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*Review Article***Durability of HDPE geomembranes**

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Abstract

This paper summarizes the basic concepts and mechanisms related to the durability of HDPE geomembranes and discusses the factors influencing the service life of geomembrane liners. Geomembrane durability is addressed in terms of field performance and laboratory test results under various conditions. It discusses their projected service lives that may range from many centuries to less than a decade depending on the type of material and exposure conditions. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Geomembranes are often included as part of the engineered barrier system for modern landfills (Rowe, 2001). As defined in ASTM D4439-00, a geomembrane is "an essentially impermeable membrane used with foundation, soil, rock earth or any other geotechnical engineering-related material as an integral part of a man-made project, structure or system". There are various types of geomembranes including polyvinyl chloride (PVC), chlorinated polyethylene (CPE), chlorosulphonated polyethylene (CSPE), ethylene propylene rubber (EPDM), polypropylene (PP), linear low-density polyethylene (LLDPE), medium-density polyethylene (MDPE) and, more recently, the bituminous geomembrane. It is important to note that the so-called HDPE geomembranes discussed in this paper are in reality MDPE in terms of resin density; however, with additional carbon black the density of the geomembrane itself falls within high-density range defined by ASTM D 883.

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The selection of a geomembrane liner depends upon the application in which it will be used (Peggs and Thiel, 1998). High-density polyethylene (HDPE) geomembranes have been used exclusively in landfill applications, especially for bottom liners, because of their relatively high resistance to aggressive leachate components (August and Tatzky, 1984; Haxo and Nelson, 1984; Rowe, 2001). In general, HDPE geomembranes consist of 96–97.5% of polyethylene resin, 2–3% of carbon black and 0.5–1.0% of other additives such as antioxidants and stabilizers (Hsuan and Koerner, 1995). The resin used is basically a linear copolymer polymerized using ethylene and α -olefin as comonomer under low pressure with appropriate catalysts (Hsuan and Koerner, 1995). The typical structure of the polyethylene consists of a monotonous progression of linked carbon atoms that are bonded to hydrogen (Apse, 1989).

The polyethylene in a geomembrane may take the form of crystal lamellae where the polyethylene chains are neatly folded and tightly packed, and looser amorphous layers where the chains or chain segments are pendant or disordered (Apse, 1989). The lamellae are linked via tie molecules that start and end in the adjacent lamellae. Thus, some of the inherent properties of polyethylene depend on the packing structure and consequently, any changes in the molecules and/or molecular packing may alter the durability and the overall field performance of the geomembrane.

This paper summarizes the basic concepts and mechanisms related to the durability of HDPE geomembranes as well as the current research trends, and provides a brief review of the key relevant literature.

2. Degradation of HDPE geomembranes

2.1. Aging and degradation

A well-designed and installed intact geomembrane liner may be expected to experience some degradation or aging with time that will lead eventually to its failure. The aging process of HDPE geomembranes can be envisioned as a simultaneous combination of physical aging and chemical aging (Hsuan and Koerner, 1995, 1998). In physical aging, the material attempts to establish equilibrium from its as-manufactured non-equilibrium state. As a consequence, there are no primary (covalent) bonds broken and for semi-crystalline polymers like HDPE, there is an increase of the material crystallinity (Petermann et al., 1976). In contrast, chemical aging involves bond scission in the backbone of the macromolecules, intermolecular cross-linking and/or chemical reactions in the pendant groups or side-chains (Schnabel, 1981) that will eventually lead to a decrease in mechanical properties and eventually to failure. Thus, from an application perspective, chemical aging is the most important degradation mechanism and therefore requires particular attention. Koerner et al. (1990) have provided a detailed description of the different types of degradation to which an HDPE geomembrane may be subjected as a result of its environmental exposure that varies with the application in which the geomembrane is used. A review of potential exposure

conditions in landfill and other containment applications has been provided by Haxo and Haxo (1989). The degradation mechanisms include swelling, UV degradation, degradation by extraction, biological degradation, and oxidative degradation.

Degradation by swelling arises when a geomembrane exposed to any liquid (including leachate) increases in volume due to sorption. This type of degradation is reversible to some extent because when the material is removed from the medium, there will be some desorption of the sorbed chemical. This type of degradation is generally not a concern for HDPE geomembranes in landfill applications, provided that the leachate in contact with the geomembrane has low concentrations of contaminants compared to the concentrations typically used in tests to assess the effect.

UV degradation (photodegradation) is induced by irradiation with UV or visible light. The consequences of long-term exposure include discolouration, surface cracks, brittleness and deterioration in mechanical properties (Schnabel, 1981; Beach and Kissin, 1986). The susceptibility of HDPE geomembranes to UV degradation is reduced by the use of carbon black or chemical-based light stabilizers that prevent the UV light from penetrating the polymer structure (Koerner et al., 1990). With respect to protection against UV, Koerner et al. (1990) indicated that a 0.15 m soil over the geomembrane would be sufficient to protect it from UV light.

Degradation by extraction is a type of degradation where one or more components are removed from the material due to long-term exposure to chemicals and liquids. In the case of HDPE geomembranes, additives incorporated into the polymer formulation (Koerner et al., 1990) may be extracted. According to Doyle and Baker (1989), the consequences associated with the extraction are essentially the progressive increase in brittleness of the geomembrane. The effects of extraction become important when stabilizers and antioxidant are leached out leaving the geomembrane unprotected and rendering the material susceptible to subsequent oxidative degradation.

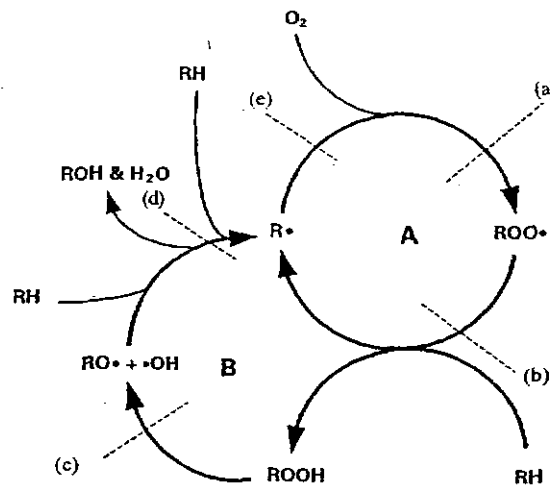
Biological degradation arises from the polymer being attacked by microorganisms (Hawkins, 1984). Koerner et al. (1990) indicated that it is highly unlikely because of the high molecular weights (30,000–100,000) of common geomembrane resins.

Oxidative degradation is the form of degradation that is the most harmful to HDPE geomembranes. In this type of degradation, the polymer chains undergo reactions with oxygen leading eventually to changes in molecular structure and morphology (Hawkins, 1972). As a result, critical mechanical, dielectric or esthetical properties may change beyond acceptable limits. Although oxidation reactions proceed slowly throughout the service life of the geomembrane, it is enhanced under service conditions that feed the polymer with energy. In general, the oxidation is either triggered or accelerated in the presence of thermal or radiation energy and the mechanisms will be discussed in the following sections.

Furthermore, geomembranes may be simultaneously subjected to several types of degradation during their service life. These different degradation mechanisms may have synergistic effects that could accelerate the overall rate of HDPE geomembrane degradation.

2.2. Oxidative degradation

Oxidation can have a particularly severe impact on polyethylene materials (Hawkins, 1984). It is generally agreed that the fundamental process underlying the oxidation of a polymeric material like HDPE is a free radical chain mechanism (Kelen, 1983; Grassie and Scott, 1985). As can be seen from Fig. 1 the oxidation mechanism involves two interacting cyclical processes (Grassie and Scott, 1985). The first cycle (A) is the alkyl/alkylperoxy chain reaction and the second (B) involves the homolysis of hydroperoxides, which feeds the chain reaction with the new radicals. If any of the interactions between the two cycles are broken, the oxidation can be retarded and can even be stopped if all the links are impeded. Antioxidants and stabilizers are often used to retard the oxidation, and can be classified into two distinct groups referred to as primary and secondary antioxidants (Chirinos-Padrón and Allen, 1992; Fay and King, 1994). Primary antioxidants function by trapping the free radical formed in the presence of oxygen while the secondary antioxidants reduce the active hydroperoxides to inactive alcohol (Yachigo, 1992). The effectiveness of the antioxidants depends on various factors including the total



RH: Polyethylene polymer chain
 R•: Reactive free radical
 ROO•: Hydroperoxy radical
 ROOH: Hydroperoxid

(a) (b) (e): Primary antioxidants
 (c) (d): Secondary antioxidants

Fig. 1. Oxidation cycles in polyethylene (modified from Grassie and Scott, 1985).

amount, the types and the combination used and the service temperature of the geomembrane (Chirinos-Padrón and Allen, 1992; Fay and King, 1994). If oxidation occurs, the resulting chain scission leads to a decrease in molecular weight making the material brittle, and more prone to environmental stress cracking (Tisinger and Giroud, 1993).

The oxidative degradation of HDPE geomembranes appears to proceed in three relatively distinct stages (Hsuan and Koerner, 1995, 1998) as shown in Fig. 2. The first stage (A) corresponds to the depletion of antioxidants and is due to either their consumption as a result of their chemical reactions with the oxygen, free radicals and alkyl peroxides and/or their physical loss by diffusion, extraction or volatilization (Luston, 1986). The time required for the depletion of antioxidant will, in part, depend on the type and the amount of antioxidants in the new geomembrane. The amount of antioxidant in the material is often measured in terms of the oxidative induction time (OIT). Two types of tests may be used: the standard-OIT (ASTM D3895-95) and high-pressure OIT (ASTM D5885-97) tests. A good discussion of these two methods has been provided by Hsuan and Koerner (1998).

Entering into the induction period (Stage B: Fig. 2), the antioxidants are completely depleted and hydroperoxides' concentration starts to accumulate. Once the concentration of hydroperoxides reaches a critical level, decomposition of hydroperoxides and accelerated chain reactions begin, signifying the end of the induction period (Rapoport and Zaikov, 1986). At this second stage, evaluating changes in molecular composition provides a logical method for measuring the course of polymer degradation. Among the available methods, the molecular composition is usually studied by Fourier transform infrared (FTIR) spectroscopy that has long been recognized as a powerful tool for polymer characterization. This technique gives quantitative and qualitative information about the physico-chemical composition of polymers, copolymers, polymer blends, composites and additives

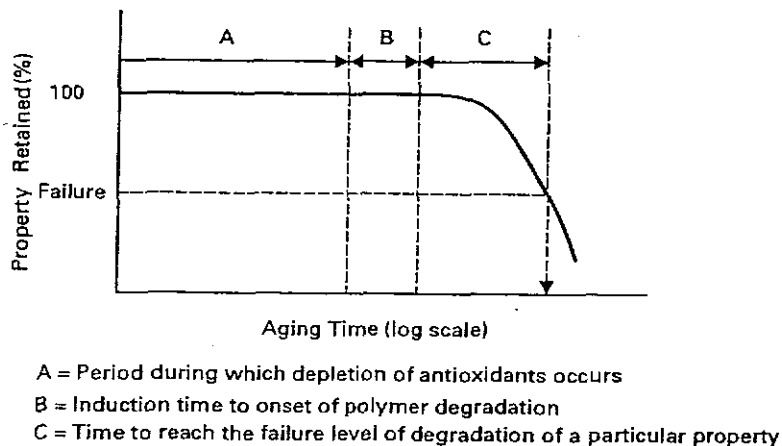


Fig. 2. The three conceptual stages in chemical aging of HDPE geomembranes (modified from Hsuan and Koerner, 1998).

used in these materials. It is used to study the functional groups formed as the by-product of material oxidation. The application of FTIR analysis to study the degradation of polyethylene has been described in great detail by Hamid and Prichard (1988).

During Stage C (Fig. 2), hydroperoxides start to decompose yielding abundant free alkyl radicals and leading to an accelerated oxidation (Kelen, 1983; Hsuan and Koerner, 1995). In the early stage of this acceleration, cross-linking occurs in these alkyl radicals due to oxygen deficiency (Hamid et al., 1992). Consequently, the molecular weight increases while mechanical properties appear relatively unchanged. As the oxidation advances further, the reaction of oxygen within the material with alkyl radicals change to chain scission causing a reduction in molecular weight as the chains shorten. Such changes in the molecular size (weight) can be detected by the melt flow index test (ASTM D1238-00) since the melt flow index is inversely related to the molecular weight. They can also be assessed in terms of environmental stress cracking test known as "Single Point Notched Constant Tensile Load Test" (SPNCTL) and described in ASTM D5397-99-Appendix.

A direct consequence of the degradation that occurs during Stage C is the decrease of both stress and strain at break while tensile modulus and yield stress increase. The test usually used to assess the changes in tensile properties is ASTM D638-99. As the degradation progresses further, the geomembrane will become increasingly brittle and the tensile properties change to the point that cracking occurs in stressed areas. Once sufficient cracks have developed to significantly increase flow through the geomembrane, the geomembrane may be considered to have reached the end of the so-called "service life".

2.3. Factors affecting the oxidative degradation

There are several factors that affect the oxidative degradation of HDPE geomembranes including the geomembrane properties, exposure medium, exposure conditions, and applied mechanical stress field.

2.3.1. Geomembrane properties

The chemical structure of a polymer strongly affects its ability to resist oxidation degradation. The rate of degradation increases with chain branching density because "branchy" materials contain more tertiary hydrogen atoms than pure linear materials (Kelen, 1983). This is due to the fact that tertiary hydrogens possess lower dissociation energy than other hydrogen atoms, thus making it easier to convert to free radicals than primary or secondary hydrogen atoms. In other words, polyethylene with greater branch density will generate more free radicals than those with fewer branches under the same conditions (Hsuan and Koerner, 1995).

It is well known that oxidation is initiated in the amorphous phase of semi-crystalline polymers because crystalline regions in polyethylene are sufficiently dense to severely limit oxygen diffusion within the material (Michaels and Bixler, 1961; Kelen, 1983). The effect of crystallinity on reducing the degradation of a geomembrane is twofold. First, the crystalline zones act as diffusive barrier to

oxygen. Secondly, the alkyl radicals formed during the oxidation tend to be trapped in the crystalline matrix and therefore are unable to progress further (Billingham and Calvert, 1986). This suggests that a geomembrane with high crystallinity will be less vulnerable to degradation than a geomembrane with low crystallinity. However, as it will be discussed later, a geomembrane with higher crystallinity is more susceptible to stress cracking.

It has also been shown that the geomembrane thickness has a significant effect on its oxidative degradation. Kelen (1983) indicated that the rate of oxidation decreases with increasing polymer film thickness and that thick films displayed longer induction time than thin ones. This is because oxidation is a function of the number of oxygen molecules available to attack the polymer chains. Since the availability of oxygen in the geomembrane is essentially diffusion controlled, increasing thickness reduces the potential for oxygen to attack the polymer. In addition, the outward migration of antioxidants will be slower for a thick geomembrane than a thin geomembrane. Similar effects of geomembranes thickness on their degradation has been reported by Lopes et al. (1998) who observed, from laboratory investigations, a greater reduction in the tensile strength for the thin geomembrane (1.0 mm thick) compared to the thick geomembrane (2.0 mm).

In addition, the presence of transition metals (e.g., Co, Mn, Cu, Al and Fe) can increase the rate of oxidation because they break down hydroperoxides via redox reactions and create additional free radicals (Osawa and Ishizuka, 1973; Osawa, 1992). The source of these elements usually comes from residual catalysts used to polymerize the resin although they are also present in landfill leachate. Although, the concentration of these elements is very low, they are still a concern regarding the long-term durability of the polymer.

2.3.2. *Exposure conditions*

The oxidation reaction in polyethylene is rather sensitive to the surrounding ambient environment. Any condition that provide oxygen and accelerate the formation of free radicals, particularly the decomposition of hydroperoxides, increase the rate of oxidation.

Energy is needed to activate the degradation and to break the chemical bonds. Sunlight, heat and radiation are three types of energies, which can affect a geomembrane during its service life. For an exposed geomembrane, sunlight is the major concern. Coupled with heat, there is a great potential for free radical formation. Heat, however, can come from other sources than direct sunlight. High temperatures of about 50–70°C have been reported within several landfills (Ramke, 1989; Lechner and Lanher, 1991; Barone et al., 1997; Bleiker, 1992; Yoshida et al., 1996) implying that geomembranes may undergo some thermal degradation or thermo-oxidation. All other things being equal, if one accepts that the degradation is an activated chemical reaction, a geomembrane will degrade faster at higher temperatures than lower temperatures.

Another important factor that affects the oxidation rate is the availability and the abundance of oxygen. In fact, it is well known that the concentration of available oxygen is an essential component to any oxidation reaction. The abundance of the

oxygen depends on the location of the geomembrane and the application. For exposed geomembranes, the availability of oxygen is high and the oxygen concentration is at its maximum. In contrast, for landfill base liners, the available free oxygen will be extremely limited. In the case of a liner for municipal solid-waste landfill, biodegradation of the waste will probably consume most of the available oxygen during the anaerobic phase of biodegradation of organic matter in waste. In surface impoundment applications, the portion of geomembrane that is covered by liquid is only exposed to about one-eighth of the oxygen in comparison with that exposed to air (Hsuan and Koerner, 1995). Consequently, as indicated by Verdu (1992), the oxidation may proceed faster when the material is exposed to atmosphere than when covered by liquid.

2.3.3. *Exposure medium*

It may be hypothesized that the medium (soil or liquid) in direct contact with the geomembrane would have a significant effect on the oxidation rate. If the adjacent soil contains transition metals at significant concentrations and there is moisture or liquid present, the transition metals can diffuse into the geomembrane (Hsuan and Koerner, 1995). The role of metals or metallic compounds in the degradation of polymers is extremely complicated and is modified by various factors such as the nature of the polymer substrate, environmental conditions, the type and valency of metal, and the anion of ligand or metallic compounds (Osawa, 1992).

Another exposure condition that may significantly enhance the oxidation of a geomembrane is the presence of transition metals such as Cu, Mn and Fe in leachate. These metals break down hydroperoxides via redox reactions and create additional free radicals (Osawa and Ishizuka, 1973; Osawa, 1992) similar to the case where they exist as impurities in the geomembrane. A thermo-oxidation study on a polypropylene immersed in metal-rich (FeCl_2 , MnSO_4 , CuCl_2 , etc.) aqueous solutions undertaken by van Langenhove (1990) showed that the degradation was accelerated by a factor of 10, or more, depending on the metal. The greatest decrease in the induction time (by more than a factor of 10) was observed in the presence of Cu, followed by Fe (a factor of 10), and Mn (a factor of 2) at concentrations up to 20 g/kg.

One may hypothesize that the influence of transition metals on the degradation would be less when they are contained in the adjacent medium (leachate, soil, etc.) than if they are impurities from manufacturing process. This is because metals cannot readily diffuse through the geomembrane as noted by August et al. (1992). However, since the degradation initiates at the surface and then progresses through the material, their effect may not be negligible. More research is required to evaluate the effects of transition metals in the adjacent soil or leachate on the service life of HDPE geomembranes.

2.3.4. *External mechanical stresses*

The application of a large external stress or loading on a polymer will result in a decrease in its useful lifetime, primarily via physical creep, although it is possible that chemical degradation mechanisms may also be enhanced (Horrocks and D'Souza,

1992). Studies on degradation of stressed polypropylene rods at temperatures up to 130°C (Czerny, 1972) suggested the presence of a safe stress level below which no increase in the degradation occurs due to increasing applied stress. Above this safe stress, the applied stress caused an appreciable acceleration of polymer embrittlement. Liavanova et al. (1979) found that, for a polypropylene stressed at 130°C, the durability isotherm in terms of applied stress versus induction time could be divided into three distinct regions. At low stresses the rate of oxidation is the dominant factor; at intermediate stresses the mechanical stress accelerates the oxidative degradation; and finally at high stresses the mechanically initiated rupture of stressed bonds is the determining factor. Undoubtedly, these observations identify the importance of the stress levels to be used in accelerated laboratory aging tests as a factor requiring consideration.

Little has been reported regarding the effect of stress on the degradation of HDPE geomembranes. Laboratory investigations conducted by Surmann et al. (1995) on 1.5 and 2.0 mm HDPE geomembranes strained at 5.6–8% revealed no strain (stress)-induced accelerating effects when immersed in leachate. Similar observations have also been reported by Maisonneuve et al. (1997) who strained the geomembrane to 5%.

3. Reported field performance

The relatively short history of geomembrane use in waste or liquid containment applications makes case records relatively rare. A study by Brady et al. (1994) examined the behaviour of HDPE in different environments over a period of 30 years. The results of tests on unaged and 30-year old specimens showed no substantial changes in density, water adsorption, water extractable matter content and tensile properties. The impact resistance changed only after 15.5 years with a reduction of about 50%.

Schmidt et al. (1984) conducted a series of physical index tests (examining tensile and tear properties) on samples of polyethylene liner material from exposed and submerged geomembranes that had been in use for up to 16 years. The results showed a stiffening of the polymers with age and a related decline in elongation at break with time, which was less significant for buried/unexposed geomembrane. The major cause of failure to the liners was from physical/mechanical damage, rather than weathering/aging effects.

Hsuan et al. (1991) conducted a study of the performance of an HDPE geomembrane after 7-yr use for solid-waste leachate storage in a surface impoundment. The samples were obtained from four different locations in the lagoons, ranging from areas continuously exposed to the atmosphere to those at the bottom of the impoundment, continuously covered by liquid. The results indicated that: (1) no substantial macroscopic change in the geomembrane sheets or seams after 7 yr exposure at the site; (2) no substantial changes in the internal structure of the material due to the constant outdoor exposure; and (3) no affect on the engineering/hydraulic containment properties of the geomembranes.

A similar study was conducted by Rowe et al. (1998) on a 14-year old HDPE geomembrane from leachate storage lagoon. They observed very low OIT values for the exposed geomembrane accompanied by a reduction in tensile break properties and stress crack resistance of the geomembrane. The results of the melt flow index tests suggest that the degradation was induced by chain scission reactions in the polymer. The geomembrane was severely cracked indicating that the material was highly susceptible to stress cracking as confirmed by the single point notched constant tensile load tests (SP-NCTL: ASTM D5397-99-Appendix). For geomembranes that were covered by soil or leachate, the depletion of antioxidant was slower than for the exposed and partially exposed geomembranes suggesting that the amount of antioxidant present in these geomembranes had been sufficient to protect the geomembrane from oxidation degradation over the 14 years of service under these less-severe exposure conditions. Rowe et al. (1998) suggested that OIT tests and stress cracking resistance might be effective in assessing the degradation of HDPE liners. The diffusion and sorption tests conducted on these samples by Sangam (2001) indicated that the permeation properties of the organic MSW contaminants are 2-5 times lower than those measured by Sangam and Rowe (2001) for a new unaged modern HDPE geomembrane. This implies better diffusion characteristics for the 14-year old geomembrane than the modern new geomembrane. However, this was offset by the brittleness and cracking that had occurred which resulted in leachate coming into direct contact with the underlying clay liner. Thus, significant migration of inorganic contaminants observed in the underlying compacted clay appears to have been due to the premature damage to and cracking of the HDPE geomembrane.

Rollin et al. (1994) have reported a case of an HDPE geomembrane after 7 years of use in landfill application. The geomembranes was part of a composite liner clay/geomembrane/clay system that was used to contain a contaminated soil. Tensile tests performed revealed that while the strength at yield increased slightly (0-8%), the properties at break (strength and strain) experienced an average decrease of 16% for samples from the slope, 25% for cover samples and 60% for samples collected from the bottom of the cells.

Eith and Köerner (1997) also described a case in which an HDPE geomembrane was used as part of a double liner system for a landfill. During the 8 years of service, the geomembrane had been exposed to various concentrations of leachate constituents. The physical, mechanical and endurance test results indicated no apparent degradation of the HDPE geomembrane properties since they were still within the range of data generated for the original material at the time of installation.

4. Environmental stress cracking

One of the concerns raised regarding the use of HDPE geomembranes is their susceptibility to stress cracking which, in turn, is a consequence of their high crystallinity (typically about 40-50%). According to ASTM D 883, stress cracking is

“an external or internal rupture in a plastic caused by tensile stress less than its short term mechanical strength.”

There are three stages in crack development (Peggs and Carlson, 1989). First, the crack is initiated via a craze that is a planar defect, then it opens in the presence of tensile stress and finally propagates through the geomembrane. In most cases, the propagation is accompanied by other crazes that will initiate further cracks. Thus, failure due to stress cracking is associated with defects or imperfections where the stresses are enhanced to higher values with an up to 6-fold magnification of tensile stress (relative to the average global stress) depending on the geometry of the defect (Halse et al., 1989; Peggs and Carlson, 1989). The defects may be of various types and shapes and generally include surface scratches, grinding gouges, patches, seams, etc. In addition, the presence of external chemical environment such as detergents, (surfactants), leachate, polar vapour, liquid, etc. may accelerate stress cracking. This type of stress cracking in the presence of chemicals is called “environmental stress cracking” (Kulshreshtha, 1992).

The molecular structure of the polymer controls its susceptibility to stress cracking. Lustiger et al. (1981) and Lustiger and Corneliussen (1986) report post-failure analyses of polyethylene pipes which showed that the failure is caused by the lack of tie molecules. Therefore, it appears that the number of tie molecules that are abundant in the amorphous zone controls the stress-cracking behaviour. The direct consequence of this dependence is that polymers with high degree of crystallinity (e.g. HDPE) and hence low number of tie molecules will be more prone to stress cracking than the same type of polymer with low crystallinity (e.g. LLDPE).

The other polymer properties that affect its susceptibility to stress cracking include the molecular weight and the comonomer content (Lu and Brown, 1990, 1991). Higher molecular weight corresponds to longer chains (Apse, 1989) resulting in more tie molecules and more effective tie molecule entanglements (Lustiger and Rosenberg, 1989). Similarly, high comonomer content and longer comonomer short-chain branches provide better cracking resistance, probably because portions of the long-branch chains cannot be folded into the lamellae and therefore contribute to the amorphous tie molecules (Lustiger and Rosenberg, 1989).

Several investigators have reported field evidence of the vulnerability of HDPE geomembranes to stress cracking. Peggs and Carlson (1989) have reported in detail several field observations of different polyethylene geomembranes. Rowe et al. (1998) have reported field observation of cracks on a 14-year old geomembrane used as a liner for leachate lagoon. Hsuan (1999) summarized field cases of stress cracking in HDPE geomembrane liner exhumed from 16 sites. The main observations from these three papers are that: (1) the majority of the field cracking failures were associated with exposed geomembranes suggesting that temperature-induced stresses may have played a significant role; and (2) cracks mostly appear at the discontinuities formed by overlapping seams, patches, scratches and gouges where stress concentrations are readily established.

Stress cracking is important because: (a) even short cracks can allow excessive leachate through the geomembrane that may readily move laterally in areas of poor contact between the geomembrane and the underlying clay; and (b) short cracks can

grow with time eventually allowing excessive leakage through the geomembrane even in areas of good contact with the clay. In either case, once the leakage increases substantially, the geomembrane ceases to perform the barrier function for which it was designed as discussed by Rowe et al. (1998).

5. Laboratory studies of geomembranes durability

Several investigators have conducted laboratory tests to examine durability and degradation issues related to geomembrane liners for landfills. For instance, Duquennoi et al. (1995) examined the aging of 2.0 mm thick HDPE geomembrane in different solutions. The experiment consisted of immersing the geomembrane samples in two different leachates and in distilled water. The first leachate was collected from a compacted municipal waste landfill while the second was sampled from a shredded uncompacted municipal waste landfill. The immersion tanks were lightproof and air free (methods not indicated) and the leachate solutions were replaced every 3 or 4 months. Incubation temperatures were 20°C (room temperature) and 50°C. Tests used to assess the aging include tensile tests (uniaxial and biaxial) and FTIR. After 50 months of aging in leachate and distilled water at room temperature, no changes were observed either in mechanical properties or FTIR spectroscopy, while at 50°C a small loss of the ester-type antioxidant was noted. These authors did not address service life prediction, probably because only one elevated temperature was used.

Surmann et al. (1995) reported aging studies that used superposition of mechanical stresses with various leachate strengths at temperatures of 23°C and 40°C using 1.5 and 2.0 mm thick geomembranes. Two aging experiments were conducted. First, geomembranes, while immersed on site in leachate from a domestic refuse landfill, were submitted to a constant one-dimensional strain of about 5.8% for the small device and varying between 7% and 8% for the big device. No failure was observed after two years and none of the analytical methods revealed any differences between the new and aged geomembranes. In the second experiment, the geomembranes, while strained at 7%, were placed over a 100 mm thick compacted clay layer and were covered by 87 mm gravel layer. The composite system was subjected to a vertical pressure varying from 250 to 300 kPa and a leachate or gasoline head, and temperatures of 23°C and 40°C. After one year of testing, the chemical composition of the HDPE geomembrane had not changed although mechanical test data showed that the material had been weakened at locations where it was dimpled and where ruptures were observed, especially for samples at 40°C.

Cazzufi et al. (1995) performed tests to assess the effect of natural and laboratory weathering exposure of different geosynthetics including a 2.0 mm HDPE geomembrane. Laboratory weathering tests consisted of submitting samples to simulated cycles of irradiation in the UV spectrum of sunlight with cycles of moisture obtained by heat condensation. The experiment conducted at 50°C and 60°C used an UV-fluorescent condensation test device equipped with UV-B-type lamps. The residual tensile properties (tensile peak strength, peak strain and secant

modulus at 5%) were used to assess the material. After 24 months, the geomembrane showed a decrease of <20% in its tensile peak properties and 10% in tensile modulus.

Maisonneuve et al. (1997, 1998) presented results for a series of tests conducted on HDPE geomembrane sheets and seams (properties not specified) in a simulated immersion medium at a temperature of 60°C and under 5% tensile strains. For the geomembrane sheets, the results show that only antioxidants were depleted and no significant physico-chemical changes were observed after about 8 months of immersion. The oxidative induction time was reduced by about 67% from 30 to 10 min. For the seamed material, a plasticizing effect that renders the material softer was observed after 4 months. As a consequence, the yield strength decreased and the strain increased as observed for the geomembrane sheet.

None of the investigations summarized above identified or directly considered the three stages of aging defined by Hsuan and Koerner (1995). Studies dealing with the depletion of antioxidants have been reported by Hsuan and Koerner (1998). The investigation conducted consisted of two series of tests in which samples of a single specific geomembrane were incubated at four elevated temperatures (55°C, 65°C, 75°C and 85°C). In the first, HDPE samples were fully immersed in four water baths while in the second series, the geomembrane is located between two 100 mm thick layers of sand, saturated on top, and dry at the bottom. The geomembrane is subjected to 0.3-m water head and a vertical compressive stress of 260 kPa. The OIT results indicated that depletion of antioxidants proceeds at rates 1.2–2.2 times faster than in the first series due to the extraction of the antioxidants.

Sangam (2001) has also reported laboratory-accelerated aging tests that involved the exposure of the geomembrane to air, water and leachate at 22°C (control), 40°C, 55°C, 70°C and 85°C. The results from the OIT tests suggested that first-order decay kinetics rates are higher in liquid-exposed samples than for samples exposed to air. In water-immersed samples, the depletion rate is about 1.6–2.4 times the rate of consumption in air-exposed samples. For leachate-exposed samples the depletion is about 4 times faster than in air and 1.6–3.2 times than in water. These observed high rates demonstrate the susceptibility of the antioxidants to extraction and the role played by the leachate constituents in facilitating the removal of antioxidants from the geomembrane.

6. Estimation of geomembranes service life

The short history of geomembranes in civil engineering applications renders difficult the estimation of their service lives. Often, the service life is predicted based on laboratory-accelerated tests using a time-temperature prediction model known as Arrhenius modeling (e.g. see Koerner et al., 1992). Gray (1990) compared two methods of accelerated aging, which both use elevated temperature to simulate long-term HDPE exposure. The paper reviewed the work carried out by the wire and cable industry which indicates that the service life of HDPE insulation on cables (at a temperature of 40°C) is in the order of several hundred years.

Lord and Halse (1989) reviewed the work carried out by the plastic pipe industry on the service life of HDPE pipes used in natural gas pipeline applications. These studies used elevated temperatures and stresses to determine the ductile/brittle transition point of HDPE pipe, and predicted a service life of >50 years for pipes under relatively high stresses (>7000 kPa). For a geomembrane at the base of a landfill, the stresses will be much less and it is expected that accelerated aging tests at these lower stresses would indicate a longer service life (likely in the order of several hundred years).

Koch et al. (1988) have applied their pipe research expertise to the geomembrane area and conclude that the interaction with leachate is the largest concern in the service life of geomembranes. Although the stress fields in an HDPE pipe are different than those in a geomembrane liner, they conclude that considering all of the other factors (leachate interaction), the service life of HDPE geomembranes could be expected to be considerably >100 years.

Jessberger and Heibroek (1997) indicated that at 20°C and under steady oxygen supply, the service life of an HDPE geomembrane might be over 300 years. However, when the temperature increases at 40°C for the same oxygen conditions, the service life is predicted to be over 45 years.

If one assumes that the degradation of the geomembrane is essentially due to oxidation and that the three-stage model proposed by Hsuan and Koerner (1995) holds, then the overall service life should be a summation of the duration of each stage. Hsuan and Koerner (1995) estimated that, at 25°C, the time to consume the antioxidants in the geomembrane examined will be about 40 years for the samples immersed in water and 120 years for samples overlaid by a saturated sand layer and underlined by an unsaturated sand layer with an applied compressive stress of approximately 260 kPa. When the temperature decreases to 20°C this time will increase to 200 years (Hsuan and Koerner, 1998). Using the three-stage degradation model, Rowe (1998) reanalyzed the data reported by Hsuan and Koerner (1995) and estimated that the service life of HDPE geomembrane in landfill applications would be about 150 years for the primary geomembrane at <25°C while for the secondary geomembrane it would be expected to exceed 300 years at 15°C and 400 years at 10°C.

Sangam (2001) examined the service lives of HDPE geomembranes under various exposure condition scenarios that the geomembranes may be subjected to when used as bottom liners for MSW landfills. These estimates were based on: (i) antioxidant depletion rates inferred for the accelerated tests and (ii) the induction time reported by Viebke et al. (1994) for an unstabilized HDPE, and (iii) an assumed degradation time of 25 years (e.g. see Rowe, 1998). It was estimated that, provided that the landfill is well maintained such that the temperature is not higher than 15°C, the primary geomembrane would last at least 200 years whereas for the conditions where the temperature is at 33°C, the service life is estimated to be about 70 years. For the typical groundwater temperature range of 7–10°C, it is estimated that the geomembrane used as a secondary liner will last at least 400 years provided that it has a suitable antioxidant package, is not subjected to significant tensile stress and is covered by an adequate protection layer.

The key findings of the work reported by Hsuan and Koerner (1995, 1998) and by Sangam (2001) are that the service lives of the HDPE geomembranes are essentially controlled by the antioxidants in the material and the service temperature. However, there is the potential for debate regarding the property (s) to be assessed with respect to the degree of polymer breakdown and the level used as the failure level. In landfill base liner applications, the real service life depends on the hydraulic and diffusive properties of the geomembranes and hence, a geomembrane may lose strength while still performing satisfactorily as a barrier. Therefore, the “hydraulic and diffusive service life” of a geomembrane may exceed the service life as determined by the degradation of physical and mechanical properties, especially if tensile stresses are minimal.

7. Summary and conclusions

A review on the degradation and field long-term of HDPE geomembranes has been presented. The oxidative degradation process of HDPE geomembranes has three main stages. First, the protective agents, called antioxidants, are depleted either by simple reaction with oxygen or loss by volatilization or leaching. At the end of this stage the material becomes vulnerable to any oxygen present. The second stage is the induction time that corresponds to the time required before the relevant properties start to be altered. The third stage corresponds to the elapsed time before the geomembrane fails. Therefore, the overall service life should be a summation of the duration of the three stages.

The oxidative degradation model discussed above calls for more comprehensive laboratory investigations to better understand the degradation that takes place in geomembranes as a result of their exposure. Therefore, the future investigations should be able to incorporate conditions that will allow the identification and quantification of the three stages of the oxidative degradation process under conditions that provide a closer approximation to field conditions.

Examination of both laboratory and field data indicate that the projected service lives of HDPE geomembranes may range from many centuries to less than a decade depending on the material and exposure conditions.

8. Introduction to references

Koerner et al. (1990) provide a detailed overview of different types of geosynthetic degradation. References Hsuan and Koerner (1995), Hsuan and Koerner (1998) and Sangam, (2001) describe the oxidation degradation of HDPE geomembranes. Grassie and Scott (1985) explain the oxidation cycles with references to stabilization by the use of antioxidants. References Haxo and Haxo (1989) and Rowe (1998) provide a good summary of the conditions that geomembranes may be subject to in landfill applications. Excellent discussions on stress cracking are presented in Hsuan (1999) and Peggs and Carlson (1989). The potential use of Arrhenius modeling of the

estimation of geosynthetics service life is discussed by Koerner et al. (1992), while Sangam (2001) presents its application to the oxidative degradation of geomembranes in landfill leachate.

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