IMPROVING INDOOR AIR QUALITY BY REDUCING RADON AND VAPOR INTRUSION THROUGH THE USE OF ETHYLENE VINYL ALCOHOL (EVOH)

R. B. Armstrong[1], M. ASME, M. SPE, M. IGS.

Department of Research and Technical Services, Kuraray America Inc., 11500 Bay Area Boulevard, Pasadena, TX 77507; PH (281) 474-1576; FAX (281) 474-1572; email: robert.armstrong@kurarayamerica.com

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Abstract

Ethylene Vinyl Alcohol (EVOH) is a random copolymer of ethylene and vinyl alcohol, commonly used as a barrier to hydrocarbons in automotive fuel systems and agricultural pesticide and herbicide solvents. EVOH provides extremely high resistance to the migration of gases and volatile organic compounds (VOC's). The incorporation of EVOH in radon resistant new construction has the potential to dramatically reduce the diffusion of radon and other harmful vapors into building spaces and significantly improve indoor air quality. Recent tests of the radon diffusion coefficient of EVOH are compared to previously published results, which show EVOH has radon barrier properties several orders of magnitude better than polyethylene such as LDPE or HDPE. For radon resistant new construction (RRNC) the use of EVOH in a composite with commonly used materials such as HDPE, LLDPE or PP would dramatically reduce the diffusion of radon and VOC's through plastic sheeting or vapor retarders. Potential applications for a high barrier vapor retarder (HBVR) include radon and vapor barrier membranes for RRNC and brown field remediation.

Introduction

Radon is a naturally occurring gas, which decays with a half life of approximately four days and emits radioactive alpha particles that are now known to be the primary cause of lung cancer in non-smokers, and the second most important cause of lung cancer after smoking. The International Agency for Research on Cancer (IARC), a World Health Organization (WHO) agency specializing in cancer, and the US National Toxicology Programme has classified radon as a human carcinogen. In 2009 the WHO Handbook on indoor radon reported that recent estimates of the proportion of lung cancers attributable to radon range from 3 to 14%. In the United States approximately 21,000 people die each year from radon-related lung cancer. The dose-response relation seems to be linear without evidence of a threshold, meaning that the lung cancer risk increases proportionally with increasing radon exposure(WHO, 2009) The WHO recently reduced the recommended maximum level of radon gas to 100 Becquerel's per cubic meter

[1] The author is an employee of Kuraray America, Inc. a producer of ethylene vinyl alcohol (EVOH) resin.

(Bq/m^3) or 2.7 picoCurie per liter (pCi/L), which is ten times lower than the recommended maximum level corresponding to a 10^{-3} risk level in 1996 (WHO, 1996). In the US and Canada a recommended action level of 4 pCi/L has been established for a number of years. In the US and Canada national agencies set guidelines for radon levels in residences and workplaces, and guidelines for radon mitigation and radon resistant new construction. In the US each state sets local guidelines or standards which vary significantly. Radon resistant new construction and overall indoor air quality are also within the scope of several of the new "green" building standards which address the related issue of vapor intrusion into buildings sited on or adjacent to brownfield sites. Vapor intrusion or VI is defined as the migration of volatile chemicals in building spaces from groundwater or soil. The chemicals of primary concern were either hydrocarbons such as benzene, ethyl benzene, toluene and xylene (BTEX) or chlorinated solvents such at trichloroethylene (TCE) or perchloroethylene (PERC). The chronic effects of long term exposure to very low levels of these chemicals motivated the EPA to issue guidelines for limits on vapor intrusion in 2002 to 2005, which are now being acted upon by most states, with California, Colorado, Wisconsin, New York and New Jersey being the most active. The action level for remediation or mitigation based on VI is often very low, typically being the level of a volatile chemical with a one in a million chance of causing cancer over a 20 year period (translates to 1 μg/m^3 for toluene in indoor air).

To prevent radon and vapor intrusion into residential and commercial buildings a variety of techniques are employed, typically a passive barrier or active venting system or a combination of the two, which can be part of building construction or mitigation after radon or vapor intrusion is detected. A passive barrier system normally includes a membrane that forms a barrier between the ground and the foundation of the building. The installation of the barrier membrane must be carried out with care so gas cannot enter via overlaps and pipe penetrations that are not sealed. To prevent gas build-up beneath the membrane, it is necessary to provide a means for gas to disperse into the atmosphere. Radon testing and mitigation efforts are not keeping pace with construction of new houses that suffer from radon problems, so promoting radon resistant new construction is becoming much more important. Current EPA guidelines suggest using 3mil (75 micron) polyethylene sheeting as a radon barrier in conjunction with an active vent system, however houses built to the current standard can exceed the action limit and require additional mitigation efforts. Several groups including the Czech Technical University have tested a variety of materials offered as radon barrier membranes and suggested that determining the radon diffusion coefficient of barrier membranes is a key step in determining the optimum type and thickness of radon barrier membranes.

Properties of EVOH

Ethylene Vinyl Alcohol (EVOH) is a random copolymer of ethylene and vinyl alcohol 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). EVOH offers extremely good resistance to the migration of volatile organic compounds (VOC's), hydrocarbons and organic solvents, with the rate of solvent diffusion in EVOH being several orders of magnitude lower than in polyethylene.

Many polymers exhibit softening, swelling or environmental stress cracking when exposed to solvents, while EVOH retains key physical properties in the presence of organic solvents, acid and alkali solutions and non-ionic surfactants. The morphology of EVOH is a combination of a highly ordered crystalline structure interspersed with disordered amorphous regions. The permeability of EVOH is controlled by factors such as crystallinity, chain stiffness, free volume, cohesive energy density, and extrinsic factors such as temperature and moisture (Koros, 1990). Like other hydrophilic polymers, EVOH can exhibit large permeability increases as temperature or moisture content rises due to an increase in the free volume (Lopez-Rubio et al 2003). By varying the ethylene content (mol % of ethylene) and volume fraction of crystallinity (Φ) of EVOH this effect is minimized (Armstrong, 2003). Table 1 illustrates the magnitude of differences in material properties by comparing the permeability of EVOH and HDPE to common gases.

Table 1 Gas barrier properties of 32 mol% 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.20μ/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

Published data shows that the barrier property of EVOH to VOC's is extremely good. Table 2 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 2 Diffusion coefficient (D_g) of TCE and Toluene in EVOH vs. HDPE

Solvent	EVOH *	HDPE**
Trichloroethylene	$3.1x10^{-17}$	$4.0x10^{-13}$
Toluene	$3.1x10^{-17}$	$3.0x10^{-13}$

Diffusion coefficient D_g in m^2/s

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

** Sangam and Rowe, (2001) Geotextiles and Geomembranes 19 329-357

Experiments & Results

To determine the radon diffusion coefficient of ethylene vinyl alcohol (EVOH) and compare this material property with other materials commonly used as radon barrier membranes, samples of 44mol% EVOH film of 0.6mil (15 microns) produced by the Kuraray Company Limited of Japan and designated 'EF-E' were submitted to the radon test laboratory in the Civil Engineering Department of the Czech Technical University in Prague. To determine the radon diffusion coefficient of these samples the laboratory followed the method K124/01/09 which is accredited by the Czech Accreditation Institute, and allows for the determination of the radon flux through the tested material placed between two cylindrical containers. Radon diffuses from the lower container, which is connected to the radon source, through the sample to the upper container. From the known time dependent curves of the radon concentration in both containers the radon diffusion coefficient can be calculated. The details of the method are outlined in the test report and also in be found in published papers (Jiránek, 2008).

The results of tests conducted by the Czech Technical University are in Table 3, with the radon diffusion coefficient D reported in units of m^2/s. The radon diffusion coefficient is reported as a material property of the composite or monolayer sample in all cases.

Table 3 Radon Diffusion Coefficient (D) in EVOH vs. other barrier materials

Material	**Radon diffusion coefficient (D) ***
EF-E (EVOH)	1.3×10^{-14}**
Bitumen coated Al foil	3.9×10^{-14}
Polyurethane (PU) coating	2.3×10^{-12}
Chlorinated polyethylene	3.5×10^{-12}
High density polyethylene (HDPE)	5.8×10^{-12}
Polyethylene (PE)	1.0×10^{-11}
Plasticized polyvinylchloride – (PVC-P)	1.9×10^{-11}
Low density polyethylene (LDPE)	2.5×10^{-10}

*Radon diffusion coefficient D in m^2/s
**Czech Technical University Test Report No 124008/2010 1-4-2010
All other values from Jiránek, Rovenská and Froňka (2008)

The radon diffusion coefficient for the EF-E sample of 1.3×10^{-14} m^2/s with uncertainty of ± 0.1 m^2/s is one of the lowest values ever reported by the laboratory, even lower than bitumen coated aluminum foil. The reported uncertainty in result for EF-E (EVOH) sample was also significantly lower than for the bitumen coated foils which is attributed to the excellent flex crack resistance of EVOH.

Discussion

The significance of these results can be illustrated using several of the design methods that determine radon barrier membrane thickness. The design methods currently utilized for such purposes and used for this comparison include:

- Method that requires the radon diffusion coefficient D of the radon barrier membrane must be below a strict limit value, which has been suggested should be $<1 \times 10^{-11}$ m^2/s.
- Method that requires that the thickness d of the radon-proof membrane must be at least three times greater than the radon diffusion length.
- Method that requires the thickness of the membrane be calculated for each house according to the radon diffusion coefficient in the membrane itself, radon concentration in the soil on the building site and house parameters (ventilation rate, area in contact with the soil etc).

In the case of the first design method, 44mol% EF-E EVOH has a radon diffusion coefficient of 1.3×10^{-14} m^2/s which is three orders of magnitude lower than the suggested limit of <1x10^{-11} m^2/s. If the second design method is employed, EVOH can be compared to HDPE and LDPE using the design factor requiring that radon barrier membrane thickness should be three times greater than the diffusion length. The diffusion length itself is a function of material properties and the established equation:

$$l = (D/\lambda)^{1/2} \quad [m]$$

Equation 1

Where

l is the diffusion length in meters (m)
D is the radon diffusion coefficient (m2/s)
λ is the radon decay constant which is 0.00756 hr^{-1} or 2.1x10^{-6} s^{-1}

The results of diffusion length design method calculations are in Table 4. The required thickness for EVOH is within the capabilities of existing producers of radon barrier membranes, however a 236 micron (9mil) thick barrier membrane of EVOH would be relatively expensive and would not possess other functional characteristics such as flexibility during installation and easy heat sealability that typical polyolefins such as LDPE, HDPE and PP possess.

Table 4 Radon barrier membrane thickness by diffusion length method

Material	l (m)	3l (m)	3l(microns)	3l (mil)
EVOH	7.86x10^{-5}	2.36 x10^{-4}	236	9
HDPE	166.2x10^{-5}	49.86x10^{-4}	4986	196
LDPE	1091.0x10^{-5}	327.3 x10^{-4}	32733	1289

The third design method detailed by others (Jiránek, Rovenská and Froňka 2008) involves a calculation of the minimum thickness of membrane required to control diffusion of radon into a defined control volume (house or building), assuming intrusion of radon by convection to be negligible. By way of a performance comparison the minimum thickness of membrane required for a typical two storey house with a full basement using EVOH, HDPE or LDPE was calculated using the design calculation proposed by Jiránek, Rovenská and Froňka.

$$d \leq l.\operatorname{arcsin} h \frac{\alpha_1.l.\lambda.C_s\left(A_f + A_w\right)}{C_{dif}.n.V} \quad [m]$$

Equation 2

Where

d is the minimum thickness of radon barrier membrane in meters (m)
l is the diffusion length (m) established by Equation 1
α_1 is a safety factor that accounts for inaccuracies in soil gas radon concentration measurements. Values of α_1 can be estimated according to the soil permeability (for highly permeable soils $\alpha_1 = 7$, for soils with medium permeability $\alpha_1 = 3$ and for low permeable soils $\alpha_1 = 2.1$)
λ is the radon decay constant which is 0.00756 hr^{-1} or 2.1x10^{-6} s^{-1}

C_s is the radon soil gas concentration (Bq/m^3)
A_f is the floor area in direct contact with the soil (m^2)
A_w is the area of the basement walls in direct contact with soil (m^2)
n is the air exchange rate (h^{-1})
V is the interior air volume (m^3)
C_{dif} (Bq/m^3) is a fraction of the reference level of indoor radon concentration C_{ref} caused by diffusion. In accordance with the method detailed by Jiránek, Rovenská and Froňka the value of C_{dif} was set at 10%, meaning that the radon diffusion into the house will be limited to 10% of indoor radon concentration, with the balance reserved for radon intrusion by convection.

The design calculation input for a typical size two story house with a full basement was:

α_1 - safety factor was 3 for soils with medium permeability
λ - radon decay constant was 0.00756 hr^{-1} or $2.1x10^{-6}$ s^{-1}
C_s - the radon soil gas concentration at 74,000 (Bq/m^3) or 2000 (pCi/L)
A_f - the floor area in direct contact with the soil was 220 m^2
A_w - the area of the basement walls in direct contact with soil was 98 m^2
n - the air exchange rate was 15 h^{-1}
V - the interior air volume was $600m^3$
C_{dif} – was 0.1

The results of specific membrane thickness design method calculations are in Table 5. The thickness of EVOH required in this typical case was only 3.7 microns (0.14 mil), which is at least two orders of magnitude lower than the thickness of HDPE and four orders of magnitude lower than LDPE. This is consistent with all established data and experience with the material properties of EVOH, with barrier properties being typically several orders of magnitude better than polyolefins.

Table 5 Radon barrier membrane thickness by specific membrane thickness method

Material	d (m)	d (mm)	d(microns)	d(mil)
EVOH	3.67×10^{-6}	0.0037	3.7	0.14
HDPE	1.45×10^{-3}	1.45	1447.7	57.0
LDPE	2.80×10^{-2}	28.00	28000.4	1102.4

Although material property data and design calculations indicate that a minimal thickness of EVOH would be sufficient to provide significantly improved protection from radon and vapor intrusion, very thin films of EVOH are not practical for installers of radon and vapor intrusion systems. A potential answer lies in the use of coextrusion. Coextrusion allows for the combination of materials in a composite with properties optimized for a target application. In industries as diverse as food packaging, agricultural chemical containers, automotive fuel tanks, pipe and tube, flexible or rigid coextrusions of five to seven layers and varying geometries exist. Utilizing materials such as EVOH in a radon barrier membrane would require at least three layers in a coextrusion, although five or six layer structures would allow for optimizing the amount of EVOH at perhaps no more than 2 to 4% of the total thickness of a radon barrier film – such as a 3 mil PE (75 micron) film with 4% EVOH. Making this technology transfer less of a challenge is the fact that many of the equipment manufacturers and suppliers well known within the barrier membrane industry, including Gloucester Engineering, Brampton Engineering, Cloeren Inc., Davis Standard Inc and Extrusion Dies Industries LLC also supply equipment to industries that are currently utilizing multilayer coextrusion. A model high barrier radon or vapor membrane structure containing a layer of EVOH is presented below in Figure 1. It should be noted that there is a wide variety of possible structures and manufacturing methods that could be employed to produce radon and vapor barrier membranes, and this example by no means exhausts the design possibilities.

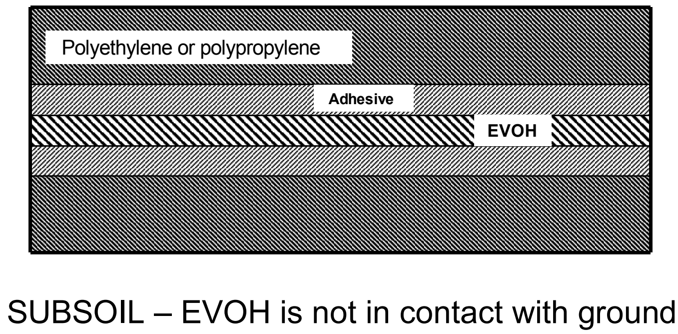

Figure 1 Model radon and vapor barrier membrane with EVOH

Conclusion

Tests of the radon diffusion coefficient of ethylene vinyl alcohol (EVOH) have shown that EVOH has radon barrier properties several orders of magnitude better than polyethylene such as LDPE or HDPE. Designers, builders and regulators could take advantage of these properties for radon resistant new construction (RRNC) where the use of EVOH in a composite with commonly used materials such as HDPE, LLDPE or PP would dramatically reduce the diffusion of radon through plastic sheeting or vapor retarders. An opportunity exists to create and utilize a superior passive radon barrier membrane that consistently and reliably controls radon levels in buildings and houses to < 1 picoCurie per liter. To realize this goal will require more than lab scale testing of the radon barrier properties of EVOH alone. A demonstration of a model high performance radon and vapor intrusion barrier membrane in a housing development or subdivision may be required to overcome conventional thinking that all vapor barriers (polyethylene) are the same, and must always be supplemented with an active venting system. Other potential applications for a high barrier membranes incorporating EVOH include VOC barriers and in brown field remediation, where EVOH could dramatically reduce the diffusion of harmful vapors into building spaces and significantly improve indoor air quality.

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