The durability of HDPE geomembranes

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Excellent papers have been written on the durability of high density polyethylene (HDPE) geomembranes. Since the subject is very complex, however, many of these papers can be understood only by polymer scientists. Because information on the durability of HDPE geomembranes is very important, such information needs to be presented to the wide range of geomembrane users.

In this article, aspects of materials' durability that relate to the composition and/or structure of the material used in the geomembrane will be discussed. Mechanical actions, including stress cracking, and aspects related to the durability of the geomembrane seams will not be addressed.

From low to high density

Polyethylene is a polymer. A polymer is a molecule that has many units (from the Greek, poly, which means many, and meros, which means part). In contrast, a monomer is a single unit (from the Greek monos, which means single). Polymers are made from monomers through a reaction called polymerization.

For example, a polyethylene polymer results from the polymerization reaction of the ethylene monomer (Seymour and Carraher, 1981).

Production of polyethylene began in the mid-1930s from a process using high pressure and high temperature (Brydson, 1982). In the mid 1950s, new reaction conditions were introduced in which polyethylene was produced at lower pressures and lower temperatures than before.

As a result, a new variety of polyethylene was made that had a higher softening point, a higher density and more rigidity than earlier types.

This new variety of polyethylene was appropriately named high density polyethylene, while the name low density polyethylene (LDPE) became used to designate the type of polyethylene produced with the early process.

Anatomy of HDPE

The high density of HDPE results from the presence of many crystals of polyethylene molecules within its structure. Crystals are regions in which matter is ordered and densely packed.

The crystalline regions are connected by less organized, or amorphous regions, hence the terminology semicrystalline structure. The amount of crystalline regions in a material is typically expressed as crystallinity, a ratio that varies between 0 percent for a totally amorphous material and 100 percent for a totally crystalline material. Crystallinity, measured by differential scanning calimetry, is the ratio of the energy required to melt a given HDPE to the energy required to melt a totally crystalline HDPE.

Because they are composed of densely packed matter, crystals are essentially impermeable to liquids and chemicals. Clearly, a relationship exists between the number of crystals, the density of polyethylene and the impermeability of the geomembrane.

HDPE used to produce geomembranes is made not only from ethylene. It also contains some comonomer (a monomer in addition to ethylene at a proportion of approximately 1 percent to 3 percent), such as butene, hexene or octene. Comonomers result in more branching on the polyethylene molecules of HDPE, which usually improves HDPE materials' flexibility and environmental stress cracking resistance (Bourgeois and Blackett, 1990).

As more branching slightly increases the distance between parallel long-chain molecules, however, it increases HDPE material permeability and reduces its chemical resistance, but by amounts that are generally considered insignificant.

HDPE geomembranes are not made from HDPE only. They also contain additives, such as carbon black and antioxidants. The resulting material is called the HDPE compound and it contains approximately 97 percent HDPE, 2.5 percent carbon black, and 0.5 percent antioxidants. Note that HDPE geomembranes do not contain plasticizers.

Chemical reactions

HDPE is chemically resistant for two reasons. First, as all members of the polyethylene family, HDPE is essentially inert. Second, as discussed earlier, because of its high density, HDPE has a low permeability; therefore, it resists penetration by chemicals. Under certain conditions, however, HDPE can react with chemicals. A chemical reaction between a material and a chemical occurs when the chemical modifies the structure of the molecules making up the material.

Reaction of HDPE with chemicals is generally limited to oxidizing agents, such as nitric acid and oxygen. In other words, oxidation is the predominant mechanism of chemical reaction of HDPE. Oxidation is a step-wise process.

The polymer first absorbs energy, provided by heat, UV radiation and/or high-energy radiation (radioactivity). This absorption excites the polymer molecules, causing them to break, forming highly reactive fragments referred to as radicals. This mechanism is called chain scission. The radicals then react with oxygen, forming even more radicals.

As the process proceeds, an increasing number of radicals are formed. The process is terminated only when the radicals either react with antioxidants or recombine, or when energy is no longer supplied (Brydson, 1982; Rodriguez, 1970; and Seymour and Carraher, 1981). If oxidation occurs, it causes the molecular weight of molecules to decrease, making the HDPE material soften and embrittle, thereby becoming subject to stress cracking. Oxidation occurs only if two conditions are present.

The first condition is a high concentration of the oxidizing agent. The second condition is that the material must receive a sufficient supply of energy to activate the reaction.

When the conditions are not present—which is often the case—HDPE is not attacked. This is confirmed by reported cases of EPA 9090 tests conducted to evaluate the chemical compatibility between HDPE geomembranes and municipal waste or hazardous waste leachates from modern waste disposal facilities, which indicate no detectable deterioration of the properties of HDPE geomembranes (Ojeshina et al., 1984; and Dudzik and Tisinger, 1990).

Physical interaction

Another potential mechanism of HDPE degradation is physical interaction. Physical interaction of HDPE with a chemical occurs when HDPE, without experiencing change in the structure of its molecules, absorbs the chemical, usually organic. Organic chemicals can interact with HDPE, because like HDPE, they are nonpolar, and therefore, have similar intermolecular forces (cohesive forces) holding adjacent molecules together. The most typical mechanism of physical interaction involving HDPE is solvation.

Solvation Solvation is a physical process by which solvent molecules are absorbed into a material. Solvation causes a polymeric material to swell (which increases its permeability) and to soften, a process often referred to as plasticization. A limited degree of swelling and softening is, to some extent, reversible: The geomembrane more or less retrieves its original dimensions and properties if the solvent is removed by evaporation. The ultimate degree of solvation is dissolution, where the molecules of the initially solid material are dispersed in the solvent. Of course, this mechanism is not reversible.

Typical solvents that may cause solvation of HDPE are aromatic solvents, such as benzene, toluene, xylene and halogenated solvents, such as chloroform, methylene chloride and trichloroethylene. These solvents cause some degree of solvation of HDPE at ordinary temperature. Dissolution of HDPE by these solvents, however, will not occur at ambient temperature.

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In fact, no known solvents can dissolve HDPE at room temperature. Typical waste disposal facility temperatures should not exceed 50 C, which is significantly below 80 C, the temperature at which some solvents may begin to dissolve HDPE. These solvents should, therefore, not cause complete dissolution of HDPE geomembranes under waste disposal facility conditions.

Moreover, the solvents must be present at very high concentration to affect HDPE, a condition that is not observed in waste disposal facilities.

Extraction Extraction is a mechanism of physical interaction between polymeric compounds and chemicals. It is a process by which chemicals and heat cause additives, such as plasticizers and antioxidants, to leach out of the polymeric compounds.

HDPE compounds used to produce geomembranes do not contain plasticizers; however, their antioxidants can be extracted. Such an extraction typically requires a very high concentration of chemical, a condition typically not present in a waste disposal facility. Moreover, most modern antioxidants have a high molecular weight and are physically entangled among the polyethylene molecules. Such physical entanglement greatly reduces the ability of chemicals to extract antioxidants. As a result, HDPE geomembranes do not undergo significant loss of antioxidants by extraction.

Energy and environment

In all the potential mechanisms of degradation described above, energy plays a crucial role. In geomembrane applications, the most typical sources of energy are heat and ultraviolet (UV) radiation; both conditions often occur through direct exposure to sunlight. Also, exposure to high-energy radiation (radioactivity) can induce reaction of HDPE with oxidizing agents. High-energy radiation also may cause HDPE to crosslink, that is, to form chemical bonds between adjacent polyethylene molecules. As a result, HDPE may harden and become brittle. Again, for this to happen, HDPE would have to be exposed to large doses of high-energy radiation (Whyatt and Farnsworth, 1990).

In the absence of either oxygen or energy, oxidation, the predominant mechanism of chemical reaction of HDPE, cannot occur. Typical waste disposal facility environments are anaerobic, eliminating the possibility for oxidative degradation of HDPE geomembranes once they are buried (Haxo and Haxo, 1989).

In addition, the supply of energy is limited, because there is no light and because geomembranes are usually protected by a layer of soil, which insulates them from heat generated by decomposition of waste.

Some oxidation of HDPE geomembranes can occur as the result of their exposure to sun during installation. Such oxidation is limited and superficial, however, because carbon black, which is an additive used in most HDPE geomembranes, absorbs sunlight, preventing it from penetrating the geomembrane (Whitney, 1988).

Furthermore, the effects of oxidation should be limited, because HDPE geomembranes contain antioxidants, additives that stabilize radicals generated by HDPE's absorption of energy. Information on the durability of HDPE geomembranes that are permanently exposed can be obtained from experience gained in observing the performance of existing facilities.

If not attacked, could HDPE simply age?

Aging refers to changes that occur in materials when they are subjected to the type of temperate conditions in which a human could survive (but would age)—no contact with liquid chemicals, moderate ambient temperature, no exposure to UV radiation or radioactivity, no supply of oxygen beyond that naturally present in air, etc. Studies have indicated that the effect of such conditions on HDPE materials is very slow.

For example, test results obtained from polyethylene films stored in a ventilated box exposed to desert, temperate and tropical environments for 15 years, have shown negligible changes in crystallinity and minimal evidence of oxidation (Moakes, 1976).

Resistance to aging is best evaluated by observations of actual performance in service. Polyethylene has a long track record of successful uses. Polyethylene was first synthesized in 1933, and became commercially available in 1937.

The use of polyethylene for cable sheathing began in 1942 (Gilroy, 1985). Since then, polyethylene has been the material of choice for the protection of transatlantic cables.

The first HDPE geomembranes were used in 1973 in Europe (Knipschild, 1984) and in 1974 in the United States. To date, HDPE geomembranes have been used, exposed or buried, for 20 years. Wherever they have been properly protected against mechanical failures (including stress cracking), HDPE geomembranes have performed satisfactorily. The performance of HDPE geomembranes for 20 years confirms the successful performance of HDPE in other outdoor applications, such as cable sheathing and buried pipes, for more than 40 years.

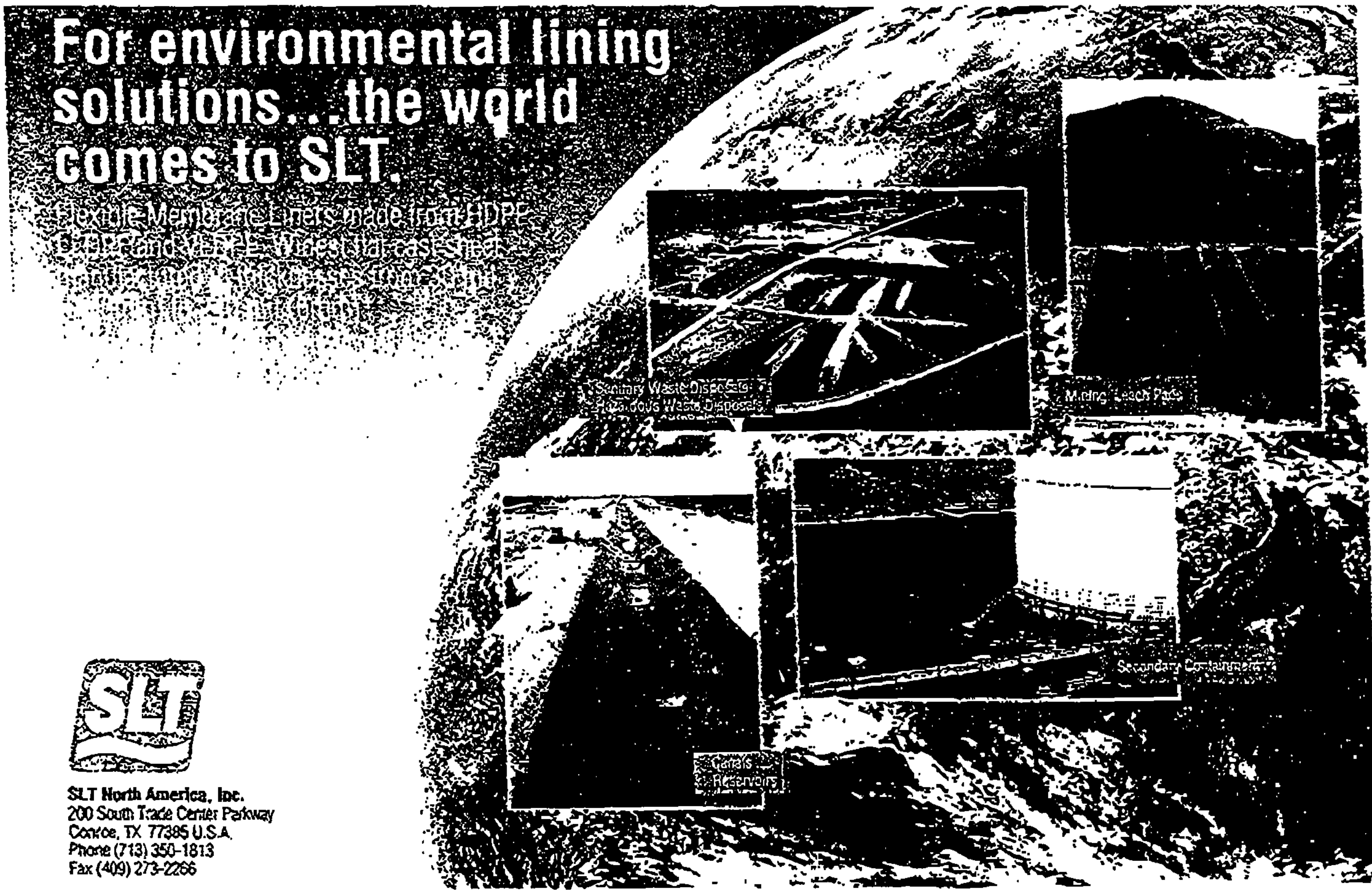
How long will geomembranes last?

A question frequently asked about geosynthetics and geomembranes in particular is, "How long will they last?" To answer this question, some clear conclusions can be drawn from the facts presented earlier.

Experience has shown that exposed HDPE materials, including geomembranes, can perform satisfactorily for decades if they are protected from mechanical aggressions.

In waste disposal facility environments, once HDPE geomembranes are buried, only little energy should be acting on them, and in addition, the supply of oxygen should most likely be very low. In the absence of an aggressive environment, therefore, HDPE geomembranes should last for a very long time in waste disposal facilities.

A U. S. Environmental Protection Agency (USEPA) ad hoc committee on the durability of polymeric landfill lining materials has concluded that the polymeric landfill lining materials should maintain their integrity in waste disposal facility environments in "terms of hundreds of years" (Haxo and Haxo 1988). This conclusion is consistent with durability evaluations made using the Arrhenius model (Koerner et al., 1990). One can conclude, then, that in properly designed and constructed facilities, HDPE geomembranes should be able to protect ground water from leachate for hundreds of years, which is long after leachate generation has stopped.



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