

# Properties of ethylene vinyl alcohol and value for select geomembrane applications

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**ABSTRACT:** Ethylene Vinyl Alcohol copolymer (EVOH), a random copolymer of ethylene and vinyl alcohol has found application in the packaging of perishable food, as a barrier to hydrocarbons in automotive fuel systems and containment of agricultural pesticides and herbicides. EVOH offers extremely good resistance to the migration of volatile organic compounds (VOC's), hydrocarbons and organic solvents, with the rate of diffusion in EVOH being several orders of magnitude lower than polyethylene. Many polymers exhibit softening, swelling or environmental stress cracking when exposed to solvents, while EVOH retains its physical properties in the presence of organic solvents, acid and alkali solutions and non-ionic surfactants. EVOH has been coextruded with other polyolefin's on conventional cast and blown extrusion systems for over twenty years in applications ranging from food packaging to consumer non durables and automotive fuel tanks. For geomembrane applications in a composite with materials such as HDPE, LLDPE and TPO, EVOH would dramatically improve the capability of geomembranes to control the diffusion of gases, hydrocarbons and solvents. Potential applications for a high barrier geomembranes (HBGM) in building and construction field include radon and vapor intrusion barriers and in brown field remediation as volatile organic compound (VOC) and chemical barrier. HBGM would protect agricultural and municipal drinking water reservoirs from contamination, and improve containment of odor and efficiency of methane production in waste disposal systems. In mining and energy extraction operations there are applications for protection and remediation where use of EVOH as part of a HBGM geomembrane liner or cap would provide a level of environmental protection that does not currently exist.

## 1 INTRODUCTION

Ethylene Vinyl Alcohol copolymer (EVOH), a random copolymer of ethylene and vinyl alcohol, is widely used to protect materials from oxidation and for containment of volatile organic hydrocarbons because of its outstanding barrier to gases, solvents and hydrocarbons (Lagaron et al. 2001). Because of its very low permeability, EVOH is widely used as a minor component in a multi-layer composite of thermoplastic polymers. The composite is typically formed by the coextrusion of multiple layers of thermoplastics into a sheet or film. The inclusion of EVOH in a co-extruded geomembrane would significantly enhance the capability of geomembranes to minimize the migration of gases, hydrocarbons and solvents. The addition of EVOH into geomembranes is expected to greatly enhance key properties

without causing any significant changes in existing form and functionality of geomembranes. Production of HBGM can be achieved with the application of suitably sized coextrusion equipment and well established technology utilized in adjacent fields of food packaging, automotive fuel systems and hazardous chemical containers.

## 2 BACKGROUND

Within the field of geosynthetics, geomembranes were first conceived as a means to augment key properties, such as the hydraulic barrier, of clay soils or geosynthetics clay liners (GCL's) or replace scarce and expensive raw material resources. Geomembranes have been utilized to accomplish the separation and reinforcement of soils, to separate two dissimilar materials and finally to prevent liquid leachate movement from a given containment area such

as a solid waste landfill. A typical composite liner system is comprised of a least a compacted clay liner (CCL) and a geomembrane (GM). The CCL hydraulic barrier is often augmented by a geosynthetic clay liner (GCL) containing bentonite. The hydraulic conductivity of a GCL is typically in the range of 1 to  $5 \times 10^{-11}$  m/s or twenty to one hundred times lower than a CCL. Geomembrane permeability to water vapor is lower again than a CCL or a GCL. Effectively this allows for the selective use of thinner higher performance materials to meet design criteria. As an example 5mm of a GCL often substitutes for 600mm of compacted clay based on reduced conductivity or simply higher barrier per unit thickness. We will return to this concept when comparing the diffusive migration barrier properties of EVOH to commonly used geomembrane materials such as HDPE.

Geomembranes themselves are ostensibly thin impervious sheets of polymeric materials used for containment or protection from liquids or vapor. According to ASTM D4439 a geomembrane is defined as a very low permeability synthetic membrane liner or barrier used with any geotechnical engineering related material so as to control fluid or gas migration in a human made project, structure or system. Municipal solid waste (MSW) landfills have evolved from unregulated ad hoc dumps to tightly regulated and well engineered structures. Globally the majority of countries that regulate HSW and MSW disposal require the use of a combination of a compacted clay liner (CCL) and a geomembrane (GM) as part of the liner system beneath waste (Koerner & Koerner 2007). These CCL/GM composite liners are intended to contain landfill leachate, which has been shown to often contain a wide variety of toxic volatile organic compounds (VOC's) known to be hazardous to human health. (Friedmann 1988, Gibbons 1992, Krug & Ham 1995, Tuncer 2003). While the monolayer high density polyethylene (HDPE) typically used for such liner systems provides a satisfactory barrier to advective migration of all types of leachate contaminants, and to diffusion of inorganic compounds such as heavy metals, HDPE and other polyethylene geomembranes provide very low resistance to the diffusion of VOC's. A variety of studies (Park & Nibras 1993; Prasad et al. 1994, Rowe 1998, Sangram & Rowe 2001) have determined that many organic compounds diffuse readily through existing geomembrane liners. It has been suggested that some of the most common contaminants include chlorinated hydrocarbons such as dichloromethane, 1,2 dichloroethane, trichloroethylene and aromatic hydrocarbons such as benzene, toluene and ethylbenzene. Contamination of ground water

and aquifers with VOC's has been reported and studied in both the United States and Europe, (Reinhard & Goodman 1984, Baun et al. 2000, Kjeldsen et al 1998) and by the World Bank which in a 2005 report concluded that degradation of the quality of the world's water supply for irrigation of crops and human consumption was a serious threat to maintaining and improving the quality of life of a majority of the world's population. With the goal of protecting groundwater quality, and preventing expensive remediation measures a number of efforts to augment the barrier of existing liner systems to VOC's have been proposed (Kolbasuk 2008, McWatters & Rowe 2009, Sangam & Rowe 2005). One of the options described has been the incorporation of a polymer with very high barrier to diffusion of VOC's and chlorinated hydrocarbons as a minor component into existing geomembranes by coextrusion. A focused review of the properties, relevant applications and techniques required to produce a composite high barrier geomembrane (HBGM) incorporating EVOH that would meet such a requirement is the objective of this paper. The potential improvements in barrier properties and implications for the design of landfill liners are also presented.

### 3 ETHYLENE VINYL ALCOHOL COPOLYMER (EVOH)

#### 3.1 *Structure and Properties*

EVOH (ethylene vinyl alcohol) is a random copolymer of ethylene and vinyl alcohol produced by saponification of solution polymerized ethylene vinyl acetate. The saponification of EVOH involves the substitution of alcohol groups in place of vinyl acetate groups after the polymerization of ethylene vinyl acetate (EVA) has occurred. The structure of EVOH after extrusion is semi-crystalline. Semi-crystalline thermoplastic polymers have a complex structure that combines crystalline domains in an amorphous matrix at a length scale of approximately 10nm. The crystalline structure of EVOH varies continuously due to the disordered packing of randomly arranged ethylene and vinyl alcohol units along polymer chains. It is the combination of the highly ordered crystalline structure interspersed with disordered amorphous regions that causes EVOH to possess the desirable properties of high resistance to diffusion of gases and solvents.

As has been described by others (Park & Nibras 1993, Sangram & Rowe 2001) the migration of organic solvents through polymers such as HDPE and EVOH is a three step process of absorption or parti-

tioning of the solvent from solution into the polymer, diffusion of the solvent through the polymer and then desorption into environment. The migration of organic solvent is controlled by material properties such as crystallinity, chain stiffness, free volume, cohesive energy density, polarity and extrinsic factors such as temperature and moisture content. Typically the principle of solubility where like dissolves like can be used as a guide to the resistance to migration of organic solvents in polymers and in general the more similar the solvent and solute are, there will be a corresponding increase in diffusion and permeation coefficients (Sangram & Rowe 2001). A common measure of solubility is the solubility parameter, a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density of the solvent which is in turn derived from the heat of vaporization. One of the simplest and most convenient relative measures of solubility is the Hildebrand solubility parameter. The solubility parameter of a polymer is more difficult to predict. The division of the Hildebrand parameter into three component Hansen parameters (dispersion force, polar force, and hydrogen bonding force) considerably increases the accuracy with which non-ionic molecular interactions can be predicted and described, but in many cases the combined Hildebrand parameter is used with success to predict the interaction of solvent and solute. Upon examination of the solubility parameters of a select group of solvents commonly found in landfill leachate (Rowe 1998) in Table 1 and polymers in Table 2 it can be seen that while HDPE and other non-polar thermoplastics should provide excellent diffusion resistance to water, which is the primary constituent of leachate, they should not be expected to provide significant resistance to the diffusion of chlorinated and aromatic hydrocarbons.

**Table 1** Solubility parameters for common leachate solvents

Solvent	Solubility Parameter $\delta$ (SI) [MPa]
Dichloromethane	20.3
1,2 dichlorethane	20.0
trichloroethylene	19.0
benzene	18.7
Toluene	18.2
ethyl benzene	18.0
m-xylene	18.0
Water	47.9

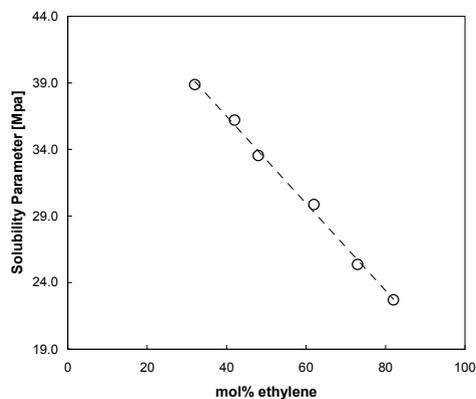
Considering the solubility parameter as a simple measure for the affinity between solvents and polymers, if the SP values are close we can expect that a polymer will be dissolved or absorb a large amount of the solvent. Many organic solvents, including

those in Table 1 have SP values ranging from 18 to 20, while many polymers have SP values from 16 to 20 leading to poor resistance to organic solvents. Nylon 6 has an SP value of 26, which provides greater resistance to organic solvents. The SP value of a 32mol% ethylene EVOH is 39 due to the presence of hydroxyl groups in the main chain and high cohesive energy density. The large difference in SP values between organic solvents and 32mol% EVOH leads to the excellent resistance to sorption and consequent swelling and diffusion of these species.

**Table 2** Solubility parameters for common polymers

Polymer	Solubility Parameter $\delta$ (SI) [MPa]
Polypropylene	16.2
Polyethylene	16.4
Polyvinylchloride	19.6
Polyurethane	20.5
Nylon 6	26.0
Nylon 66	27.8
EVOH (32mol%)	38.9

EVOH is a copolymer of ethylene and vinyl alcohol and thus one would expect the solubility parameter to vary with the ethylene content. This proves to be the case, as can be seen in Figure 1.



**Figure 1** Ethylene content of EVOH vs. Solubility Parameters

The derivation of the relationship between the mass flux due to diffusive migration and the solubility, diffusive and permeation coefficients has been described in detail by many others. Suffice to say that the final relationship between the mass flux  $f$ , the solubility diffusion and permeation coefficients ( $S_{gf}$ ,  $D_g$  and  $P_g$ ) can be stated as:

$$f = -S_g D_g \frac{d_{c_f}}{d_z} = -P_g \frac{d_{c_f}}{d_z} \quad (1)$$

Where  $c_f$  = solution concentration and  $z$  = position through membrane.

The diffusive barrier properties of a membrane, including geomembranes can be established through several methods including sorption weight gain, time lag and diffusion permeation experiments (Sangam & Rowe 2001). Low permeation coefficients or low permeation rates (mass or volume flux) are indicative of a geomembrane that will be a more effective barrier to a given contaminant. A number of studies are currently under way to establish the solubility, diffusive and permeation coefficients of EVOH or geomembranes containing EVOH. Published data currently available shows that the barrier property of EVOH to VOC's found in landfill leachate will be extremely good. Table 3 compares the diffusion coefficients of trichloroethylene and toluene in EVOH and HDPE. Note that the EVOH testing was conducted at 100% solution concentration, while the HDPE tests were conducted with dilute solution concentrations ranging from only 2 to 5 mg/L.

**Table 3** Diffusion coefficient ( $D_g$ ) of TCE and Toluene in EVOH vs. HDPE

Solvent	EVOH *	HDPE**
trichloroethylene	$3.1 \times 10^{-17}$	$4.0 \times 10^{-13}$
toluene	$3.1 \times 10^{-17}$	$3.0 \times 10^{-13}$

Diffusion coefficient  $D_g$  in  $m^2/s$

\*Kiwa NV report April 2008 for EVAL Europe N.V

\*\* Sangam and Rowe, Migration of dilute aqueous organic pollutants through a HDPE geomembrane, (2001) Geotextiles and Geomembranes 19 329-357

### 3.2 Performance of EVOH in VOC containment applications

Given the material properties of EVOH outlined above, it is not surprising that this polymer has been utilized in a wide variety of applications where the containment and control of diffusion of gases or VOC's is desirable. A select number of these applications and relevant performance data are presented here to illustrate the improvement in performance when EVOH is utilized to compliment the properties of polyethylene. The first examples include food and beverage packaging, athletic footwear, vacuum insulation panels and vapor intrusion barrier membranes where controlling the ingress or egress of gases from a controlled environment is critical. EVOH is used in coextrusions with a variety of materials including HDPE, linear low density polyethylene (LLDPE), polypropylene (PP) and polyamides to produce articles such as films, formed sheet, in-

jected and extrusion blowmolded containers. Table 4 illustrates the magnitude of differences in material properties by comparing the permeability of EVOH and HDPE to common gases. The permeability is reported as a permeation rate in  $cc.20\mu/m^2.day.atm$  which is the volumetric flow through a defined thickness and over a unit area under a constant driving force of one atmosphere pressure over the course of 24hours.

**Table 4** Gas barrier properties of EVOH vs. HDPE

Gas	EVOH*	HDPE**
Nitrogen	0.019	190
Oxygen	0.25	2300
Carbon Dioxide	0.6	17526
Sulfur Dioxide	0.3	21844
Methane	0.4	2845

Volumetric permeation rate in  $(cc.20\mu/m^2.day.atm)$

Conditions: 23°C – 0% RH (ASTM D1434T)

\* ASTM D1434 at Kuraray lab – 32mol% EVOH

\*\*Permeability Properties of Plastics and Elastomers, Massey, 2nd Edition

EVOH is also commonly utilized in coextrusion blowmolded containers for agricultural chemicals that contain high percentages of aromatic hydrocarbon solvents such as xylene and toluene. In such containers EVOH is normally the innermost layer of the bottle, protecting the HDPE from swelling and elution that would occur if exposed to high concentrations of such solvents. The barrier of EVOH to diffusive migration of solvent liquid and vapor also serves to retain solvents within the container. As a demonstration of the properties of a coextruded HDPE and EVOH structure, a standard chemical resistance test was conducted on one liter chemical extrusion blow molded containers that were either monolayer HDPE or a coextrusion (from the outside) of HDPE/Regrind/Adhesive/32mol% EVOH with EVOH layer thickness being no more than 4% by thickness at any spot in the sidewall of the container. Three replicates of each sample were subjected to the chemical resistance test outlined in CFR 49.173.24 Appendix B, which involves 30 days of storage at 50°C in an explosion proof oven after being filled with 100% m-xylene. The weight loss of the HDPE containers after 30 days was 9.6% while the coextruded containers with EVOH inside had a weight loss of less than 0.05%. It was also observed that the monolayer containers suffered from paneling (deformation) in the oven, while the EVOH barrier containers retained physical integrity.

One of the major applications for EVOH is in automotive fuel systems to control emissions of hydrocarbons from fuel lines and tanks. The use of EVOH in a coextrusion blowmolded tank with high molecu-

lar weight HDPE (HMWPE) originated in the United States in response to mandates of VOC emission reductions by the US Environmental Protection Agency (EPA) and the California Air Resources Board (CARB), and has now been in widespread use for fifteen years in more than 100 million vehicles with zero failure. Following adoption in the US, the same coextrusion technology spread geographically to Europe, Latin America and is now entering China and India. Table 5 illustrates the dramatic difference in permeation of ethanol, toluene and isooctane between monolayer HMWPE and a coextrusion of HMWPE and 32mol% EVOH. The permeation is reported as the rate of mass transport through a model fuel tank sidewall in grams/m<sup>2</sup>.day. The testing was conducted as an isostatic permeation test by MOCON Inc. The experimental setup was comprised of a two chamber cell, separated by the model tank sidewall. The test cell and the test sample were maintained at a temperature of 40°C. The lower chamber was filled with a mixture of 45% toluene, 45% isooctane and 10% ethanol. The upper chamber of the test cell was swept with an inert carrier gas which carried any vapors diffusing through the sample to first a capillary column and then to a flame ionizing detector (FID). The fuel in the lower chamber was refreshed periodically to maintain a constant driving force. The testing was conducted for a period of 8 weeks or until equilibrium rate of permeation was observed. For these experiments the samples were monolayer HDPE of total thickness 220 μm and a coextrusion of HDPE and EVOH, with total thickness 220μm and EVOH thickness 20μm in the center of the coextrusion.

**Table 5** Solvent barrier of HDPE vs. EVOH/HDPE coex

Solvent	EVOH coex	Monolayer HDPE
Ethanol	0.0880	10
Toluene	0.0005	92
Isooctane	<0.0001	34

Mass permeation rate in (grams/m<sup>2</sup>.day)  
Conditions: 40°C – 0% RH

### 3.3 Coextruding geomembranes with EVOH

Coextrusion allows the combination of complimentary materials in a composite with properties optimized for a target end use or application. The development and use of coextrusion has varied between different industries. In the food and beverage packaging industry, seven layer composite films are now commonplace, and nine to eleven layer structures are commercially available. In other industries as diverse as agricultural chemical containers, automotive fuel tanks and municipal water supply piping, flexible or rigid coextrusions of five

to seven layers and varying geometries exist. In contrast the use of coextrusion within the geomembrane industry was well established by the mid 1990's, but has generally remained limited to three layers. Utilizing materials such as EVOH in a HBGGM would require at least three layers in a coextrusion, although five or six layer structures would allow for the most economical use of material, by optimizing the amount of EVOH at perhaps no more than 2 to 4% by thickness of a typical geomembrane. What is required to produce a HBGGM is a transfer of existing coextrusion technology from other industries. Making this technology transfer much less of a challenge is the fact that many of the equipment manufacturers and suppliers well known within the geomembrane industry, including Battenfeld Gloucester, Brampton, Cloeren, Davis Standard and EDI are also supplying the equipment to industries that have progressed further in the use of coextrusion. Designing and manufacturing a commercial scale cast or blown geomembrane line is an engineering exercise that does not require any fundamental changes or breakthroughs in coextrusion technology or practice.

## 4 A MODEL HIGH BARRIER GEOMEMBRANE (HBGM)

There have conceivably several means to improve the resistance of GM to organic solvents, including fluorination of HDPE (Sangram & Rowe 2005), laminations with aluminum foil and coextrusion with polymers such as EVOH. Given a goal to create high barrier geomembrane that will provide the established properties of flexibility, durability and ease of installation of current geomembranes while also providing superior resistance to migration of liquid and vapor VOC's, there is a case to choose coextrusion with EVOH. The inclusion of EVOH in a coextruded geomembrane would significantly enhance the capability of geomembranes to minimize the migration of gases, hydrocarbons and solvents. The barrier properties of EVOH to a wide range of VOC's typically found in landfills is so great, that in the same way that a relatively thin GCL substitutes for a great depth of compacted clay, a very thin layer of EVOH within a polyethylene or polypropylene geomembrane will effectively reduce diffusive migration of organic contaminants. Two possible model high barrier geomembrane structures containing a layer of EVOH is presented below in Figure 2. A three layer structure could include two layers of polyethylene or polypropylene blended with compatibilizers or extrudable adhesives sandwiching the EVOH. Alternatively a five layer structure could include two discrete layers of the adhesive resin (typi-

cally maleic anhydride grafted HDPE or LLDPE) to provide physical and chemical bonding between the outer polyolefin layers and an EVOH core. It should be noted that there is a wide variety of possible structures and manufacturing methods that could be employed to produce HBGM structures, and these examples by no means exhaust the design possibilities.

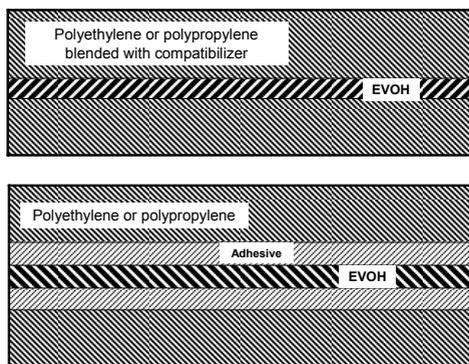


Figure 2 Model HBGM with EVOH

## 5 CONCLUSION

The primary function of a composite liner system in municipal solid and hazardous water landfills is containment of liquids and vapor that should not migrate into the surrounding environment. Polymeric geomembranes are not impermeable, only relatively impermeable when compared to soils. While existing monolithic geomembranes comprised of polypropylene, polyethylene and polyvinylchloride unquestionably are excellent hydraulic and heavy metal barriers, it is becoming increasingly apparent that these materials are not good barriers for volatile organic compounds migrating by diffusion from landfills and posing a threat to groundwater. The inclusion of EVOH by coextrusion into existing geomembrane designs would greatly improve the long term performance of landfills by significantly minimizing diffusive migration of VOC's, and offers a cost effective alternative to expensive remediation of contaminated sites. A HBGM with EVOH offers the potential for significantly improved protection of soil and water quality.

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