BARRIER ENHANCEMENT USING ADDITIVES

Peter Maul
President
Nanocor, Incorporated

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Introduction

Three decades of explosive growth have made plastic a dominant form of packaging worldwide. Among plastic's attributes are flexibility, clarity, low cost, shelf appeal, and ease of transport, storage and use. But the most important feature for food and beverage packaging is delivering to the consumer products that are fresh and safe. This often involves maintaining performance over long intervals between actual production and eventual consumption.

This time interval, commonly known as "shelf life", is increasing as food and beverage producers seek to distribute their products on a global basis and as plastics encroach upon areas previously the bastions of metal and glass packaging. For many foods and beverages the limiting shelf life factor is the package's resistance to gas intrusion, exemplified by oxygen and water vapor. For other situations it is retention of gases, CO_2 for example, and aromas. In either case the solution is providing barrier to the movement of molecules through the plastic matrix comprising the package.

This paper overviews general approaches to enhancing plastic package barrier and provides details about the use of additives to accomplish the goal. Particular emphasis is given to the role of nanotechnology in barrier packaging.

General Barrier Approaches

Even novice package engineers know all plastics are permeable, and significant work has been done to devise ways to improve it. The most common approaches are outlined below.

Make a plastic article and coat it. Both flexible film and rigid containers are coated with ultra thin layers of materials that provide high intrinsic barrier. A variety of vapor deposition technologies are used to adhere coatings of aluminum and silicon oxides. A newer variant uses microwave plasma deposition to deliver amorphous carbon coatings onto the interior surfaces of beverage containers. Another approach consists of coating the outside surface of a package, usually a bottle, with high barrier epoxies, using spray or dip technology. Coated articles have an established niche, but they are limited by the level of adherence between the coating and plastic substrate. The rigors of filling and transporting can compromise the coating and hence shelf life. Exterior coatings can scratch off. Interior ones can crack or delaminate due to package creep after filling.

Blend high barrier plastics into medium barrier ones. Modern compounding technology affords the engineer opportunities to blend high and medium barrier plastics. This cost-driven approach requires intimate incorporation so that small micelles of high barrier polymer are created and evenly distributed. Generally high barrier plastics have miscibilities and refractive indices quite different from their medium barrier hosts. Unfortunately, blend levels are only in the high single digits before clarity suffers, limiting this approach to shorter shelf life applications.

Multilayer structures containing barrier layers. This approach has grown rapidly in the last decade. It consists of embedding a thin (3-10%) layer of high barrier plastic within at least two layers of structural plastics. By properly choosing the candidates, one can fully utilize intrinsic barrier and protect the barrier layer from high relative humidity. Because the barrier is embedded, it is also protected from abrasion. Miscibility problems are avoided, and clarity is good. Layer adherence can be a problem and tie adhesives may be needed. Resins must be chosen with thermal stability and process window in mind. A final issue is recyclability, because barrier layers may need to be delaminated and removed before reuse. These limitations aside, a finished article can be filled and transported with ease. Long shelf life can be attained at reasonable cost.

Upgrade plastics with barrier-enhancing additives. Although this concept is not new, it has only recently become feasible with the advent of advanced material technology. Two commercial approaches are in use: oxygen scavengers and nanoclays. As the additive term implies, the approach consists of incorporating functional materials directly into a plastic matrix, then using the upgraded plastic as a component of an article. In the case of oxygen scavengers, the upgraded plastic may be the only component. In the case of nanoclays, it is usually, but not always, used as a barrier layer of a multilayer structure. Commercial oxygen scavengers are incorporated into PET or polyamides while commercial nanoclays are incorporated primarily into polyamides. Because these additives become part of the polymer matrix, concerns about adherence, scratching and delamination are virtually nil. The additives are used at levels of 2-8% and they are miscible, so clarity is good.

Oxygen Scavengers

The moniker, "scavenger" is not scientifically correct because these products work by consuming oxygen in a classic oxidation reaction. An oxidizable plastic is used for the reaction, which is catalyzed by a transition metal, usually cobalt[1]. Typically the oxidizable plastic is PET or polyamide. The reaction is triggered by humidity moving through the plastic matrix.

Oxygen scavengers are called active systems because the reaction begins immediately upon exposure to humidity and of course oxygen. They become "active" and stay active until there is insufficient catalyst to sustain the oxidation reaction. At this point they are spent. Therefore oxygen scavengers have a specific life after which they cease to provide meaningful barrier. However, scavengers are highly effective at removing oxygen, especially during the first half of their life cycle. Scavengers not only remove oxygen as it ingresses into the package, but also as it egresses from the package headspace into the wall. And because dissolved oxygen in beverages tends to migrate into the package due to gradient affect, it is likewise removed. In a properly designed package and under the right conditions, scavengers can easily hold product oxygen at 1ppm for a six month shelf life.

Barrier performance for active systems is highly dependant on package surface area/volume ratio. Large surface/volume limits cost effective performance. For this reason oxygen scavengers have primarily been used for bottled products.

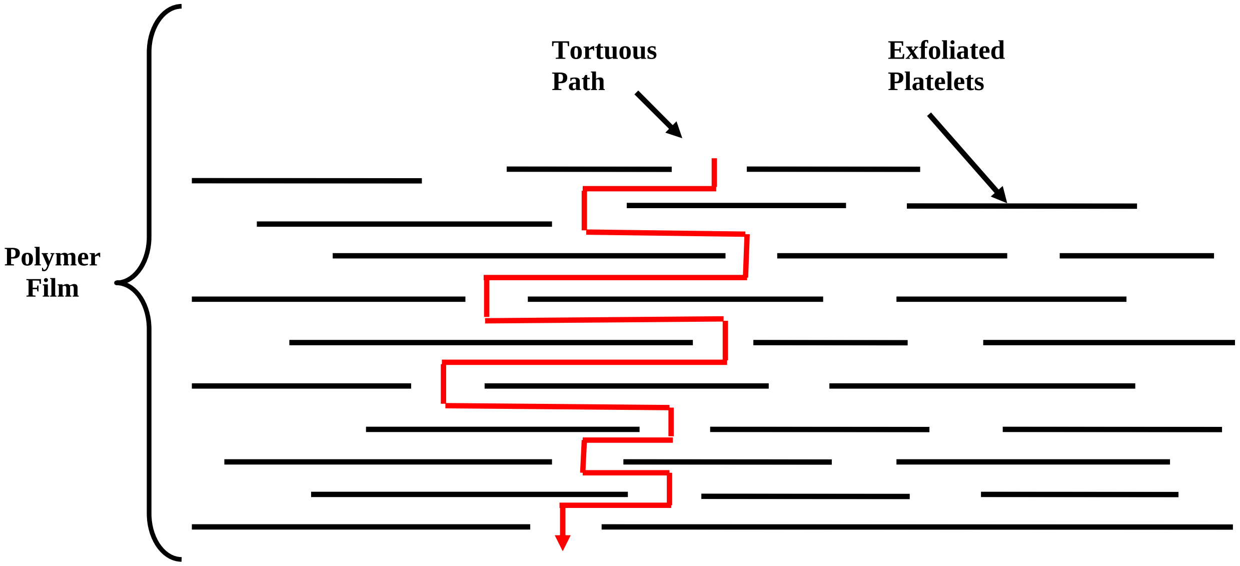
There are five significant producers, offering scavenging systems in different formats. One offers the scavenger in a PET masterbatch, which can be dosed into any bottle grade PET during manufacture. Another supplies the entire PET resin containing scavenger. A third offers scavenger incorporated into a polyamide blend for use as the barrier layer in multilayer bottles. Finally, two bottle producers sell multilayer bottles containing proprietary scavengers in the polyamide inner-layer.

Scavenger Products & Producers:

PRODUCT	REGION	PRODUCER	RESIN BASE (FORMAT)	WEBSITE
Amosorb™ DFC	**All**	**ColorMatrix**	**PET (Masterbatch)**	**www.colormatrix.com**
Polyshield™	**Europe**	**Invista**	**PET (Resin)**	**www.invista.com**
Aegis™ OX	**All**	**Honeywell**	**Polyamide Blend (Resin)**	**www. honeywell.com**
Oxbar™	**All**	**Constar**	**Polyamide MXD6 (Bottle)**	**www.constar.net**
Bindox™	**Europe**	**Amcor**	**Polyamide MXD6 (Bottle)**	**www.amcor.com**

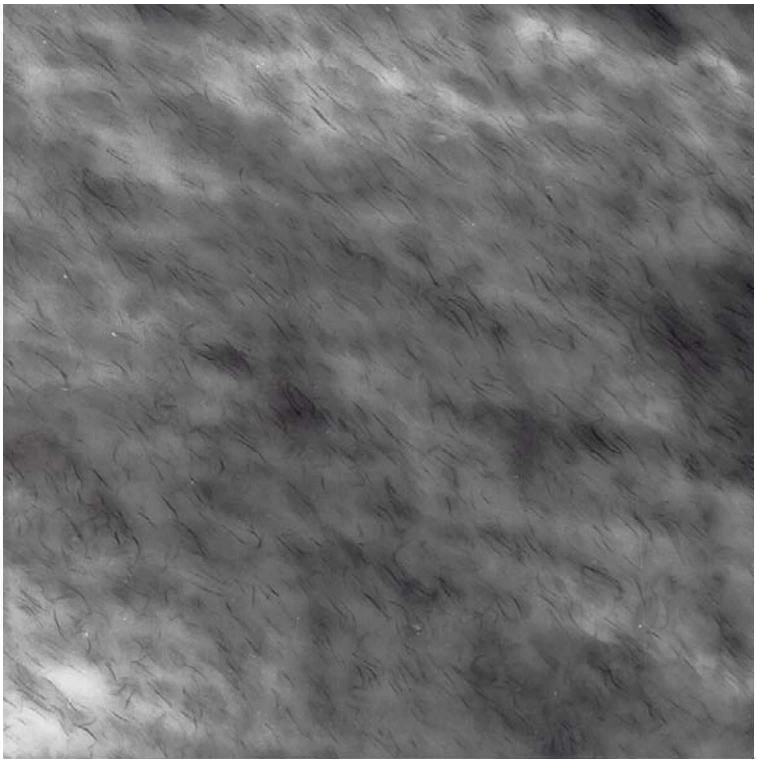
Nanoclays

Nanoclays refer to a category of clay minerals with a specialized structure, characterized by a platey morphology. The platelets have submicron dimensions, excepting their thickness, which is only about one nanometer. This dimensional disparity results in large aspect ratio, a property conducive to barrier enhancement based on the principle of tortuous path migration.[2]



Nanoclays create a “passive” barrier by impeding the diffusion of gases and aromas as they attempt to permeate through a plastic matrix. In this manner they differ from oxygen scavengers. Rather than being specific to just one gas, ie oxygen, passive barriers impede all gases to one degree or another. A second distinction is that they do so over time without losing activity. Nanoclays deliver the same rate of barrier enhancement regardless of time.

In their natural state nanoclays exists as agglomerated bundles, consisting of thousands of platelets held together by van der Waals forces. To optimize barrier and promote good clarity, the platelets must be separated in the plastic matrix through a process termed exfoliation.



PA6 Nanocomposite by TEM

By combining surface compatibilizing agents and process shear, commercial nanoclays can achieve 95%+ exfoliation and even distribution within polyamide plastics. The result is known as a plastic nanocomposite.

Proper control of exfoliation is best done by polyamide producers and compounders. There are currently eight nanocomposite barrier products available. Seven are based on polyamide 6 and one is a specialized polyamide known as MXD6.

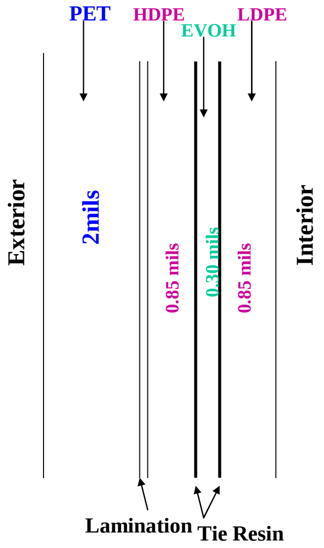
Polyamide Nanocomposite Products & Producers:

PRODUCT	REGION	PRODUCER	RESIN BASE	WEBSITE
Durethan® LDPU	**Europe**	**Lanxess**	**PA6**	**www.lanxess.com**
NycoNano™	**US**	**Nycoa**	**PA6**	**www.nycoa.net**
Aegis™ NC	**US**	**Honeywell**	**PA6**	**www.honeywell.com**
Nanoblend™	**Europe**	**PolyOne**	**PA6**	**www.polyone.com**
Nanomide™	**Asia**	**NanoPolymer**	**PA6**	**www.nanopolymer.com**
Ecobesta®	**Asia**	**Ube Industries**	**PA6 copolymer**	**www.UBE.com**
Systemer	**Asia**	**Showa Denko**	**PA6**	**www.showadenko.com**
Imperm®	**All**	**Nanocor**	**MXD6**	**www.nanocor.com**

PA6 Nanocomposites. The nanoclay content of commercial nanocomposites varies from 2-8%. Above this range exfoliation becomes increasingly difficult and its effect on polymer rheology creates processing problems during package conversion. Commercial products fall into two general categories: regular and high load. Regular products have nanoclay loading in the 2-4% range and high load 5-8%. Regular load products bring 2 times barrier improvement for oxygen and water vapor transmission. High load products are 4-5X better than neat polymer and about 2X better for CO_2.

Standup Pouch Application. Standup pouches have grown ten-fold in the past decade with nearly half of their consumption in Europe. Pouches are competing successfully against metal cans because they consume only half of the energy during production and require only half of the shelf space. In general, pouch construction must be robust to provide the “stand-up” feature. Many pouches consist of seven layers with a total thickness of 4 mils (100 microns). Many also contain an oxygen barrier, usually EVOH.

Current Pouch Construction



✓4 mils total
✓7 layer structure
✓OTR: 0.583 cc/100in^2 day

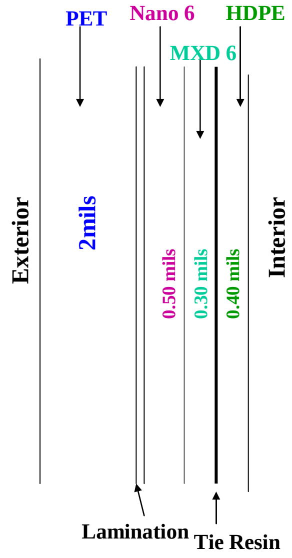
High load nanocomposite PA6 is an obvious candidate for structure down-gauging, because it provides increased longitudinal stiffness in addition to increased barrier. Stiffness is expressed as Young's Modulus, which increases five-fold over neat PA6, the same magnitude as its barrier increase.

PA6 Versus Nano-PA6

Material	Young's Modulus (Mpa)	OTR (cc mil/100 in^{2}day)
PA6	140	2.91
Nano-PA6 (5% nanoclay)	705	0.58

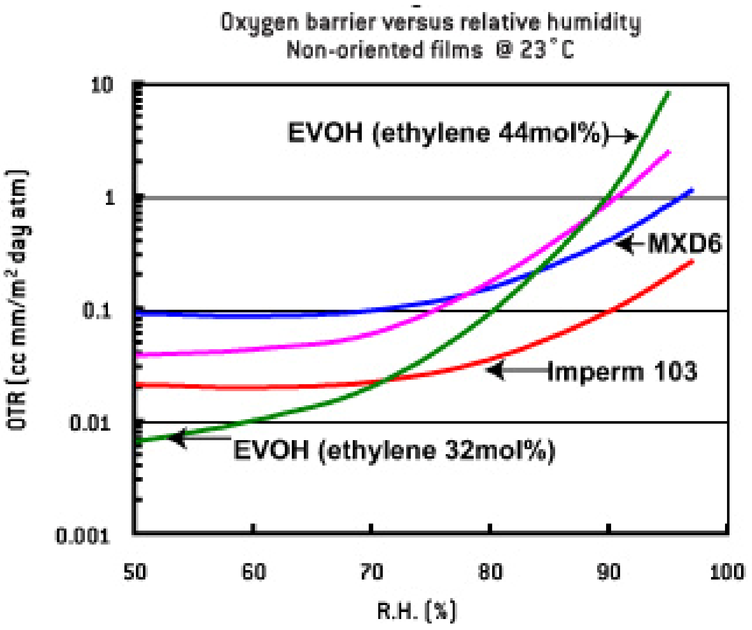
In this example, the desire was to cost-reduce a standup pouch containing barbeque sauce. The incumbent barrier was EVOH. By substituting a nano PA6/MXD6 combination and by taking advantage of the beefed-up Young's Modulus, the total structure was down-gauged 20% and the number of layers was cut from seven to six without compromising barrier or shelf life. Overall cost savings were nearly 7%.

Down Gauged Structure



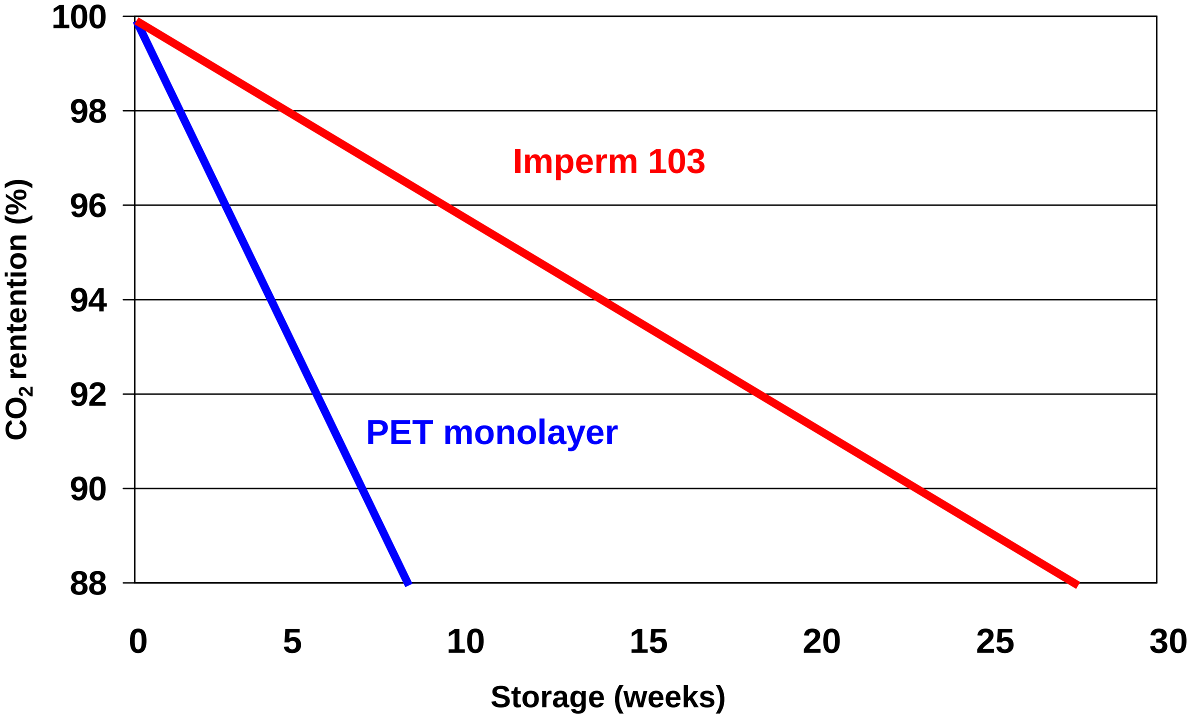
✓3.2 mils total
✓6 layer structure
✓OTR: 0.600 cc/100in^2 day

<u>MXD6 Nanocomposites (Imperm®).</u> Imperm is based on a unique polyamide called meta-xylylene adipamide (tradename MXD6), which is itself a high barrier plastic. With the addition of nanoclay, it exhibits exceptional barrier. Oxygen barrier improves by a factor of 5 times and exceeds ethylene vinyl alcohol (EVOH), particularly at high relative humidities and especially at high ambient temperatures. Water vapor transmission is cut in half. Aroma permeation is very low. CO_2 barrier exceeds any and all commercially available resins.



Imperm's impact on CO_2 retention makes it attractive for the rapidly advancing plastic beer bottle sector, as well as smaller portion carbonated soft drink (CSD) bottles. Both applications utilize PET multilayer construction, ideal for marriage to polyamide barriers. PET is a relative newcomer to beer packaging, but it has been used for decades in CSD. What is different now is that small CSD bottles must have higher barrier built into them to satisfy their high surface/volume ratio. Small portion monolayer CSD bottles have short (8 weeks) shelf life. But the addition of 3% Imperm nearly triples it, providing ample shelf life for problem-free distribution.

Bottle Shelf Life

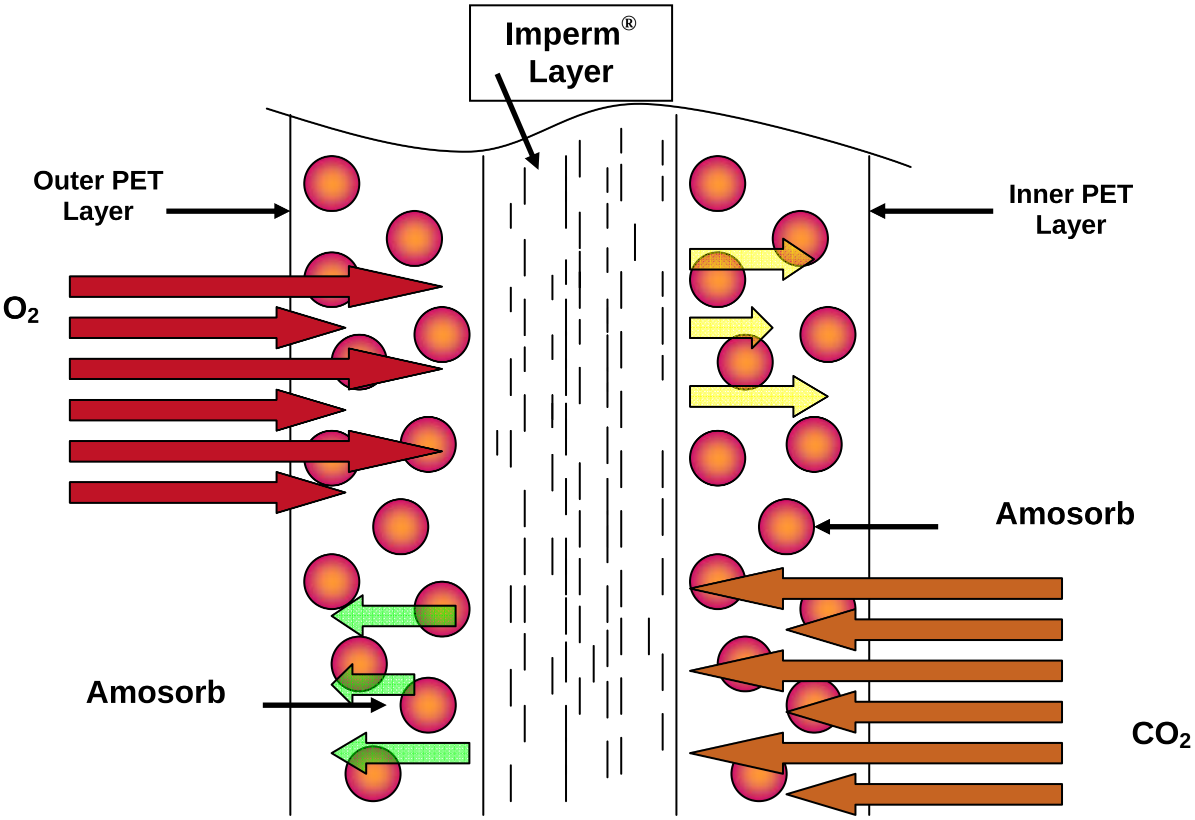


Imperm Application. Plastic beer bottles of volume 500 ml or less require significant barrier protection against oxygen ingress. In addition they require considerable barrier to CO_2 loss. In this respect beer packaging is perhaps the most demanding for barrier enhancement. A European producer wished to package lager beer in a 330 ml bottle and achieve five month's shelf life. During this period total oxygen ingress was limited to 2 ppm and CO_2 loss could be just 10%. Finally the producer wanted to position himself with a recyclable bottle.

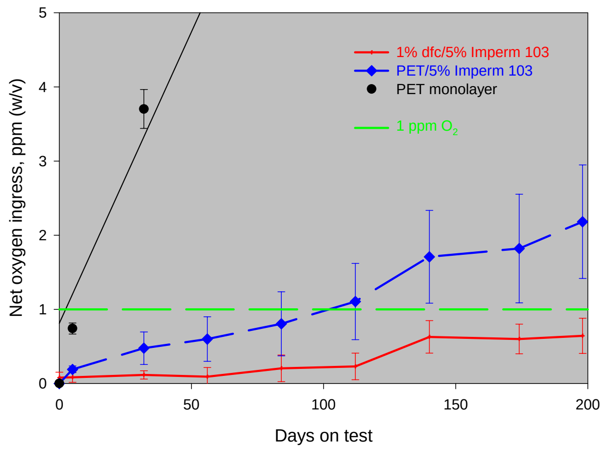
The solution is a 30 gram weight bottle with a simple PET/Imperm/PET construction. Imperm is used at 5% of the total structure. No tie adhesive is required. The bottle exhibits about 3% haze. Recycling studies show 93% of the barrier layer can be removed using a standard recycling protocol. The bottle cost is about 10% premium over a can.

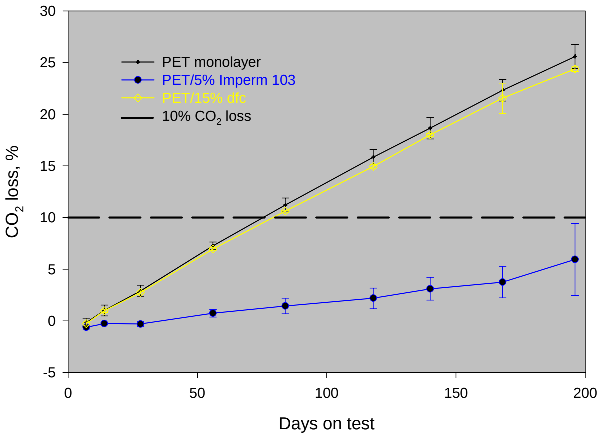
Active/Passive Combination Systems

European beer producers are pushing the limits of package barrier technology by requiring shelf life of six months or greater for premium beers. These beers are especially sensitive to oxygen. Add to this the requirement of no more than 10% CO_2 loss and one confronts a sizable technical challenge. Add to this the economic goal of creating a bottle with a cost premium over cans of no greater than 15% and the challenge might seem insurmountable. Not so.



A combination barrier system has been devised to meet these criteria by using Amosorb™ DFC oxygen scavenger to augment the O_2 barrier of Imperm. Barrier synergism is depicted in the schematic above. 1% Amosorb is added to the PET layers and 5% Imperm constitutes the core layer. Most of the ingressing oxygen is scavenged by the Amosorb in the outer PET layer, while Imperm with its passive barrier "protects" scavenger located in the inner PET layer. This inner-layer scavenger is consequently available to take care of headspace and dissolved oxygen. Meanwhile Imperm also does its usual job in retaining CO_2.





Courtesy of ColorMatrix Corporation

As the left graph shows, the combination system holds oxygen ingress to less than 1 ppm over six months, something that could not be accomplished with Imperm alone. Likewise Imperm achieves the CO_2 loss goal (right graph), something Amosorb is incapable of doing. But together the goals are met. From an economic standpoint oxygen synergy is crucial to reducing the use level of Amosorb. Without this synergy bottle cost will exceed the 15% premium criteria.

Summary

Material technology advances have paved the way for use of additives to enhance barrier in plastic packaging. Both oxygen scavengers and nanoclays are well into commercial use with established applications. Scavengers excel for O_2 barrier, but care must be exercised to correctly estimate their effective life. Nanoclays excel for CO_2 barrier, while also delivering good O_2 barrier, making them ideal for carbonated beverage packaging. Combining scavengers and nanoclays creates synergistic systems that take package barrier to the next level.

References

[1] US Patent # 5,021,515, issued June 4, 1991

[2] L.E. Neilson, Journal of Macromolecular Science (Chem), A1 (5), 920-942, 1967.

[3] US Patent # 6,232,388, issued May 1, 2001.