common needs.);
- The product itself and its compatibility with the packaging materials (For example, many options can be ruled out if the product contains water, is chemically active, or is sharp.);
- The equipment that will be used to process the packaging material;
- The sterilization method (if applicable);
- Specific environmental and/or disposal requirements;
- The cost of the packaging system.

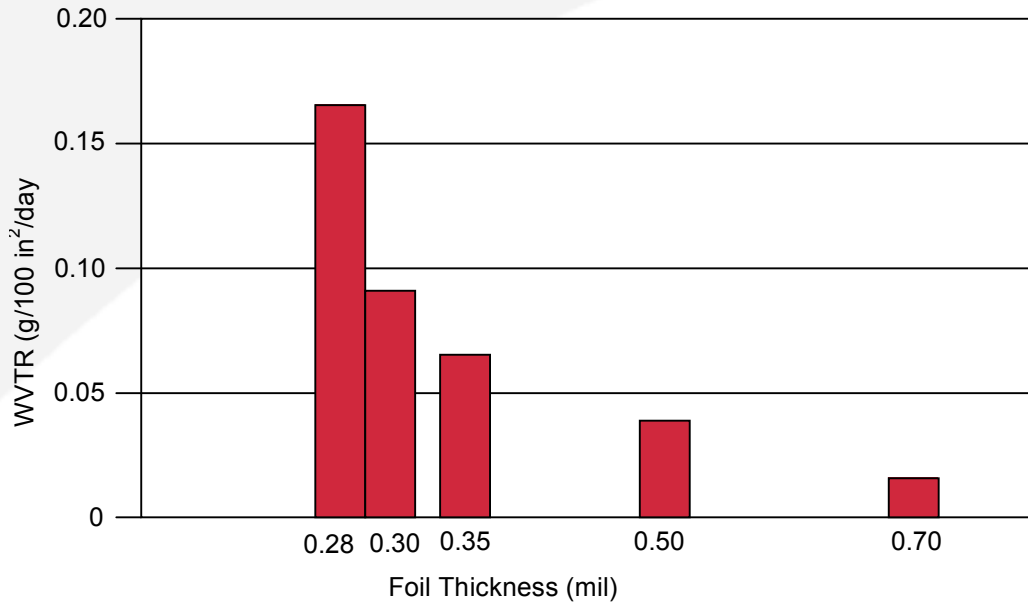


Chart 1: Barrier Properties of Thin Gauge Foils

In order to understand the barrier that will be provided by the finished package, it is important to factor in not only the permeation through the face of the material but also the ingress through the seal. The sealants used in packaging materials often provide little barrier to gasses and ingress through the seal can result in a significant barrier loss. Figure 1 shows the cross-section of a foil composite made from a laminate of 0.00048" polyester/ 0.001" aluminum foil / 0.002" low density polyethylene. While oxygen is unable to permeate through the face of the aluminum foil, oxygen will pass through the edges of the seal.

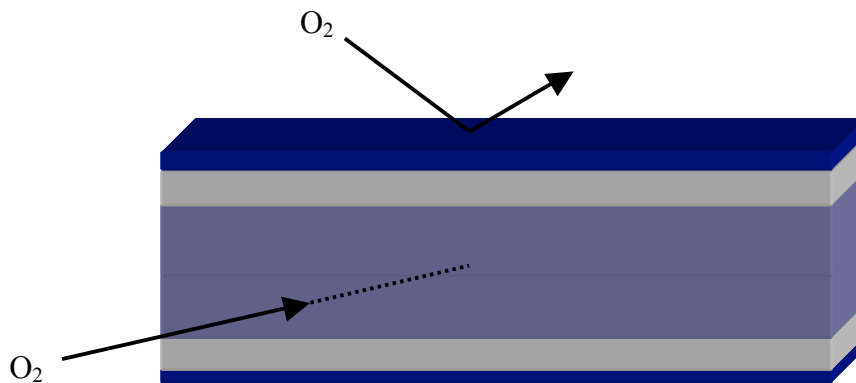


Figure 1: Ingress Through the Seal

Ingress of oxygen through the seal can be theoretically calculated or determined through whole package barrier testing.



CLEAR HIGH BARRIER MATERIALS

Clear high-barrier materials are available in two forms, barrier films and barrier coatings. For more complex applications, combinations of films and coatings may be required.

Films

Ethylene Vinyl Alcohol

Ethylene Vinyl Alcohol (EVOH) is one of the most common clear high barrier films used today. It is applied as a discrete layer in a coextrusion. EVOH provides excellent oxygen barrier, in the range of 0.006 – 0.12 cc-mil/100 in²-day. The barrier that a particular EVOH film provides is dependent upon a number of factors:

- Mole percent – as the ethylene mole percent increases, the barrier decreases;
- Degree of crystallinity – as the degree of crystallinity increases, the barrier properties improve;
- Thickness – as with all films, as the thickness increases, the barrier increases;
- Temperature – as the temperature increases, the barrier decreases;
- Humidity – at high humidity levels, the barrier provided by EVOH drops rapidly. Note: it is the humidity level at the EVOH interface rather than ambient humidity that is critical.

In addition to providing excellent oxygen barrier, EVOH is also an excellent odor and aroma barrier. It has the added advantage of being thermoformable making it popular for 3D applications. EVOH has a long history and is well understood.

Polyacrylonitrile

Polyacrylonitrile (Barex[®]) is a good oxygen barrier, in the neighborhood of 0.7 cc-mil/100in²-day. What makes polyacrylonitrile unique is that it can also be used as a sealant. Because Barex can also be thermoformed, it is a very versatile product. It is ideal for very sensitive applications where oxygen ingress through the seal is a concern.

Cyclic Olefin Copolymers

Cyclic Olefin Copolymers (COC) or Cyclic Olefin Polymers (COP) are a good moisture barrier providing approximately 0.2 g-mil/100in²-day. When using COCs/COPs to achieve barrier, they can be coextruded as a discrete layer or, for improved economics, blended to a level of 60 – 70 percent with polyolefins. COCs/COPs will enhance stiffness making them ideal for use in stand-up pouch applications. They have excellent clarity, can be thermoformed and, if the appropriate grade is selected, can be used in retort/autoclave applications.

COCs/COPs are not appropriate for all applications. They are attacked by nonpolar solvents such as toluene and naphtha and have limited resistance to ethyl acetate. COCs also tend to be brittle although blending can reduce that issue.

Polychlorotrifluoroethylene

Polychlorotrifluoroethylene (PCTFE or Aclar[®]) provides excellent moisture barrier. It is available as a copolymer or a homopolymer with water vapor transmission rates of approximately 0.038 g-mil/100in²-day and 0.016 g-mil/100in²-day respectively. These grades of PCTFE are commonly used in blister (thermoformed) packages where moisture barrier is required.



Machine direction oriented (MDO) PCTFE is specifically designed for pouch or non-forming applications. MDO PCTFE, sold under the trade name Aclar Flex, provides a WVTR of approximately 0.010 g-mil/100 in²-day. While not thermoformable, MDO PCTFE maintains PCTFEs excellent properties. It is inert, chemically resistant, has excellent clarity, and, unlike many barrier materials, it is flex-crack resistant.

Nanocomposites

Nanocomposites are polymer structures that contain fillers, typically silicate nanoclays, with at least one dimension in the nanometer range. The fillers separate into tiny platelets that disperse into a matrix of layers. Because the matrix of layers create a tortuous path for gasses trying to permeate through the film, the barrier properties of the modified polymer are improved. However, the challenge is to ensure that that the filler dispersion is consistent. In addition to better barrier properties, nanocomposites modified films also have improved dimensional stability and stiffness and, because crystallinity is increased, enhanced clarity.

Nanocomposite masterbatches are commercially available for nylon and polyolefins. The oxygen barrier of nylon nanocomposite films can as much as 50 percent higher than a nonmodified nylon. Polyethylene and polypropylene nanocomposite structures have shown improvement in gas barrier of 25 to 50 percent and in water vapor of 10 to 15 percent in laboratory settings. Achieving consistent barrier properties on a commercial scale remains challenging.

Nanocomposite technology is very much an emerging science. It shows a great deal of promise and as more options become available for film applications it will have a significant impact on barrier material options.

Coatings

Polyvinylidene chloride

Polyvinylidene chloride (PVdC) is a widely used barrier material with a long history. While PVdC is available as an oriented film and a discrete layer in coextruded films, it is more commonly used as a barrier coating. PVdC has good oxygen and moisture barrier properties and provides an excellent aroma and flavor barrier. Common transmission rates for PVdC coated substrates are shown in Table 1.

Material	O ₂ TR (cc/100in ² -day)	WVTR (g/100in ² -day)
PVdC-coated PET	0.5	0.5
PVdC-coated OPP	1.3	0.3
PVdC-coated Nylon 6,6	0.5	0.6

Table 1: Barrier Properties of PVdC Coated Substrates

The barrier level of PVdC coatings are dependent upon the coating thickness. Much lower transmission rates can be achieved by applying significantly more coating as is common in the pharmaceutical industry.



Because PVdC contains chlorine, hydrochloric acid can be generated under certain conditions. As a result, specialized equipment must be used to apply the coating and the proper equipment must be used if the packaging material is to be incinerated.

Polyvinyl Alcohol

Polyvinyl alcohol (PVOH) is also available as a film or a coating. As a coating, PVOH provides excellent oxygen barrier as shown in Table 2.

Material	O ₂ TR (cc/100in ² -day)
PVOH-coated PET	0.2
PVOH-acrylic-coated OPP	1.3

Table 2: Barrier Properties of PVOH Coated Substrates

The barrier of a PVOH coating is dependent upon the coating thickness. PVOH is moisture sensitive and will dissolve when exposed to water or high humidity.

Silicon Oxide and Aluminum Oxide

Silicon Oxide (SiO_x) coatings are generally applied as a vacuum deposition onto films such as polyester and nylon. SiO_x coatings provide excellent oxygen and water vapor barrier properties in a variety of ranges as shown in Table 3.

Material	O ₂ TR (cc/100in ² -day)	WVTR (g/100in ² -day)
ClearFoil [®] A*	0.04	0.04
ClearFoil [®] F**	<0.003	0.02
ClearFoil [®] B	0.04	0.04
ClearFoil [®] B2*	0.02	0.02

* Retortable/Autoclaveable

**Excellent Flex-crack resistance

Table 3: Silicon Oxide Coated Substrates

A concern is often expressed regarding the ability of silicon oxide coatings to maintain their barrier when flexed. The reality is that most grades perform favorably when compared to aluminum foil and metallized composites. For more demanding applications, there are grades available that provide tremendous flex-crack resistance. Table 4 details the transmission rates of a variety of substrates before and after flexing.



Material	Flat O ₂ TR (cc/100in ² -day)	Flexed O ₂ TR (cc/100in ² -day)
48 ga oPET / 35 ga Foil / 2 mil LLDPE	0.03	3.2
48 ga oPET / Met / 2 mil LLDPE	0.1	0.7
48 ga oPET/ ClearFoil [®] A / 2 mil LLDPE	0.04	0.5
48 ga oPET/ ClearFoil [®] F / 2 mil LLDPE	<0.003	<0.003

Table 4: Barrier Properties After Flexing

Aluminum oxide (Al₂O₃), coated substrates provide similar properties and are used for the same applications as silicon oxide coated substrates. Unlike the slight amber tint seen in SiO_x coated films, these films are clear. However, they may have a slightly gray cast when many layers are stacked. Table 5 shows the barrier values of common aluminum oxide coated materials.

Material	O ₂ TR (cc/100in ² -day)	WVTR (g/100in ² -day)
ClearFoil [®] M	0.045	0.03
ClearFoil [®] M2*	0.04	0.3
ClearFoil [®] X	0.004	0.0016
ClearFoil [®] Z	0.0008	0.0008

* Retortable/Autoclaveable

Table 5: Aluminum Oxide Coated Substrates

SiO_x and Al₂O₃ coating are available in grades appropriate for retort/autoclave applications.

The conventional wisdom is that composite packaging materials that use SiO_x or Al₂O₃ coatings as the barrier will be more expensive than aluminum foil composites. This conclusion is often reached after comparing the cost of the base aluminum foil (unlaminated) to the base SiO_x or Al₂O₃ coated product. However, it ignores that fact that aluminum foil must be protected on both sides whereas the SiO_x or Al₂O₃ coated product may only need a sealant. The cost of the additional layer and processing necessary for aluminum foil often results in a composite structure that is more expensive than a comparable SiO_x or Al₂O₃ composite. Table 6 provides a relative cost comparison of various structures.



Material	O ₂ TR (cc/100in ² -day)	WVTR (g/100in ² -day)	Cost*
48 ga PET / 2 mil LDPE	4.5	0.3	1.00
48 ga PVOH-coated PET / 2 mil LDPE	0.2	0.3	1.07
48 ga metallized PET / 2 mil LDPE	0.1	0.05	1.12
48 ga saran-coated PET / 2 mil LDPE	0.5	0.3	1.14
48 ga ClearFoil [®] B / 2 mil LDPE	0.04	0.03	1.25
48 ga ClearFoil [®] X / 2 mil LDPE	0.004	0.0016	1.83
48 ga PET / 50 ga Foil / 2 mil LDPE	0.02	0.01	2.07

*Relative cost as compared to 48 ga PET/2 mil LDPE. Actual ratios may vary dependent upon order quantity and widths.

Table 6: Cost versus Barrier Comparison

Active Packaging

Oxygen Scavengers

When products are extremely sensitive to presence of oxygen, oxygen scavengers provide an excellent way to extend product shelf-life and ensure freshness and/or product efficacy. Oxygen scavengers reduce the level of oxygen in the headspace of the package and ensure that any oxygen permeating through the package is consumed. Because oxygen scavengers have a finite absorption capacity, they must be used with a passive barrier. The appropriate passive barrier material will be dependent upon the percent oxygen permissible in the headspace and the shelf-life of the product. The oxygen scavenger must be separated from the product with a function barrier.

Two types of oxygen scavengers are commonly used. The first are ferric compositions. They are moisture activated. Because a relative humidity greater than 40 % RH is required to initiate the reaction, they are not appropriate for dry products.

The second approach is to use oxygen scavenging polymers. In this case, an oxidizable polymer is extruded with a transition metal catalyst (used to promote the formation of free radicals) and a photoinitiator (to activate the reaction). Ultraviolet light is used to trigger the oxidation mechanism.

Oxygen scavengers are very effective in reducing the oxygen level in a package as illustrated in Chart 2.

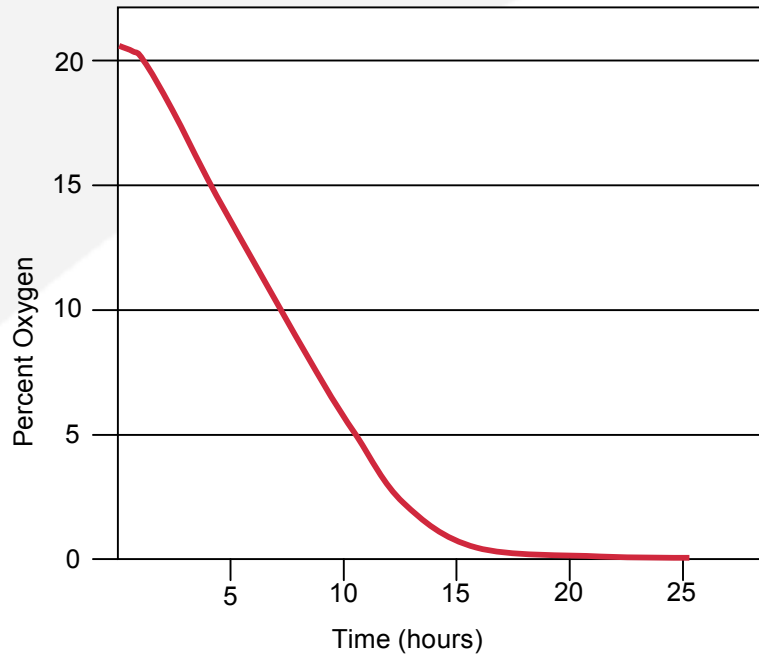


Chart 2: Oxygen Consumption

Moisture Scavengers

Moisture scavengers are created by incorporating a desiccant into a polymer layer. The choice of the desiccant is dependent upon the end humidity desired. If the goal is to maintain the humidity at a specific level, hydrate forming salts are used. These salts will not absorb water until the relative humidity at which the first hydrate forms is reached. The reaction is reversible so the salts “breathe” allowing relative humidity to be maintained.

Chemically reactive agents are used when the level of humidity is to be minimized. The reaction that consumes the moisture is irreversible. Chemically reactive agents have a finite absorption capacity that is dictated by the concentration of the agent and the thickness of the layer containing the agent. Because chemically reactive agents will continue to take up water until the reactant is consumed, extremely low humidity levels may be achieved.

CONCLUSION

There is no one ideal barrier material for all products. Achieving the correct balance of barrier, performance, and economics is very much application dependent. Fortunately, we have a wide variety of clear high barrier materials from which to choose.

With the advances in SiO_x and Al_2O_3 coated products, clear barrier options exist that can provide barrier properties comparable to or even better than aluminum foil and often at a lower price. Package performance can be further enhanced through the use of active packaging. Today, even the most demanding products can be packaged in clear materials.