New EVAL® EVOH Resins for Flexible Packaging

Robert B. Armstrong
EVAL Americas (USA)

ABSTRACT

Due to higher productivity, lower cost, and diverse function, coextrusion coating has come to be regarded as an excellent method of manufacturing composite packaging. An important application for EVOH (ethylene vinyl alcohol) barrier resin is in coextrusion coating, where EVOH is used in conjunction with paper, foil and other plastics for flexible and semi-rigid containers. Taking advantage of EVOH's high speed processability and superior pinhole resistance, plus flavor, odor and gas barrier properties, EVOH/Paper, EVOH/Polyolefin, and EVOH/Paper/Aluminum containers and flexible have been very successful in the marketplace. This paper is a review of the balance of processability, thermal stability and barrier properties in various EVAL EVOH (ethylene vinyl alcohol) resins typically used in coextrusion coating. This paper will discuss the use of EVOH of varying mol% ethylene, including new grades of EVOH optimized for high speed coextrusion coating and laminating, including basic properties and processability, gas, flavor and aroma barrier properties, thermal stability, and an overview of applications and structures.

INTRODUCTION

The high barrier packaging market in the United States continues to experience strong sustained growth. EVOH (Ethylene vinyl alcohol copolymer) barrier resin is often used in new applications in high barrier flexible packaging because of its outstanding gas barrier properties, excellent organoleptic properties, and easy processability on a wide range of conventional coextrusion processing equipment.

Coextrusion coating and laminating is a technology originally developed in the nineteen forties and fifties, which has constantly evolved in the years since into a technologically sophisticated synthesis of equipment, materials and processing knowledge. Today coextrusion coating and laminating offers high productivity, low cost, and diverse function. Progress has been driven by response to consumer demands for greater convenience, variety and improved product quality. Developments to improve the original Dupont coextrusion coating die technology include automatic profile control dies, multi manifold feed blocks, gravimetric feed systems and computerized process control systems.

The development of improved equipment must be matched by improved materials, and resin suppliers of EVOH are striving to improve the barrier, thermal stability, degradation resistance and processability of EVOH resins to meet the needs of a demanding and competitive segment of the packaging industry. This paper will review the need for barrier, particularly to oxygen in flexible packaging, the value that EVOH offers in high barrier flexible packaging and the properties of EVOH which are desirable in coextrusion coating and laminating. The combination of improved coextrusion technology, processing knowledge and EVOH resins is expected to allow for continued replacement of metal and glass packaging with high barrier flexible packaging.

EXAMPLE of MARKET APPLICATION

Packaging and Degradation of Food

While innovative packaging continues to amaze in the ways that it promotes product, offers ease of opening, increases consumer convenience or differentiates one supplier from another, the primary purpose of packaging remains to contain and preserve the packaged product. Foods are by their nature perishable, and the period of time during processing and storage when foods are still of acceptable quality is defined as the useful shelf life of that foodstuff. There are three primary ways by which food products degrade, to the point where they are either unpalatable, or could be harmful to the person consuming them. The first degradation route is physical damage or bruising, which is not significant for the purpose of this paper.

The second route is through chemical changes that can cause deterioration of the food and reduce shelf life. The chemical changes can include oxidative reactions, lipid oxidation, and enzymatic actions that can change the appearance of food, and make it unfit for consumption. For example dried snacks such as potato chips are susceptible to enzymatic degradation and biological attack. Fat, which contributes to the chips flavor and texture must be protected from oxidative degradation (rancidity).

The third route is through microbiological changes, since microbes can multiply rapidly under favorable conditions, and many food products have low resistance to microbe growth once they are harvested or processed. Microbiological growth eventually results in unsavory food taste and appearance and can also cause food to become unsafe for human consumption. Some microorganisms such as *Salmonella* and *Escherichia coli* directly cause infection, while *Clostridium botulinum* and *Staphylococcus aureus* produce toxins that directly affect humans.

To maximize shelf life of food, several key environmental factors including temperature, water content and composition of atmospheric gases surrounding a product should be controlled. Given that both chemical changes such as oxidation, and microbiological growth can be accelerated in the presence of oxygen, controlling the oxygen content in a package or the rate of oxygen ingress into a package is often one of the most critical attributes of barrier packaging. A starting point for a package design could be the permeation targets' in the table below, which show the maximum acceptable oxygen gain in several different types of food.

Table I. Permeation Targets for Selected Foods

Food or Beverage	Maximum Oxygen Ingress permissible ppm (mass basis)	Maximum Water Gain or Loss % (mass basis)
Canned milk, meats, fish and poultry	1 – 5	3% loss
Beer, ale, wine	1 – 5	3% loss 20% CO_2 or SO_2 loss
Canned vegetables, soups, spaghetti, catsup, sauces	1 – 5	3% loss
Canned fruit	5 – 15	3% loss
Dried foods	5 – 15	1 % gain
Carbonated soft drinks	10 – 40	3% loss
Fruit juices, drinks	10 – 40	3% loss
Oils, shortening	50 – 200	10% gain
Salad dressings	50 – 200	10% gain
Peanut butter	50 – 200	10% gain
Jams, jellies, syrups, pickles, olives vinegar	50 – 200	3% loss

While these targets and the subsequent calculations should not be considered definitive, they can be used as a guide, and the starting point for creation of a barrier package. As an example we will consider the packaging requirements of dried foods such as potato chips as being <10ppm oxygen ingress and <1% weight gain of moisture

COMPARISION and SELECTION OF BARRIER MATERIALS

Traditionally extrusion coaters have relied upon aluminum foil to meet needs of high barrier flexible packaging. Foil is an attractive option, offering barrier to gases, moisture and radiation. Packaging comprised of foil, paper and polyethylene offer outstanding attributes at a very reasonable cost. However there are negative attributes to this type of laminate, including poor flex crack resistance, non existent thermoformability or orientability, susceptibility to attack by acidic foods, non-microwavable and opaqueness, not forgetting recycling difficulties.

The negative issues with foil can be overcome by using barrier polymers such as Nylon, PVdC or EVOH. However these polymers are all permeable to small molecule gases such as oxygen, nitrogen and carbon dioxide. A table of barrier properties to oxygen and moisture would be necessary to meet the permeation targets in Table 1. Once a reliable reference table of oxygen and moisture barrier has been secured, a package designer can then choose the material, or combination of materials that will meet the barrier target initially selected.

Table II. Barrier Comparison of Various Polymers

MATERIAL	OTR @ 25°C, 65% RH (cc.mil/100 sq. in.24hrs.atm)	MVTR @ 40°C, 90% RH (gram-mil/100 sq. in.24hrs.atm)
EVOH	0.05~0.18	1.4~5.4
PVdC	0.15~0.90	0.1~0.2
Acrylonitrile	0.8	5.0
MXD6	0.15	3.2
Oriented PET	2.6	1.2
Oriented Nylon	2.1	9.0
LDPE	420	1.0~1.5
HDPE	150	0.4
Polypropylene	150	0.69
Polystyrene	350	7~10

OTR = Oxygen Transmission Rate, or permeation rate of oxygen through material

MVTR = Moisture Vapor Transmission Rate, or permeation rate of water vapor through material

Using as an example a 28 gram (~1 oz.) package that will hold potato chips for 60 days (2 months). We assume as previously stated that the maximum oxygen ingress over 60 days is 10 ppm. To provide a factor of safety of 2, the target chosen for calculation will be 5ppm. Now assuming that the package will have an exposed surface area of 400 cm, the amount of oxygen allowed to enter the package is:

$$I_M = I_p M_p$$

Equation 1

Where I_M is the maximum amount of oxygen in grams that can enter the package, I_p is the maximum allowable ingress in ppm, and M_p is the mass of product. For our example;

$$I_M = (5.0 / 10^6)(10^3 g)$$

$$= 0.005 \text{ g}$$

Example 1

The molar mass of oxygen is 32g/g mole and 1 g-mole of an ideal gas at standard pressure and temperature will occupy a volume of 22,400 cc, from which we obtain:

$$I_V = \frac{V_g}{m_g} \times I_M$$

Equation 2

Where I_V is maximum amount of oxygen in cubic centimeters that can enter the package, Vg is 22,400 cc (Volume of 1 g-mole of an ideal gas at standard conditions), and $m_{g \text{ is}}$ the molar mass of oxygen.

$$I_v = 22{,}400 / 32 \text{ x } 0.005$$

$$= 3.5 \text{ cc}$$

Example 2

So the barrier of choice must prevent more than 3.5cc of oxygen from permeating into the package over the course of 60 days. The target transmission rate is thus:

$$N_A = 3.5 / 60 \text{ days}$$

$$N_A = 0.0583 \text{ cc/day}$$

Example 3

Where N_A or 'flux' is the rate of diffusion of Substance A through a solid, being the amount of gas passing through a unit area of the polymer in a unit amount of time. Then using the Mass Transport of Gas equation, and by choosing to use 32 mol% EVOH with a permeation value P of 0.3.25µm/m^2.day.atm at 20°C and 65% RH we can determine the desired thickness of EVOH *l:*

$$\frac{\Delta M_A}{t} = P\left[\frac{A\Delta p}{l}\right]$$

Equation 4

Where $\Delta M_A/t$ is transmission rate at unit temperature, P is permeability, A is unit area of polymer membrane, Δp is partial pressure difference across the membrane, and *l* is unit thickness of the polymer layer.

Substituting what is already known into the equation:

$$0.0583 \text{ cc/day} = 0.32 \text{ cc.25 µm/ m}^2\text{.day.atm x [0.04 m}^2 \text{ x 0.21 atm / } l \text{ µm]}$$

$$l = [0.32 \times 25 \times 0.21 \times 0.04] / 0.0583$$

$$l = 1.15 \text{ µm (0.045 mil or 0.8 lb/ream)}$$

Example 4

A valid method to compare the value of EVOH in this application relative to other common barrier resins such as Nylon 6 or PVdC is to compare the thickness of each material required to meet the permeation target previously established. While the thickness of 32mol% EVOH required to meet the target of 0.0583 cc/day at 20°C and 65% RH is 1.15 microns (0.8 lb/ream), the thickness of PVdC required to meet the same target is 5.8 microns (~4 lb/ream).

It is also obvious that if we could reduce the permeation P value for EVOH, that either longer shelf life or equivalent shelf life at reduced barrier thickness would be achievable. EVOH (ethylene vinyl alcohol) is a random copolymer of ethylene and vinyl alcohol. In general, polymers with a regular structure crystallize, while those with random structure vitrify to a glass without crystallizing. EVOH is somewhat unique in that the fine structure comprises both monoclinic crystalline regions having high degree of order, and glassy amorphous regions. It is the combination of these states' which causes EVOH to be at once flexible and yet provide high barrier properties. The degree of crystallinity is strongly influenced by processing conditions during re-crystallization, especially orientation and heat treatment.

PROPERTIES and PROCESSABILITY of EVOH RESINS for COEXTRUSION COATING

Basic Properties of EVOH

Briefly the properties of EVOH vary with the relative amounts of the two components, polyvinyl alcohol (PVOH) and polyethylene (PE). As the mol% of ethylene increases, the properties of EVOH become more like that of polyethylene, and conversely as mol% ethylene decreases the material behaves more like PVOH. Selection of a suitable EVOH for coextrusion coated or laminated structure depends upon the balance of the key properties of barrier, thermal stability and processability requirements for a given application and the converting process under consideration.

Table III. Basic Properties of EVOH designed for Coextrusion Coating and Laminating

Ethylene Content	Mol% Ethylene		27	32	35	44	48
Density	g/cc	D1505	1.20	1.19	1.18	1.14	1.12
Melt Index	g/10 min	190°C		4.4	8	5.5	6.4
		210°C	9.0	10.5	16	13	14.7
		240°C	20.0	24	40	34	36
		D1238 2160g					
Melting Point	°C	DSC	191	183	179	165	158

As seen in the table above, commercially available grades of EVOH resins contain between 27 to 48 mol% ethylene. The crystalline form is predominantly monoclinic up to about 42 mol%, with structure very dense and closely packed in a fashion similar to that of PVOH. These EVOH grades will have higher gas barrier properties and higher thermoforming temperatures than PE. In EVOH having mol% ethylene ranging from 42 mol% to 80 mol% the crystalline structure is comprised of larger less dense hexagonal crystals, which offers improved orientability in secondary processing process such as thermoforming, at the expense of lower gas barrier properties.

Table IV. Oxygen Permeation of EVOH - 20°C / 65% RH

Mol% Ethylene	27	32	35	44	48
Oxygen Permeation (cc.mil/100 in2.day.atm)	0.010	0.020	0.028	0.076	0.163
Oxygen Permeation (cc.20 um/sq. m.day.atm)	0.2	0.4	0.6	1.5	3.2

Choosing a barrier material considering only the gas barrier property may be adequate for many packaging applications, but depending on package contents, additional function of odor/flavor barrier could be required. Odor and flavors, of which foods or liquids may only contain small amounts, can be absorbed into many kinds of plastic. For certain foods such as soups or juices in which any change in taste must be prevented EVOH resins are ideal for flavor barriers, because EVOH has a low absorption rate of odor and flavor, and EVOH resins have almost no odor. Furthermore, the excellent resistance of EVOH to oils and organic solvents makes EVOH suitable for packaging edible oils, oily foods such as potato chips, mineral oils, organic solvents and agricultural chemicals.

Processability of EVOH

Based on previous experiments conducted on semi-commercial coex coating and laminating equipment, the most important factors affecting quality of high speed coextrusion coating of EVOH onto paper or other substrates, that are influenced by the choice of EVOH mol% are;

- The degree of neck-in of the EVAL melt and variation of such neck-in

- The melt tension
- The thickness limitation (minimum coating weight)
- Level of output at high speeds with low motor load.

High speed processing and high temperature conditions are the status quo for coextrusion coating. Achieving consistent thickness distribution and draw down to very thin gauges at these extreme conditions are critical performance measures, as are a small degree of neck in and edge 'weave'. Production line speed of extrusion coating continues to increase, and line speeds higher than 1000 feet per minute are commonplace. Accordingly, high output stable processability in extrusion is very important for an EVOH resin for coating applications. Based on experimental results higher mol% ethylene and higher melt index or MI is a very effective way to improve processing performance. Detail of past findings is presented in Appendix 1.

A study of three different EVOH resins with varying mol% and melt indexes was made to illustrate the effect selected mol% ethylene and melt index has on processability. Items studied included extrusion output, neck-in characteristics, thickness distribution, thickness limitations, and process stability of these resins.

Coextrusion coating test. The EVOH resins selected for the study, were 32 mol%, 35 mol% and 44mol% ethylene EVOH. The first resin is a 32 mol% EVOH with melt index of 4.4 gm/10min at 190°C. the 44 mol% EVOH has a melt index of 5.5 gm/10min. Finally a 35 mol% EVOH polymer with a MI of 8 gm/10 min at 190°C was included in the sample set.

Coextrusion coated structure. The following structure was chosen as being representative of typical portion of a multilayer coextrusion coated structure. Adhesive and EVOH were coated onto PET film and then extrusion laminated with a second film of LDPE.

Table V. Trial Structure

Trial Structure: 12micron PET// Adhesive / EVOH / Adhesive //40 micron PE

Target EVOH thickness was 1, 5, and 10 micron

Target adhesive thickness was constant at 5 micron. Adhesive had MI of 5.6 g/10 min (190°C)

Process and equipment. Coextrusion coating testing was carried out on a semi-commercial coextrusion laminator. A 2 kind, 3 three layer Cloren coextrusion feed block and die was utilized for this series of tests. Details of coextrusion coating test is presented in Appendix 2.

Evaluation items. Items evaluated for each sample of EVOH resin were;

- Extrusion output and process conditions at typical coextrusion coating conditions of 150 meters/min and temperatures of 240 and 280°C.
- Neck in variation and degree of neck in.
- Thickness variation and thickness limitation (minimum thickness before web breakage or EVAL layer became discontinued)
- Extrusion stability by variation in melt pressure, motor load, or melt temperature.

Experiment results. Processability of EVOH grades during extrusion coating test was measured by two methods. First the characteristics of the Adhesive/EVAL/Adhesive melt curtain was observed and recorded, and then measurements of layer thickness and distribution was made from collected samples.

Table VI. Processability of EVOH grades - Film speed 150 meters/min

EVOH Thickness	1 micron at 280 ° C			10 micron at 240 ° C		
Mol% Ethylene	32	35	44	32	35	44
Average Thickness (µm)	1.1	1.4	1.3	10	9	10
Range of Thickness (µm)	<1	<1	<1	0	2	0
Neck in width (mm)	45	46	45	59	57	58
Variation of width (mm)	<4	<4	<4	<4	<4	<4
Web Breaks	NO	NO	NO	NO	NO	NO

The first test at extrusion temperatures of 240°C showed that all grades shared common properties of stable operation at high speed (150 meters/min). However due to low speed of EVOH extruder at target thickness of one (1) micron, extruder surging was observed, and EVOH layer variation for all grades was more than one (1) micron. The EVOH layer became thinner than one (1) micron, and completely disappeared at intervals across the film web. Web breakage was also observed. At higher melt temperature of 280°C, 35 mol% EVOH performance was similar to E105. A stable melt curtain was observed, and a consistent layer of one (1) micron EVOH was achieved. Neck in and neck in variation was similar to that seen at 240°C, and no web breakage's occurred. As can be seen from Table 7, while the processability of EVOH is satisfactory under a number of conditions, as the EVOH thickness is increased the degree of neck in and edge weave also tends to increase.

Table VI. Processability at 280°C of 35 mol% EVOH. Adhesive Layer Melt temperature at 300°C

EVOH Thickness	1 micro n	5 micron	10 micron
EVOH Mol%	35	35	35
Average Thickness (µm)	1.1	5	10
Range of Thickness (µm)	< 0.25	0	0
Neck in width (mm)	46	48	51
Variation of width (mm)	1	<2	<4
Web Breaks	NO	NO	NO

Thermal Stability of EVOH

Long term thermal Stability. While there continue to be advances in the design of coextrusion coating equipment, as equipment manufacturers have gained more experience with EVOH resins, it remains a fact that EVOH is a thermally sensitive polymer. Although more heat stable than PVdC co-polymers, EVOH which does not exit the extrusion system with majority of the polymer melt stream, but remains coated on melt surfaces, will tend to first degrade, then crosslink, until a point when it breaks loose from surface to which it has been attached, and will reappear as an inclusion in melt curtain. The propensity to crosslink tends to decrease with lower ethylene content, so an understanding of this effect, and improvements in this property are worth examining.

Table VIII. Long Term Thermal Stability of EVOH

Mol% Ethylene	27	32	35	44	48
Long run stability at 220°C (hrs)*1	50	84	110	190	525

Note: Long term thermal stability is time required to generate cross linked gels in EVOH resin when heated continuously at a specified temperature.

Short term thermal stability. Resistance to degradation at high temperature is a critical attribute in coextrusion coating, chiefly because of the high melt temperatures required to gain good adhesion to the paper or film substrate upon which the coextruded melt is being deposited. If the temperature of the sealant is too low because the EVOH encapsulated in the structure is at a lower melt temperature, adhesion strength will suffer, or productivity decrease as line speeds are lowered to reach acceptable adhesion level. Significant efforts have been made to improve the short term thermal stability or degradation resistance of EVOH. These efforts can be seen in the successful extrusion tests of 3 different EVOH resins in the preceding section, but can also be estimated by measuring the degradation temperature of the EVOH. The data shows again the trend of increasing thermal stability as the mol% increases, but it is interesting to note that even the 27mol% EVOH has a degradation temperature exceeding 300°C.

Table IX. TG-DTA Degradation Temperature of EVOH

Mol% Ethylene	27	32	35	44	48
Onset Degradation (°C)	310	363	365	387	395

APPLICATIONS

The applications for EVOH in coextrusion coating and laminating now stretches back at least to the 1980's when development of coextruded coatings of EVOH and polyethylene onto paperboard for orange juice and fabric softeners began. Since that time many applications for EVOH in coextrusion coating have been commercialized. Appendix 3 shows some typical applications of film, sheet and paper containers or packaging to which EVOH is being applied. Based on results of evaluation of current processability, barrier and thermal stability, EVOH could be easily substituted into these and many other coextrusion coating applications.

CONCLUSION

Coextrusion coating converters will continue to find applications for high barrier flexible packaging produced via coextrusion coating and lamination in applications formerly dominated by metal and glass containers. A new generation of high barrier flexible packaging serves to contain and protect products, in such demanding applications as retail dried food snacks, while offering advantages of product promotion, increased food safety and reduced distribution costs.

Barrier material choices for flexible packaging continue to expand. EVOH (Ethylene vinyl alcohol) offers flexibility, transparency and pinhole resistance in addition to extremely high barrier to gases, flavors and aromas, and easy processability. Use of EVOH in multilayer packaging can preserve food quality and flavor in convenient and attractive transparent packaging. A wider range than ever before of EVOH resins, designed for coextrusion coating and laminating process is now available. These materials, incorporating improvements in thermal stability and processability, allows package designers and processors to effectively and efficiently utilize EVOH in flexible packaging and add value to their products and applications.

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Appendix 1. Factors Affecting Coextrusion Coating Quality

	Processability	Adhesion
Equipment	Extrusion Stability Thickness Profile Cooling roll temp.	Air gap Cooling roll temperature Nip roll pressure
Coating Substrate	Tension resistance	Surface flatness Surface treatment
EVOH	Neck in variation Melt tension Thickness limitation Output at high speed	Mol% Ethylene
Adhesive resin	Viscosity matching with EVOH Neck in variation Melt tension	Grade

Appendix 2. Process Conditions for Coextrusion Coating Test

Extruder Conditions

Extruder Diameter (L/D)	50 mm (26)	
Flight	Single	
Screw pitch	50 mm	
Feed zone length, (channel depth) Compression zone length, (channel depth) Metering zone length, (channel depth)	6D (9.9 mm) 10D (9.9~2.76 mm) 10D (2.76 mm)	
Compression ratio	3.6	
Screen Structure	None	
Target EVOH Processing Temperature	240°C	280°C
Barrel temperatures °C C1 C2 C3	175 200 240	175 220 280
Adapter temperatures °C A1~A2	240	280
Feedblock / Die temperatures °C	240	280

Process Conditions

Line Speed m/min	**150**	
EVOH coating thickness (micron)	1 5 10	
Adhesive coating thickness (micron)	5	
EVOH Processing Temperature °C	240	280
Die width (mm)	620	
Die gap (mm)	0.7	
Air gap (mm)	110	
Cooling roll temp (°C)	35	
Nip roll pressure (kg/cm2)	28	

Appendix 3. Selected Applications for EVOH Coextrusion coating

1. Paper / EVOH structures

Structure	Requirement	Application
PE / Paper / Adhesive / EVOH	Chemical resistance	Chemicals
PE / Paper / Adhesive / EVOH / Sealant	Gas & flavor barrier, Pinhole resistance	Juices, Jam, Snacks
PE / Paper / Adhesive / EVOH/ Adhesive / EVOH	Gas & flavor barrier, Pinhole resistance	Juices, Soups

2. Paper / Al / EVOH structures

Structure	Requirement	Application
PE / Paper / PE / Al / Adhesive / EVOH / Sealant	Gas & flavor barrier, Pinhole resistance	Juices, Soups, Drinks

3. Plastic film / EVAL® structures

Structure	Requirement	Application
Oriented Nylon / EVOH / Adhesive / Sealant	Gas barrier, Strength	Soups, Raw meat, Lid stocks
OPP / Adhesive / EVOH / Sealant	Gas & flavor barrier, Water barrier	Snacks, spices, Jam, rice paste
OPET / Adhesive / EVOH/ Adhesive / Sealant	Gas barrier, Transparency	Snacks, Lid stock
OPP/ PO / Tie/ EVOH /Tie/PO / OPP or sealant	Gas & flavor barrier, Water barrier	Snacks, Lid Stock