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Barrier permeation properties of EVOH thin-film membranes under aqueous and non-aqueous conditions☆

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ABSTRACT

Ethylene vinyl alcohol (EVOH) copolymers can provide a superior barrier to hydrocarbons and are increasingly being used in co-extruded geomembranes for geoenvironmental applications. These thin-films behave differently under different humidity conditions. This study investigated the permeation properties of toluene through two EVOH thin-films (32 mol% ethylene and 44 mol% ethylene) for both non-aqueous and aqueous solutions. The results of this study are used to gain a better understanding of the behaviour of the EVOH layer used in co-extruded geomembranes. The thin-film results are compared with published values for co-extruded linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) geomembranes with an EVOH core. Permeation coefficients are presented over a range of contaminant concentrations from 25 ppm to 99% toluene based on almost five years of continuous testing and the effect of moisture is discussed. A number of EVOH thin-films were affected by humidity (i.e., where moisture diffused into the film) prior to diffusion testing under non-aqueous conditions. This observation led to an investigation of the effect of moisture uptake on the permeation of toluene under non-aqueous testing. In these cases, the 44 mol% thin-film had lower toluene permeation coefficient values than the 32 mol% thin-film. These values were similar to toluene permeation coefficient values from tests with aqueous solutions. When relative humidity was less than 60%, the 32 mol% had slightly lower permeability values than 44 mol% thin-film. However, even when affected by humidity, the permeability of both thin-films were considerably (two to three orders of magnitude) lower than previously observed in a water-saturated solution. Permeation of toluene from a 1/1 toluene/hexane solution was also examined for the 32 mol % EVOH thin-film at temperatures of 23–50 °C and results fit well with a conventional Arrhenius relationship of increasing P_g values with increasing temperature.

1. Introduction

Ethylene vinyl alcohol (EVOH) copolymers are excellent barriers to aromatic and aliphatic hydrocarbons and have been used in many environmental containment applications. In the automotive industry, polyethylene was traditionally used in barrier systems of rigid fuel tanks and flexible lines. However, as regulations for vehicle emissions became more stringent, multi-layered barriers that incorporate polyethylene with an EVOH copolymer inner layer were introduced (Gagnard et al., 2003; Lagaron et al., 2001).

Similarly, in geoenvironmental applications (e.g., construction on brownfield sites) EVOH is being used to design superior "vapour" barriers and geomembranes. Geomembranes are commonly used as the primary advective and diffusive barriers to leachate and landfill gas contaminants in landfill cover and base liner systems. Geomembranes that were traditionally polyethylene (typically a single layer of linear low density polyethylene (LLDPE) or high density polyethylene (HDPE)) are now being co-extruded with an inner EVOH layer. Co-extruded EVOH geomembranes or films with polyethylene or polyamide are also being produced for use as vapour barriers in buildings and at brownfield sites to reduce vapour intrusion. These barriers have a low permeability to volatile organic contaminants (VOCs) (Armstrong and Chow, 2011; McWatters and Rowe, 2015). As part of field trials, a co-extruded EVOH geomembrane has been used in the barrier systems of two Antarctic biopiles for containing hydrocarbon-contaminated soil (McWatters et al., 2016a).

Polyethylene is an excellent barrier to water, however it is not a good barrier to many hydrocarbons. Toluene has been shown to diffuse readily through conventional single-layer LLDPE and HDPE geomembranes with permeation coefficients, P_g, for toluene in dilute aqueous

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solution of 18×10^{-11} m^2s^{-1} and 2.4×10^{-11} m^2s^{-1} for LLDPE and HDPE geomembranes, respectively (McWatters and Rowe, 2009; McWatters et al., 2016b). In contrast, EVOH is an excellent hydrocarbon barrier, however its permeability to hydrocarbons is severely affected by moisture (Lagaron et al., 2001). Thus, co-extruding an outer LLDPE or HDPE layer with an interior EVOH thin-film, marries the advantageous properties of both products. The polyethylene outer layers minimize moisture migration to the hydrophilic EVOH thin-film. The EVOH film provides the primary resistance to the diffusion of hydrocarbons. The permeability of toluene through the 38 mol% EVOH layer in a 0.53 mm-thick co-extruded LLDPE/EVOH/LLDPE geomembrane was reported (McWatters and Rowe, 2015) to be 5×10^{-15} m^2s^{-1} (i.e., almost five orders of magnitude lower than that for LLDPE and four orders of magnitude lower than for HDPE geomembranes).

The EVOH is a copolymer of ethylene and vinyl alcohol typically manufactured in the range of 24 mol% ethylene/76 mol% vinyl alcohol to 48 mol% ethylene/52 mol% vinyl alcohol. The permeation properties of these thin-films are dependent on the molar composition of the polymers and the surrounding environment (Lagaron et al., 2001). With respect to molar composition, a 32 mol% ethylene copolymer has superior barrier properties and is more rigid than higher mol% copolymers and is used for standard automotive and pipe applications. A 44 mol% ethylene copolymer has more free volume, leading to greater flexibility and is therefore useful for packaging, but loses some of its diffusive resistance to permeants (e.g., oxygen) (Mokwena and Tang, 2012). A 38 mol% ethylene copolymer combines the excellent diffusive resistance with easier processing on blown-film equipment; hence its use in the co-extruded LLDPE or HDPE geomembranes.

In humid environments (> 65% RH), EVOH copolymers show decreased mechanical and barrier properties to water and oxygen (Lagaron et al., 2001, 2003; Aucejo et al., 1999, 2000; Kim and Chun, 1999; Zhang et al., 1999, 2001). The presence of water plasticizes the thin-film making it more swollen and flexible.

A high vinyl alcohol content (68–80 mol% with a corresponding ethylene content of 32–20 mol%) has excellent resistance to oxygen, nitrogen, carbon dioxide and hydrocarbons because of the increased presence of hydroxyl groups that improve inter-chain cohesion of the polymer (Lagaron et al., 2001). However, high vinyl alcohol content films will uptake more water (swell) in high relative humidity (> 65%) conditions through the following pathways: hydrogen bonding to alcohol groups; hydrogen bonding (clustering) to water already present; and water occupying the free volume spaces (Lagaron et al., 2001). The barrier performance deteriorates with swelling because water inhibits inter- and intra-hydrogen bonding of hydroxyl groups of the polymer. Inter-chain cohesion decreases, mechanical properties decrease and the free volume of polymer increases making the polymer more plastic. Plasticization, the process of a polymer rearranging to become more flexible, provides more space for permeants to more readily migrate through the polymer (Robertson, 2006). Studies have shown that the permeation of oxygen is lower for 32 mol% than 44 mol% under no/low humidity conditions (Muramatsu et al., 2003). Under higher relative humidity conditions (> 90% RH), the trend reverses and 44 mol% performs as a superior barrier to oxygen permeation over the more water-affected 32 mol% thin-film. This is largely because the 32 mol% thin-film has less free volume than the higher ethylene thin-films, where more ethylene means less hydrogen bonding interactions and therefore more flexibility in the polymer (Lagaron et al., 2001). This pattern is repeated when McWatters and Rowe (2015) showed how water environments affected the diffusion of aromatic hydrocarbons, benzene, toluene, ethylbenzene and xylenes (BTEX) and chlorinated hydrocarbons (CHCs) in dilute aqueous solution through 32 mol% and 44 mol% EVOH thin-films. With respect to toluene in aqueous solution, the permeation coefficients for 32 mol% thin-film (e.g., $P_g = 0.2 \times 10^{-12}$ m^2s^{-1}) was higher (therefore an inferior barrier) than those for the 44 mol% thin-film (e.g., $P_g = 0.03 \times 10^{-12}$ m^2s^{-1}).

Morphological changes, including decreased crystallinity, are observed under the combined influence of increased temperature and relative humidity conditions, also decreasing the diffusive barrier properties (Lopez-Rubio et al., 2003).

Aucejo et al. (1999) have shown that the effect of water on vinyl alcohol is reduced by copolymerization with ethylene, although the mechanical and barrier properties are still water dependent. Optimization studies have led to standard practices of manufacturing multilayer structures (e.g., optimum copolymer content of 4 wt% between the PE and EVOH layers) (Kim and Chun, 1999). Most research has focused on understanding moisture sensitivity and its effect on oxygen and other gas permeation through EVOH used in the food packaging industry (Mokwena and Tang, 2012). Few studies have focused on understanding moisture sensitivity and its effect on hydrocarbon permeation (Liu et al., 1988; Johansson and Leufven 1994; Gavara et al., 1996) with none studying the effect of temperature or both combined.

More research is needed to better understand the properties of EVOH specific to those being used in environmental barrier applications, including performance as a diffusive barrier for both contaminants in leachate (e.g., biopiles) and vapour phase (e.g., vapour barriers in buildings). The quantity of water (liquid or vapour) that will be absorbed and speed of absorption depends on the environmental conditions of the application in which the thin-film is used. This will depend on the nature and amount of polyethylene available to resist moisture diffusion to the EVOH core of the co-extruded geomembrane. The absorption process can vary widely between applications since it is dependent on temperature and the relative humidity of the environment. In some applications, these two factors may change over time. As co-extruded geomembranes are relatively new, it is also important to investigate the long-term durability of these geomembranes. However, studies of the long-term performance of EVOH in geoenvironmental applications are rare (McWatters et al., 2016a, Eun et al., 2014, 2017).

Understanding the sorption, diffusion and overall permeation process through the co-extruded geomembranes requires a study of the EVOH thin-film layers in the absence of PE exterior layers. To establish the effect of water on permeation resistance, sorption and diffusion tests using 32 mol% and 44 mol% EVOH thin-films were studied in dilute aqueous solutions of BTEX and CHC (McWatters and Rowe, 2015). These film compositions were chosen to better understand the difference in ethylene content with respect to permeation of volatile hydrocarbons. The two films bracket the 38 mol% film used in the co-extruded geomembrane but was not available for testing.

This study examines the permeation of toluene from a non-aqueous (hexane) solution through 32 mol% and 44 mol% EVOH thin-films (i.e., the same thin-films as examined for permeation of BTEX from an aqueous solution by McWatters and Rowe, 2015). When the EVOH film is in contact with an aqueous solution, the maximum moisture uptake is permitted and this must be regarded as a worst-case scenario. However, even in contact with an aqueous solution adjacent to a coextruded PE/EVOH/PE geomembrane, the moisture getting to the EVOH will be limited by the nature and thickness of the polyethylene layers. By testing the hexane solution, no water uptake can be expected during the test and the water content of the film will be that with which it starts. Since the moisture uptake prior to testing is a function of the humidity of the air and time of exposure, films can be conditioned to different initial water contents before testing and then tested. The likelihood of further water uptake during the tests with hexane as the base solution in both the source and receptor is nil.

The objectives of this study were to evaluate: (a) the relative permeation of dilute toluene in a hexane solution compared to that from a dilute aqueous solution; (b) the effect of different toluene concentrations (2.5–99%) in non-aqueous solution on permeation through the two thin-films; (c) the effect of relative humidity in the testing environment on permeation; and (d) the influence of temperature on permeation through 32 mol% thin-film with tests performed over the temperature range of 23–50 °C. Finally, these established permeation properties are compared with the published diffusive properties of a co-