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EVAL™

Value Proposition of Ethylene Vinyl Alcohol (EVOH) for Food and Beverage Packaging

Edgard Chow

Introduction

Ethylene vinyl alcohol (EVOH) copolymer is a thermoplastic that is best known for its high oxygen barrier properties and the associated benefit of extension of shelf life of packaged food. EVOH is a saponified copolymer of ethylene and vinyl acetate as described by the following molecular formula.

$$—[CH_2\text{-}CH_2]_m\text{-}[CH_2\text{-}CH(OH)]_n—$$

Figure 1 – Chemical Structure of EVOH

The oxygen barrier of EVOH is exponentially better when compared to polyolefins and other ethylene copolymers and is inversely proportional to its ethylene content. For example, a 32 mol% ethylene EVOH offers a higher barrier (lower permeability) than a 44 mol% ethylene EVOH.

EVAL™	Ethylene (mol%)	Density (g/cm³)	Melt Temperature (°C)	O_2 Permeability (cc.20µm/m².day.atm)
L171B	27	1.21	190	0.1
F171B	32	1.19	183	0.3
C109B	35	1.18	177	0.5
H171B	38	1.17	172	0.7
E171B	44	1.14	165	1.9
G176B	48	1.12	157	3.7

Table 1 – Basic Properties of EVOH

Relative to other traditional barrier materials such as glass, aluminum foil, and metal cans, EVOH offers advantages that have a positive impact along the food supply chain[1].

Attribute	EVOH	Glass	Foil	Metal can
Density (g/cm³)	1.12~1.22	2.4	2.7	7.8
May be used in transparent packaging	Yes	Yes	No	No
May be heated in microwave ovens	Yes	Yes	No	No
May be inspected with metal detectors	Yes	Yes	No	No
Abuse resistance	Yes, if used in thin layers with polyolefins	Breaks on impact	Tends to flex crack	Dents on impact
Tendency to be recycled	Process scrap reincorporated into rigid barrier packaging. Preferred barrier for developing post-consumer recycling infrastructure	Existing infrastructure and energy intensive	Complex to separate multiple materials	Existing infrastructure and energy intensive

Table 2 – General Properties of Barrier Materials

Background

As population density and urbanization increase, purchasing fresh goods becomes more challenging as the time available for shopping, preparing, and cooking food becomes more limited. The convenient supply of refrigerated and shelf stable food is only possible due to food preservation and high barrier packaging. Innovation in materials, coextrusion equipment, and ingenuity in packaging development have made it possible to optimize packaging with less materials while maintaining the required performance. More recently, sustainability initiatives have accelerated the development of "monomaterial" packaging targeting structures that can be recycled while still delivering the high level of performance needed to effectively protect food.

Coextrusion and Converting Technologies

Innovation in EVOH resin technology has expanded its processing window so that it can be used in most polymer converting techniques including extrusion coating and extrusion lamination, blown film, cast film, extrusion blow molding, cast sheet extrusion, pipe-extrusion, tube extrusion, injection molding, and others. The recommended processing temperature for EVOH (200 – 230°C) is similar to conditions used to process polyolefins.

The use of a "tie resin" is required for EVOH to bond to non-polar materials like polyolefins. Polyolefins serve the functions of abuse resistance, water vapor barrier, and sealant properties which are essential for the packaging to render its full protective function. For example, in a 5-layer PE/tie/EVOH/tie/PE structure, a linear low-density polyethylene (LLDPE) that is functionalized by grafting maleic acid anhydride along the polymer chain is the commonly used technology. Different adhesion mechanisms are responsible for the adhesion at PE/tie interface versus the tie/EVOH interface. The tie resin adheres physically to the polyethylene skin layers through chain entanglement and anchorage mechanisms while it adheres chemically to the EVOH layer by forming covalent bonds with the hydroxyl groups.

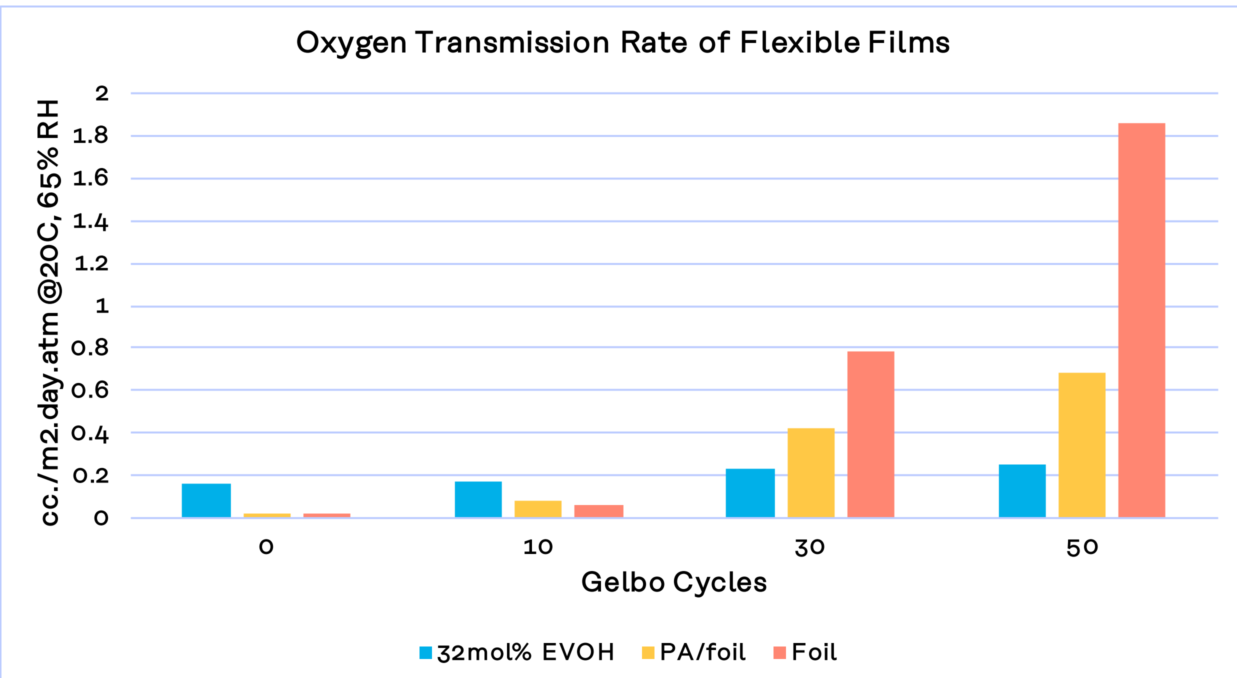
Since its inception in the 1970s, coextrusion equipment technology has continued to make inroads on innovation as simple 3-material, 5-layer systems have evolved into more sophisticated ones. This is most evident in flexible packaging where 7-layer, 9-layer, and 11-layer dies are now reliably producing films with thin layers of high-performance materials. Added to the development of these streamlined systems is the use of automatic layer correction die technology that reduce overall thickness variation. Cartridge heaters located at defined intervals (typically every 1~2") along the lip of the die is the most common technology. The heaters are used to slightly tighten or open the die gap in a localized region. It is common for auto-correction dies can produce films with overall thickness variation ranges by thickness of ±5% for annular dies and ±2% for flat dies. In blown film processes, air ring technology to make localized flow rate changes to cool the bubble has also been implemented. Adjustment in total thickness is measured by gauges that travel across the transverse direction of the film being extruded. Capacitive, X-ray or nuclear (gamma or beta) gauge sensors provide feedback to a software that optimizes the rate of adjustments as needed.

High barrier film coextrusions are often used to package dry and liquid goods in vertical form-fill-seal equipment. Barrier films may be transparent and unprinted for institutional or food service applications that are contained in a secondary packaging such as a cardboard box; or they may be pigmented, and surface printed for retail packaging. Printing of retail packaging is necessary to convey essential branding and nutritional information to the consumer.

Barrier films are also commonly laminated to oriented substrates for lidding film or standup pouch formats. In these formats, printed artwork is often reverse printed onto the oriented substrate so that it can be trapped between it and the sealant film. Historically, biaxially-oriented polyethylene terephthalate (PET) films have been used as the oriented film of choice for to its excellent transparency, dimensional stability, and heat resistance properties. Heat resistance is an important attribute to be able to seal trays and pouches at high speeds without burning or squeezing out the sealant layer. Recent circular economy initiatives have led to the development of "monomaterial" alternatives such as BOPP, BOPE and even MDO-PE films that are compatible with sealant film. To compensate for the reduction in heat resistance of the oriented PE or PP films, some varnish and other heat resistant coatings are also under development.

EVOH: A Reliable Barrier

Relative to metallic barriers, EVOH offers considerable advantage in abuse resistance. If selection of barrier materials was based solely on oxygen barrier performance and considered independently from flex crack resistance or performance in use, then foil or metallized films would dominate this application. In Figure 2 the change in oxygen transmission rate (OTR) with increasing Gelbo cycles can be observed for three structures.

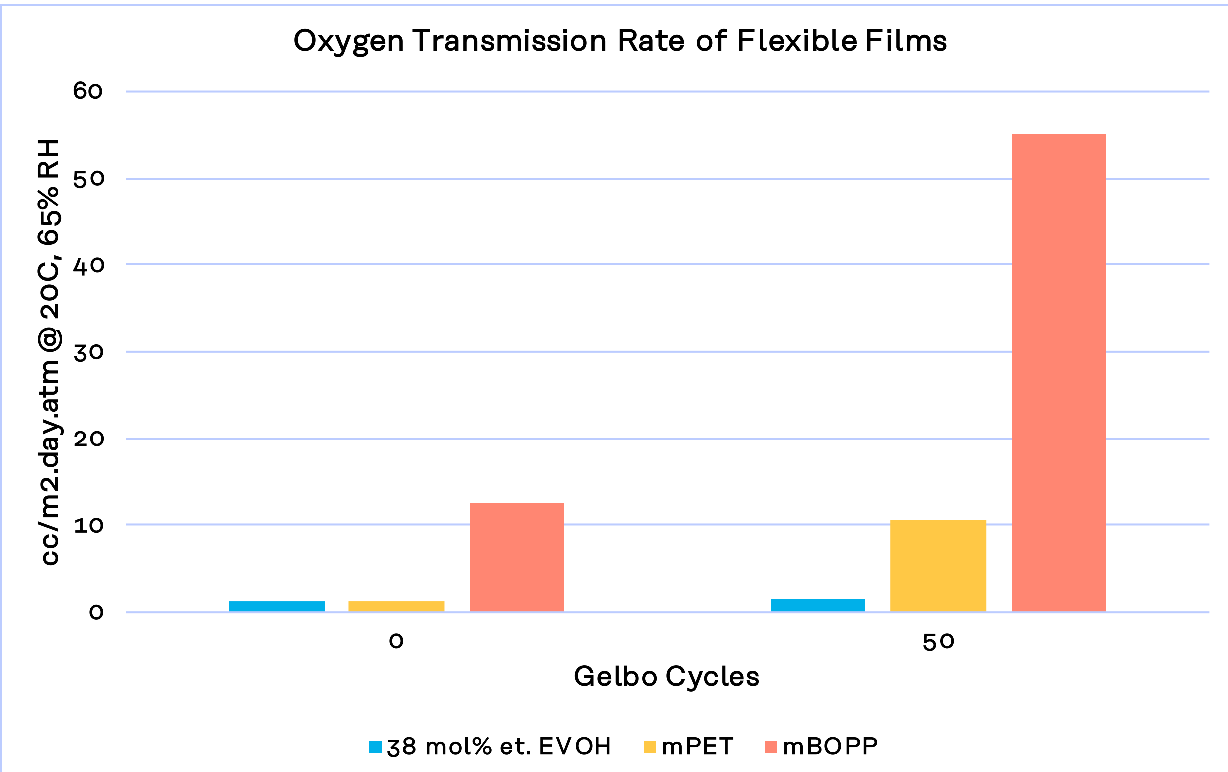


32mol% EVOH = Coextrusion of PE/tie/EVOH/tie/PE = 65/5/12/5/65 µm
PA/Foil = Extrusion lamination of BOPA/tie/foil/tie/PE = 20/12/8/12/100 µm
Foil = Extrusion lamination of PE/tie/foil/tie/PE = 65/12/8/12/38 µm

Figure 2 – Flex-crack Resistance of EVOH vs. Aluminum Foil

While the oxygen barrier of EVOH is initially lower than that of foil, due to the higher flex crack resistance of EVOH after as few as 30 cycles the barrier performance of Foil and PA/foil laminations are significantly worse than EVOH[2].

A similar result is observed when comparing the oxygen barrier and flex crack performance of a coextrusion of 32mol% EVOH versus metalized PET and metalized BOPP films. In Figure 3 the change in barrier with increasing flex crack cycles of three structures is observed.



38 mol% et. = EVOH = coextrusion of PE/tie/EVOH/tie/PE = 20/7/7/7/38 µm
mPET = lamination of PE/mPET//PE = 22/15/32 µm
mBOPP = lamination of PE/mBOPP/PE = 39/18/51 µm

Figure 3 – Flex-crack Resistance of EVOH vs. Metalized Films

It can be observed that after 50 Gelbo cycles the PET lamination exhibited a ten-fold deterioration of oxygen barrier[2]. As a guideline any application that requires a metalized PET lamination becomes a viable opportunity for an EVOH coextrusion. EVOH has replaced metalized PET in numerous liquid packaging applications including the iconic wine bag-in-box format that has been around for around 50 years.

Food Processing and Specifications

The shelf life of food is defined as the time required for food to become unpalatable in expert, organoleptic test panel evaluations. Food is subject to deterioration via chemical, physical, and microbiological changes. The combination of food preservation techniques and high barrier packaging help preserve the intrinsic properties of the food (pH, water activity, lipid content, etc.) until its point of consumption.

Low acid food can be retorted (cooked and sterilized) in PP/EVOH/PP containers to safely deem it shelf stable for 12 to 18 months. Similarly, pasteurization or hot filling provides shelf stability to high acid food such as tomato-based sauces and fruit juices. Milk can be made shelf stable if it is ultra-high temperature (UHT) treated and then filled in high barrier packaging in an aseptic environment. Keeping fried potato chips from going rancid and stale for several months requires the combination of modified atmosphere packaging (MAP), and high barrier packaging. Potato chips require packaging with high barrier to water vapor, light and oxygen that can be provided by combining opaque biaxially oriented polypropylene (BOPP) with EVOH. In the refrigerated aisle, vacuum pouches, shrink bags or vacuum-skin packaging made of PE/EVOH/ionomer or PE/EVOH/OE protect fresh meat against the proliferation of bacteria and microorganisms to significantly improve their shelf life. PE/EVOH/PE barrier films provide the right combination of moisture and oxygen barrier to minimize changes in water activity and microbial growth of the cheese for vacuum packed block and sliced cheese and MAP packaged grated cheese. Regardless of the application, limiting the amount of oxygen ingress into the packaging is key to minimizing the deteriorative reactions that alter the shelf life of food.

Emerging food processing techniques include High Pressure Processing (HPP) and Microwave-Assisted Temperature Sterilization (MATS). HPP is a process that combines radiation and conductive energy to sterilize certain foods sealed flexible packaging using a high level of hydrostatic pressure (400-600 MPa) for a short period of time (1-5 minutes) to microorganisms and pathogens by several log cycles.

The selection of the suitable grade of EVOH for a specific application depends on both the intrinsic attributes of the food and numerous extrinsic conditions that can trigger the critical index of failure that defines the shelf life of food. For most cases food formulations are unique to each brand owner and thus, there is limited published information on food requirements. Table 3 provides oxygen and water vapor sensitivity of various foods to oxygen ingress and water vapor gain or loss.[3]

Food Type	Maximum Allowable O_2 Ingress (ppm)	Maximum Allowable H_2O Gain or Loss (%)
Canned milk, canned proteins	1-5	3% loss
Beer, wine, ale	1-5	3% loss (20% CO_2 loss)
Canned fruits, tomato sauce, soy sauce	5-15	3% loss
Dried foods	5-15	1% gain
Fruit juices, drinks	10-40	3% loss
Carbonated soft drinks	10-40	3% loss (<15% CO_2 loss in 15 weeks)
Oils, shortening, salad dressings, mayonnaise, peanut butter	50-200	10% gain

Table 3 – Food Sensitivity Guidelines

Synergies of Polymers

While EVOH is often able meet the oxygen barrier requirements, other materials like polyethylene are called upon to provide the water vapor barrier to keep moisture gain or loss and changes in textural properties to a minimum. The synergy of polyolefins and EVOH make it possible to control microbial growth. The water vapor barrier of polyolefins prevents texture and agglomeration changes that affect the water activity of the food and EVOH controls the proliferation of mold and yeast.

Material	Oxygen Permeability @ 20°C, 65%RH (cc.20μm/m².day.atm)	Water Vapor Permeability @ 38°C, 90%RH (g.25μm/m².day)
EVAL™ F171 (32 mol% Et.)	0.3	45
EVAL™ E171 (44 mol% Et.)	1.9	28
PA6	45	220
PET	150	13
PP	3000	11
HDPE	2300	6.2
LDPE	10000	19

Table 4 – Permeability of Oxygen and Water Vapor through Polymers

In addition to oxygen and water vapor barrier, there are other properties that are critical in the role packaging plays in the protection of food. These include preservation of vitamins above a critical threshold and minimizing changes in flavor and aroma of the food. Fruit based products such as diced fruit, fruit pulp, fruit juice, dried fruits and even artificial flavors found in various cereals and snacks are all prime examples where EVOH adds value in preserving vitamin C and preventing the loss of citric flavor often defined by the barrier of d-limonene that polymers provide. Table 5 compares the permeability of d-limonene through various polymers. It can be noted that EVOH offers exponentially better barrier to citric flavor versus polyolefins alone.[4]

Material	D-Limonene Permeability (cc.20μm/m².day.atm)
F171B	0.039
E171B	0.059
HDPE	1219
PP	1524

Test condition: 20°C, 65%RH

Table 5 – Permeability of D-Limonene through Polymers

Table 6 shows the transmission rate of four chemical compounds through flexibles films containing a thin EVOH layer. These specific compounds have been associated via gas chromatography olfactory technology with the aroma of various food types.[4]

Chemical Compound	Aroma (Related Food Type)	Transmission Rate (g/m².day)
Allyl Sulfide	Garlic (Croutons, snacks, dressings condiments)	0.00075
Acetic Acid	Vinegar (Cheddar cheese, cheese, snacks, condiments)	0.035
Ethyl Acetate	Artificial flavor (Citrus, berries, coconut, coffee, chocolate, honey)	0.0043
Menthol	Mint (Chewing gum, peppermint candies)	0.00099
Film structure: [HDPE/tie/EVOH/tie/EVA]32, 32mol% et. EVOH Test condition: 23°C, 75%RH, 100 ppm source concentration		

Table 6 – Transmission Rate of Aroma Compounds through a Flexible Film

Extrinsic Factors that Influence Shelf Life

Understanding the effect that food preservation technique, filling method, and transportation and storage conditions are paramount to decide the packaging format and overall design of the package from its ability to withstand the thermal and mechanical abuse that it will see in its trajectory to the consumer.

Other factors such as the packaging surface area and the net product content also influence shelf-life equation. It is important to understand that all else being constant, the smaller the package, the higher the gas barrier that is required to provide the same target shelf life. That is, the higher the surface area to volume ratio of the package, the lower the oxygen transmission rate needed to reach the same shelf life for a given application. This is evident in the marketplace in the packaging used for carbonated soft drinks. Large 2L and 3L formats can be successfully distributed using monolayer PET bottles while the single serve containers are limited to aluminum can or glass bottles.

For snacks and dry foods, modified atmosphere packaging (MAP) is employed in form-fill-seal (FFS) process to help extend the shelf life of various food. Oxygen, carbon dioxide, nitrogen, and mixes thereof are often used as a flush gas within the head space of package for this purpose. As can be appreciated on Table 7, EVOH offers the additional benefit of containing the various gas mixtures which are optimized for specific food types.

Material	CO_2 Permeability (cc.20µm/m^2.day.atm)	N_2 Permeability (cc.20µm/m^2.day.atm)
F171B	0.81	0.017
E171B	7.1	0.13
PA6	205	12
PET	110	8
LDPE	42000	3100
		Test condition: 20°C, 65%RH

Table 7 – Permeability of Modified Atmosphere Gases through Polymers

The barrier properties of EVOH can be leveraged throughout the entire food supply chain. In retail packaging, EVOH is ubiquitous in high-performance films used to package meat, cheese, and snacks, including potato chips, roasted nuts, and beef jerky. Table 6 lists a few of these structures found in supermarkets.

Format	Melt Processing	Application	Food Processing	Structure
Flexible	Extrusion coating	Instant oatmeal, tea leaves	Paper coating	Paper//tie/EVOH/tie/PE
Flexible	Cast film	Processed meat, cheese	VSP, vacuum forming	PE/tie/EVOH/tie/Ionomer
Flexible	Blown film	Meat, cheese	Vacuum bags, formed	PE/tie/EVOH/tie/PE
Flexible	Blown film	Avocado puree	HPP	PE/tie/EVOH/tie/PE
Flexible	Double bubble process	Fresh meats	Vacuum shrink bags	PE/tie/EVOH/tie/Ionomer
Flexible	Triple bubble process	Processed meats	Vacuum shrink casings	PE/tie/EVOH/tie/PE
Flexible	Blown film	Milk	UHT VFFS Aseptic	w-PE/w-PE/tie/EVOH/tie/b-PE/PE*
Rigid	Sheet extrusion	Fresh pasta, prepared food	MAP	PET/tie/EVOH/tie/PE
Rigid	Sheet extrusion	Jello, pudding	Aseptic	PS/tie/EVOH/tie/PE
Rigid	Sheet extrusion	Ready-to-eat meals, pet food	Retort	PP/Regrind/tie/EVOH/tie/Regrind/PP
Rigid	Extrusion blow molding	Coffee, roasted nuts	MAP	HDPE/Regrind/tie/EVOH/tie/HDPE
Rigid	Extrusion blow molding	Nutritional beverages	Aseptic	PE/tie/EVOH/tie/Regrind/PE
Rigid	Extrusion blow molding	Fruit preserves, fruit juices	Hot filled	PP/tie/EVOH/tie/Regrind/PP
Rigid	Extrusion blow molding	Nutritional beverages	Retort	PP/tie/EVOH/tie/Regrind/PP

w-PE = polyethylene pigmented white with titanium dioxide
b-PE = polyethylene pigmented black with carbon black

Table 8 – Typical Food Packaging Structures

EVOH layers are also used in food service (hotel, restaurant, and institutional) packaging and in intermediate and bulk packaging formats. For example, following pasteurization, tomato puree used by pizza parlors is packaged in 1000 L flexible, intermediate bulk containers. The product can be later packed in smaller 3 kg, 5 kg, or 7 kg packs, also with EVOH, for safe transportation. The concept of intermediate-sized containers has also been used to package coffee beans, rice, nuts, seeds, and powdered milk in 25-75 kg formats, commonly referred to as "hermetic bags." The benefit of food preservation has also been commercialized in liners of shipping containers, or "flexitanks," with a capacity range of 8,000-36,000 L for the transcontinental shipment of various commodities, including olive oil, concentrated juice, and wine. In the wine industry, EVOH has been shown to be effective in minimizing the ingress of organic solvents, haloanisoles, and naphthalene, commonly found as tainting compounds for wine shipped in this format. Table 9 summarizes the permeability of aromatic solvents through EVOH and HDPE.[5]

Solvent	E171B (44 mol% et. EVOH)	HDPE
	x 10^{-14} m^2/s	
Benzene	2.3	1000
Toluene	2.6	3000
Ethyl benzene	1.6	5000
m&p Xylene	1.5	6000

Condition: 23°C, 50%RH
Source concentration: 25ppm for each of the four BTEX components

Table 9 – Permeability of Aromatic Solvents through EVOH and HDPE

EVOH also offers protection of food against low molecular weight components sometimes present in packaging itself such as plastics additives, adhesive components, and printing inks. There are increasing concerns about the migration of mineral oil components into food. In 2009, the BfR (the German Federal Institute for Risk Assessment) came to the conclusion that the migration of mineral oil may pose a risk to the consumers and recommended minimizing the migration of mineral oil components into food. In 2012 the EFSA (European Food Safety Authority) stated in a scientific opinion that exposure to mineral oil may pose a human health hazard and that a revision of existing acceptable daily intake is warranted.

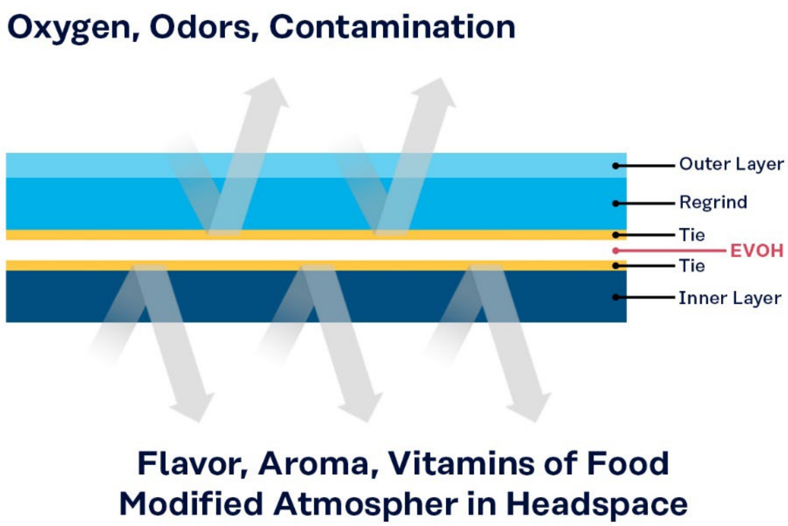
Material	Thickness (µm)	1% breakthrough @ 60°C	1% breakthrough @ 22°C (calculated)
LDPE	60	0.01 days	0.44 days
BOPP	50	0.13 days	5.9 days
PET	12	> 85 days	> 10.7 years
PA	20	> 85 days	> 10.7 years
E105B, 44mol% et. EVOH	5*	> 56 days	> 7.1 years
F171B, 32 mol% et. EVOH	5*	> 84 days	> 10.6 years
Testing conducted using Gas Chromatography on a [PE/tie/EVOH/tie/PE]60 coextruded film*			
Table 10 – Time for the Breakthrough of Mineral Oil through Various Polymer			

Permeation testing of various polymers demonstrated that EVOH can act as a functional barrier to reduce the migration of substances to a toxicologically and organoleptically insignificant level during normal or foreseeable conditions of use.[6]

Summary

As population density and urbanization increase the distribution of packaged foods becomes more and more indispensable. While food preservation techniques prevent the growth of microorganisms, and slow the oxidation of fats that cause rancidity, high barrier packaging minimizes the ingress of oxygen to retard the undesired chemical reactions in the food.

The strong presence of EVOH in food packaging stems from both its ability to limit the transport of gases and other chemical compounds that alter the safety, nutritional and organoleptic properties of food and from its ease of processing in different polymer processing methods. In general, EVOH can contain the flavor, aroma, vitamins, and freshness of the food, while it is able to minimize the ingress of oxygen and potential contaminants into the packaging.



Relative to metallic barriers such as foil and metalized films, EVOH offers considerable advantage in abuse resistance. The barrier properties of EVOH can be leveraged throughout the entire food supply chain. In retail packaging, EVOH is ubiquitous in high-performance films used to package meat, cheese, and snacks, including potato chips, roasted nuts, and beef jerky. EVOH has made its way into the food service industry in bag-in-box and intermediate flexible liners and even into bulk transportation of juice concentrates and wine in flexitanks. As sustainability and circular economy gain momentum in the packaging industry, it is anticipated that EVOH will enable packaging engineers to design structures that impart the needed functionality to reliably extend the shelf life of food, while minimizing packaging weight and cost, and overall impact on the environment.

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KAI Corporate Headquarters
2625 Bay Area Blvd. Ste 600
Houston, TX 77058

Kuraray.us.com

KAI EVAL Plant
11500 Bay Area Blvd.
Pasadena, TX 77507