

212

DB2

Géomembranes en Polyéthylène

Projet d'établissement d'un lieu d'enfouissement
sanitaire à Saint-Cyrille-de-Lessard

MRC L'Islet

6212-03-045

Il s'agit d'une géomembrane dont le composé principal est du polyéthylène (PEHD).

Le polyéthylène (PE) est un polymère obtenu lors d'une réaction de polymérisation du monomère éthylène. La découverte de ce polymère remonte aux années 1930 et la technologie moderne de production a été mise au point durant les années 1950.

Actuellement, on produit le polyéthylène dans un réacteur à des températures et pressions contrôlées permettant d'obtenir une gamme de produits de densité variable:

- le polyéthylène à haute densité (PEHD);
- le polyéthylène à moyenne densité (PEMD);
- le polyéthylène à basse densité [PEBD ou PEBDL(linéaire)] et
- le polyéthylène à très faible densité (PETBD).

Le polyéthylène est constitué de molécules présentes dans une structure plus ou moins dense; les résines utilisées dans la production des géomembranes ont un poids moléculaire moyen de 250 000 pour le PEHD et 180 000 pour le PEBD (ou PEBDL).

Afin d'améliorer les propriétés du PEHD, entre autres la flexibilité et la résistance à la fissuration sous contrainte (stress cracking), les producteurs de résines peuvent faire varier la distribution des poids moléculaires. Un poids moléculaire plus faible favorise la flexibilité et la résistance à la fissuration sous contrainte (en faveur des PEBD et PEBDL); dans ce cas cependant, certaines ramifications nuisent à la résistance chimique du produit, ce qui explique, à l'opposé, la flexibilité médiocre, le risque de fissuration sous contrainte et la bonne inertie chimique des géomembranes PEHD.

Tous ces produits sont composés de parties cristallines (zones dans lesquelles la matière est ordonnée et dense) dans un entourage moléculaire moins bien organisé nommé « zone amorphe ». On peut produire le polymère PEBDL à partir du monomère éthylène et d'un comonomère tels le butène, l'hexène ou l'octène, dans une proportion de 1 à 3 %.

La présence du comonomère augmente cependant la distance entre les chaînes moléculaires polyéthylènes, diminuant ainsi la densité du PEBDL. Il faudra donc prévoir qu'une géomembrane PEBDL aura une résistance aux attaques chimiques différente de celle du PEHD, soit approximativement 90 % plus faible. Elle est cependant plus résistante qu'une géomembrane PEBD, car les chaînes d'un PEBD(L) sont moins ramifiées que celles d'un PEBD ; d'où l'usage de plus en plus répandu des PEBD(L).

De plus, afin d'augmenter la résistance du matériau aux attaques thermiques et aux rayons ultraviolets, on inclut des additifs tels que le noir de carbone et des agents antioxydants lors de la production de la géomembrane. Une géomembrane

polyéthylène haute densité (PEHD) est constituée en moyenne de 97 % de polyéthylène, de 2,5 % de noir de carbone et de 0,5 % d'antioxydants.

Source : Géomembranes : Guide de choix

The durability of HDPE geomembranes

By L.G. Tisinger and J.P. Giroud

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 calorimetry, 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 crack-

ing. 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,

A USEPA ad hoc committee has concluded that polymeric landfill lining materials should maintain their integrity in waste disposal environments in "terms of hundreds of years."

however, will not occur at ambient temperature.

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) radi-

ation; 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 environ-

ments, 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.

For environmental lining solutions...the world comes to SLT.

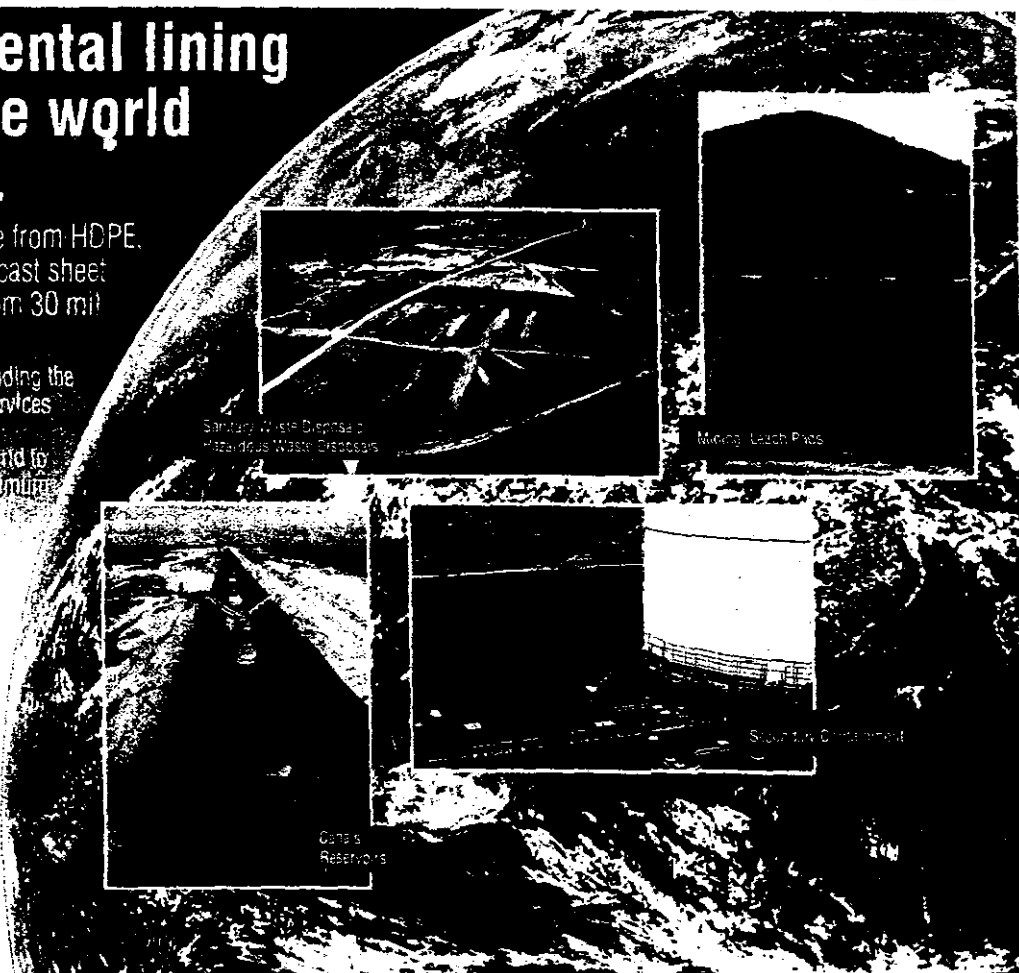
Flexible Membrane Liners made from HDPE, LLDPE and VLDPE. Widest flat cast sheet manufactured in thicknesses from 30 mil (0.75mm) to 240 mil (6mm).

Since the early 70's, SLT has been providing the highest quality liners and installation services to our clients worldwide.

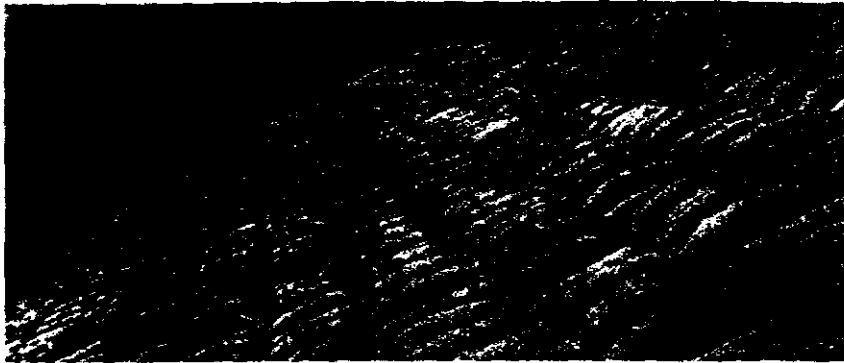
SLT has field offices throughout the world to assist clients in determining the optimum



SLT North America, Inc.
200 South Trade Center Parkway
Conroe, TX 77385 U.S.A.
Phone (713) 350-1813
Fax (409) 273-2266



CIRCLE READER SERVICE #4



Halt Waterfront Soil Erosion with Heavy Duty FABRIFORM® AB Mats

■ This Key West, Florida landfill (Stock Island) recently had a durable articulating block (AB) FABRIFORM® revetment installed which is protection, plus two thousand (2000) lineal feet of shoreline, against highwinds and waters during tropical storms. FABRIFORM® revetment meets the challenge with its nylon fabric-encased cable-reinforced staggered pattern of 40 inch (1000 mm) transverse by 24 inch (600 mm) slope by 8 inch (200 mm) thick articulating concrete blocks.

For a type or configuration of FABRIFORM® to handle your concrete forming requirements, just call Construction Techniques - the only name you have to remember for any woven industrial fabric.

Write or Call



Construction Techniques, Inc.

5353 West 161st St. • Cleveland, OH 44142
Telephone: 216-267-7310 • Fax: 216-267-7315

CIRCLE READER SERVICE #12

YOU BELONG

The North American Geosynthetic Society (NAGS) is a professional society dedicated to the development and advancement of geotextiles, geomembranes and related products and their applications. Membership is open to individuals whose activities or interests are related to geosynthetics.

As a NAGS member you:

- ◆ Are entitled to reduced registration fees at conferences and seminars organized or sponsored by NAGS
- ◆ Receive a free subscription to the Geotechnical Fabrics Report magazine
- ◆ Enjoy discounts on all NAGS publications
- ◆ Join other geosynthetic designers, manufacturers and users in the exchange of new ideas and information.

As a NAGS member you can meet with other North American members to discuss and develop specific areas of interest. NAGS members work together to contribute to the advancement of the science and technology of geosynthetics. Finally, NAGS offers you the means to reach out to designers, engineers and others involved in the international development of geosynthetics.

JOIN TODAY

For an application or more information contact:



NORTH AMERICAN GEOSYNTHETICS SOCIETY
345 Cedar St., Suite 800, St. Paul, MN 55101, USA
612/222-2508

CIRCLE READER SERVICE #13

References

- Bourgeois, J.R. and Blackett P.W., "HMW High Density Polyethylene," Modern Plastics Encyclopedia, McGraw-Hill, New Jersey, October 1990, pp. 75-76
- Brydson, J.A., "Plastics Materials," Butterworth's Scientific, Boston, 1982, 800 pages
- Dudzik, B.E. and Tisinger, L.G., "An Evaluation of Chemical Compatibility Test Results of High Density Polyethylene Exposed to Industrial Waste Leachate," Geosynthetic Testing For Waste Containment Applications, ASTM STP 1081, Robert M. Koerner, editor, American Society for Testing and Materials, Philadelphia, 1990, pp. 37-56
- Gilroy, H.M., "Polyolefin Longevity For Telephone Service," Antec, 1985, pp. 258-264
- Haxo, H.E. and Haxo, P.D., "Consensus Report of the Ad Hoc Meeting on the Service Life in Landfill Environments of Flexible Membrane Liners and Other Synthetic Polymeric Materials of Construction," Matrecon Inc., Alameda, Calif., Report # M86-155, May 1988, 55 pages
- Haxo, H.E. and Haxo, P.D., "Environmental Conditions Encountered by Geosynthetics in Containment Facilities," "Durability and Aging of Geosynthetics," Robert M. Koerner, editor, Elsevier, New York, 1989, pp. 28-47
- Knipschild, F.W., "Guidelines for the Installation of Geomembranes for Groundwater Protection in West Germany," Proceedings of the International Conference on Geomembranes, Vol. 1, Denver, Colo., June 1984, pp. 227-231
- Koerner, R.M.; Lord, A.E. and Hsuan, Y.H., "Long-Term Durability and Aging of Geomembranes," "Waste Containment Systems: Construction, Regulation, and Performance," Bonaparte, R., ASCE Geotechnical Special Publication No. 26, Proceedings of a symposium held in San Francisco, Calif., November 1990, pp. 52-83
- Moakes, R.C., "Long-Term Natural Ageing," Rapra Members Journal, March/April 1976, pp. 19-22
- Ojeshina, A., Jett, M.E. and Krecic, R., "An Assessment of HDPE Liner Durability: A Report on Selected Installations," International Conference on Geomembranes, Denver, 1984, Session 3C: Durability, pp. 317-320
- Rodriguez, F., "Principles of Polymer Systems," McGraw Hill, New York, 1970, 560 pages
- Seymour, R.B. and Carraher, C.E., "Polymer Chemistry: An Introduction," Dekker, New York, 1981, 564 pages
- Whyatt, G.A. and Farnsworth, R.K., "The High Ph and Chemical Radiation Compatibility of Various Liner Materials," Geosynthetic Testing for Waste Containment Applications, ASTM STP 1081, Robert M. Koerner, editor, American Society for Testing and Materials, Philadelphia, 1990, pp. 110-124
- Whitney, L.C., "Specifying Carbon Blacks for UV Light Protection," Plastics Engineering, December 1988, pp. 29-33

Acknowledgements

The authors acknowledge the technical assistance of J.F. Beech, F. Struve and C.E. Carraher in the preparation of this article.

TWENTY YEARS OF POLYETHYLENE GEOMEMBRANE UTILIZATION IN QUEBEC

Robert Denis, Solmax International Inc., Varennes (Qc) Canada
François Thivierge, Solmax-Textel Inc., Ste-Foy (Qc) Canada
Pascal Saunier, Solmax-Textel, Ste-Foy (Qc) Canada

ABSTRACT

A twenty year retrospective on the utilization of polyethylene geomembranes in Quebec is presented. Different applications and designs are discussed and commented along with lessons learned. Special consideration is given to the durability aspect of the materials throughout this first successful 20 year chapter of the geomembrane industry in Quebec.

RÉSUMÉ

Une rétrospective des vingt dernières années est présentée sur l'utilisation des géomembranes de polyéthylène au Québec. Différentes applications et conceptions sont discutées, accompagnées de leçons et expertises retenues. Une attention spéciale est prêtée à la durabilité des matériaux.

1. INTRODUCTION

Geomembranes are essentially bi-dimensional polymeric materials designed to reduce the hydraulic conductivity of in situ soils. Polymers come in different types, with polyethylene representing the bulk of the usage especially when corrosive contaminants are to be securely contained. Sparingly used for agricultural applications such as irrigation reservoirs and water conveyance structures as early as the 60's, it is truly only since the mid 80's that polyethylene geomembranes have revolutionized the waste containment industry in North America. Originally developed in Western Europe (Koerner 1997), polyethylene geomembranes were quickly endorsed by numerous governmental agencies, designers and users throughout the world as the materials of choice when it comes to environmental protection. This global and profound acceptance was basically achieved from the materials' intrinsic beneficial mechanical and physical properties in prolonged contact with a wide range of contaminants, along with their relatively low costs. From modest beginnings, polyethylene geomembranes are now being installed world-wide at an annual rate of over 300 million square meters. Canada is no exception to the rule, especially in the Quebec Province whereby polyethylene geomembranes have successfully been used since the mid 80's as well.

2. A SHORT HISTORY

In spite of the lack of properly documented and published case histories, it is still rather fairly safe to say that early uses of polyethylene geomembranes in the Quebec Province hail from the early 80's, more or less coincidental with the industry's official beginnings in North America as evidenced by what many consider as the first International Conference on Geomembranes held in Denver, Colorado

in 1984 (Denver 1984). To that effect, internal documentation of one of the local industry's first polyethylene geomembrane commercial venture reports the installation of both Canadian and American-made polyethylene geomembranes for non-environmental protection applications such as small water tanks and reservoirs in the early 80's for both municipal and private clients.



Figure 1. Early non-environmental polyethylene geomembrane applications.

It is also the era whereby a large contaminated soil site (a former coke gasification plant) was rehabilitated using polyethylene geomembranes as one of the very first high profile geosynthetic environmental endeavours in Quebec. This event was then quickly followed in the mid 80's by Quebec's first polyethylene geomembrane municipal waste landfill lining system, the first hazardous waste landfill cover, the first geomembrane double-lined

contaminated soil landfill, as well as the first large area secondary containment structure.

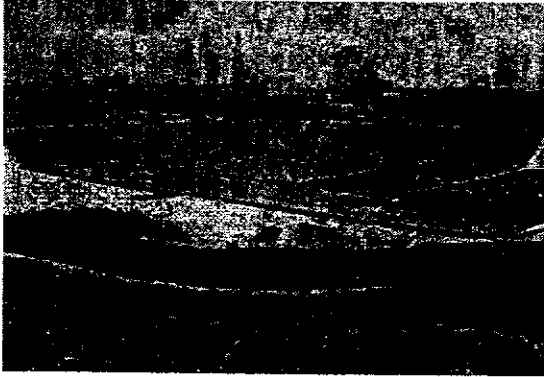


Figure 2. Quebec's first contaminated soil landfill.



Figure 3. Quebec's first municipal solid waste landfill.



Figure 4. Quebec's first large-scale secondary containment structure.

And then there was no turning back as polyethylene geomembranes have been used for all kinds of containment structures such as industrial sludge

reservoirs, mine tailing dams, waste water reservoirs, etc... leading to MSW piggyback landfill extensions in 2001.

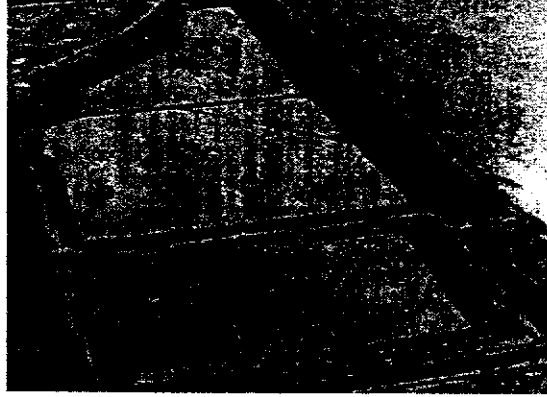


Figure 5. Industrial sludge reservoirs.

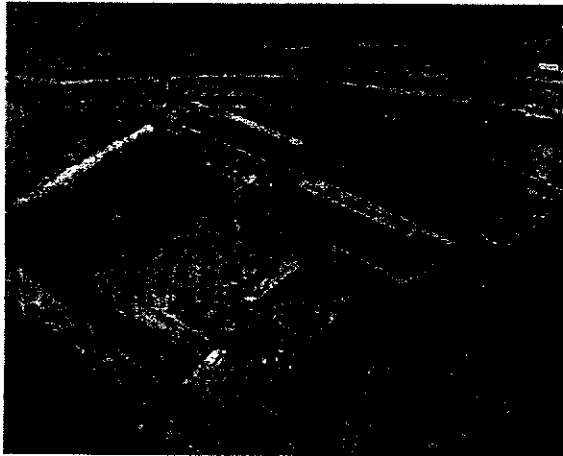


Figure 6. Contaminated soil cap closure.

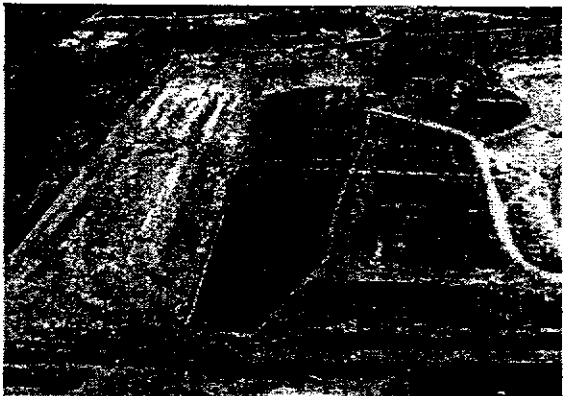


Figure 7. Quebec's first MSW piggyback installation.

Endorsed from early on by local environmental regulators and engineers, polyethylene geomembranes in the Quebec Province have thus followed the same fast track evolutionary course as in the United States, covering a wide range of applications, both environmental and operational. Conservative estimates of the total amount of installed polyethylene geomembranes in the Quebec Province since their inception are over 50 million square meters.

3. 20 YEARS WITHOUT FAILURE

According to the authors' combined experience, none of the many polyethylene geomembrane projects in Quebec has ever been the subject of a claim pertaining to premature polymer degradation and/or ensuing leakage. This feat is further enhanced by the fact that twenty years ago, polymer resins were not as performing as they are today, installation equipment not as technically advanced, and that both manufacturing and installation quality control had not been as thoroughly industry-standardized as they are now. It is also noteworthy that many different manufacturers with different proprietary resin formulations have supplied the Quebec market for the past 20 years without a single failure case, reinforcing once again that all polyethylene geomembranes regardless of their origins have successfully performed as anticipated in the Province of Quebec. This feat is really not that exceptional as the whole industry can basically vouch for the same accomplishment during the same period.

4. QUEBEC INDUSTRY IDIOSYNCRASIES

Although very much closely in line with American industry developments, technology advancements and industry standards evolution throughout the years, the Quebec polyethylene geomembrane industry has had some notable differences and uniqueness of its own. It may claim for instance to have had three geomembrane manufacturers on its territory, even offering at one point fully automated extrusion pre-fabricated roll goods as an early effort to reduce the amount of on-site welds, a technology which obviously eventually became obsolete.



Figure 8. Prefabricated polyethylene geomembrane rolls with plastic spacers.

Another significant difference in the early years when hand-held extrusion welding was but the only game in town, was the extensive utilization of the so-called European automated hot air welding method which unfortunately never truly grabbed hold in America as a bonafide welding technique in spite of conclusive scientific studies (Marcotte et al. 1993). As a matter of fact, as of today automated hot air welding still hasn't graduated beyond an industry-approved tacking method for patch work.



Figure 9. Automated hot-air welder.

Nowadays Quebec still distinguishes itself by proudly claiming the presence of the only Canadian polyethylene geomembrane manufacturer exporting to more than 40 countries throughout the world, as well as the home of a major polyethylene geomembrane resin supplier, of Canada's only exclusive geosynthetic design engineering firm, and of Canada's only fully GAI accredited laboratory. The industry is also greatly indebted to a few very distinguished emissaries such as Prof. André Rollin Ph.D. author of numerous technical papers and books on geomembranes (Rollin et al. 2002), and heavily instrumental into having École Polytechnique de Montréal offer intensive courses on the topic at graduate level for many years. The polyethylene geomembrane industry is

thus truly well established in the Quebec Province, which is also a token of its historical success.

5. TYPICAL CROSS-SECTIONS

Different cross-sections of basal liner have been used throughout the years, from simplistic early beginning approaches to today's sophisticated double-lined multi-layered imperviating systems. While non-exhaustive, Figures 10. through 14. illustrate most of the different schemes utilized during the first 20 years of the industry in Quebec. Types "1" and "2" illustrate different variations of the same theme; type "2" using natural materials in lieu of geosynthetic versions. Individual composing elements are identified as follows;

- GTX: Geotextile (filtrating function)
- GMB: Geomembrane (imperviating function)
- GCL: Geocomposite Clay Liner (imperviating function)
- CCL: Compacted Clay Liner (imperviating function)
- GNT: Geonet (lateral drainage function)
- SP: Gravelly sand (drainage & puncture protection function, may also be replaced by a geotextile or geocomposite)

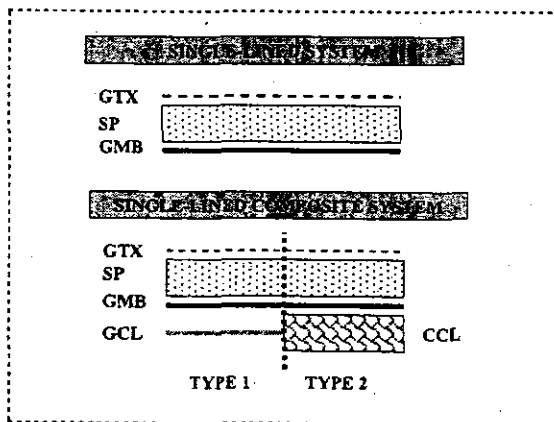


Figure 10. Typical geosynthetic single-lined systems.

Historically first to be designed and extensively used until the mid-80's prior to the advent of double-lined schemes, geosynthetic single-lined systems, are composed of a single geomembrane hydraulic barrier. Geomembrane thickness range between 1mm and 2mm. Usually directly installed on a compacted clayey subgrade free of puncturing elements, the geomembrane may also be protected from above by the addition of a so-called operational layer (in a liquid containment application) or by the addition of a drainage layer (in a solid containment application for the capture and removal of leachate). Further technological developments witnessed the coming of GCL products i.e. Geocomposite Clay Liners which may be used as a replacement for a clayey subgrade. Polyethylene geomembranes have also been left exposed without any protection or concern for their premature

polymer degradation on account of their inherent carbon black UV inhibitor.

As previously mentioned, modern waste containment designs eventually evolved into so-called double-lined systems. A double-lined system is basically comprised of two hydraulic barriers separated by a drainage layer. To that effect it is important to understand how a double-lined system works, since contrary to popular misconception, the existence of a second barrier is not justified in case the first barrier fails (Denis et al. 1988). In other words, if the design engineer has reasons to believe that the first barrier may leak (which he should since nothing is never absolutely impervious), he needs to be consistent into believing that the second barrier may leak as well! The key imperviating element in a double-lined system is actually the drainage layer in between the barriers, as it will intercept any leaks through the first barrier and rapidly direct them to a sump area in order to be pumped out prior to the formation of any hydraulic head acting on the second barrier. Since no hydraulic head exists on the second barrier, no flow may develop through it and hence, the system taken as a whole is impervious although none of the composing elements are. So in essence, efficient pumping in between barriers i.e. pumping as fast as leakage develops between barriers, is the key into achieving impermeability.

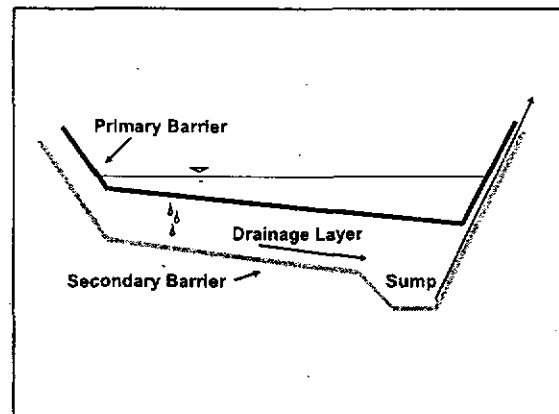


Figure 11. Schematic double-lined system.

As exemplified in the next figures, double-lined systems have also been designed using different versions of the same theme (GRI 1993). Some have exclusively used polymeric barriers, some have used so-called composite barriers (i.e. one part polymeric, one part natural materials), and some have also used GCL's as replacements for natural materials.

And finally, both hazardous and MSW landfill closures have also witnessed the numerous advantages of incorporating polyethylene geomembranes within their typical cross-sections such as their high elasticity and deformation to local subsidence, a phenomena associated with waste fermentation and consolidation.

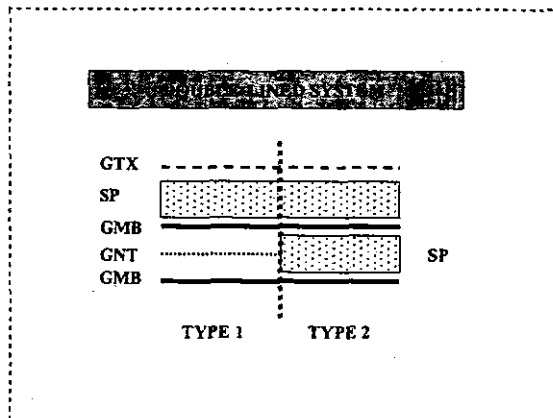


Figure 12. Typical geosynthetic double-lined systems.

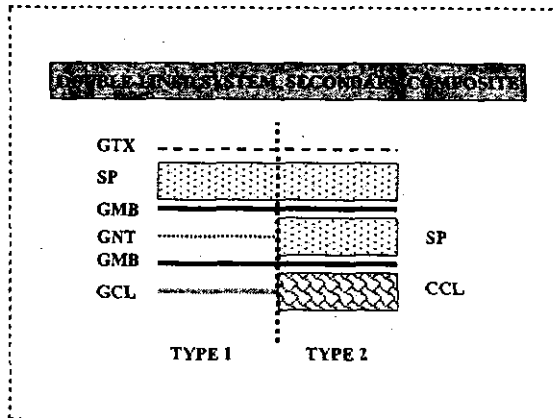


Figure 13. Typical geosynthetic double-lined systems with secondary composite liner.

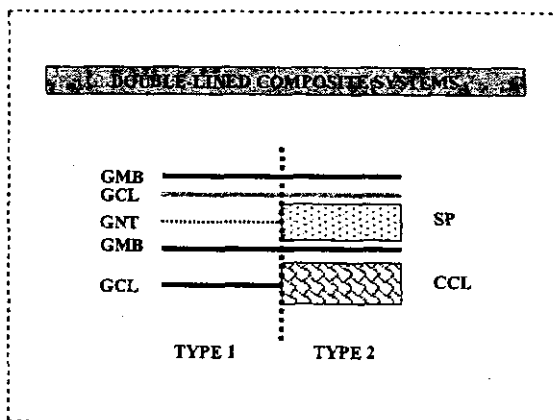


Figure 14. Typical geosynthetic double-lined composite liner systems.

6. THE NEXT TWENTY YEARS

It appears that the future of polyethylene geomembranes is very bright and secure for the next 20 years with increasing world demands especially in developing countries in conjunction for both water and waste management. Notwithstanding current and future polymer developments and save for some minor advancements, polyethylene as a primary geomembrane building material will be rather hard to dislodge for the same reasons it came to exist; excellent engineering properties at relatively low cost. New developments will probably be more along the lines of enhanced and modernized quality control and quality assurance methods such as the geoelectrical testing procedure (Rollin 2004). This procedure enables the identification and location of just about every geomembrane leak larger than 1mm in diameter, whether exposed or backfilled! This quality assurance procedure, although well proven and documented is unfortunately not currently made compulsory by governing bodies. Although it has already been used on a few projects in Quebec in recent years, it has yet to be considered as an inherent part of the geomembrane technology.

REFERENCES

- Denver 1984. "Proceedings of the International Conference on Geomembranes", IFAI, June 20-24 1984, Denver Colorado USA.
- GRI 1993. "A Survey of State Municipal Solid Waste (MSW) Liner and Cover Systems", Geosynthetic Research Institute, Drexel University, Report No. 11, August 1993.
- Koerner R. 1997. "Designing with Geosynthetics", Fourth edition, Prentice Hall, ISBN 0-13-726175-6.
- Marcotte, M., Rollin, A.L., Lagacé, S., Denis, R. 1993. "Assessment of Hot Air Fusion Welding for HDPE Geomembranes", Geosynthetics '93 Conference Proceedings, IFAI, Vancouver, British Columbia, Canada, March 1993.
- Rollin, A.L., Pierson, P., Lambert, S., 2002. "Géomembranes; Guide de Choix", Presses Internationales Polytechnique, ISBN 2-553-01023-0.
- Rollin, A.L., 2004. "Détection de Fuites dans les Ouvrages de Confinement", Comptes-Rendus Forum Géosynthétiques 2004, SAGEOS, Quebec City, February 2004.
- Denis, R., Côté, J., Chassé, A., Marcotte, M. 1988. "Les Géomembranes; Imperméables ou IMPERMÉABLES!", Comptes-Rendus, Géosynthétiques '88, Montréal and Québec City, June 1988.

LONG TERM PERFORMANCE OF POLYMERIC GEOMEMBRANES

Andre L. Rollin, ing., F_{éic}, F_{CSME}, Montreal, Canada

ABSTRACT

In the 1970's, polymeric and elastomeric geomembranes were installed as liners to contain water and contaminated industrial liquid effluents in regions where natural clay was not available. While the incentive to develop geomembranes may have originated from the substitution where shortage of natural clayed soils, now they are used worldwide. Geomembranes installed in many geotechnical and environmental works must have a short term performance in retaining liquid and gas in ponds, canals and landfills. Will geomembranes last for 5, 50, 100 years or longer? Their short term performance, survivability, is related to the engineering design of the work, to the CQA manufacture, to their installation, and the chemical nature of the products in contact.

RÉSUMÉ

Les géomembranes installées dans un ouvrage de géotechnique ou de protection de l'environnement doivent être performants à court terme pour retenir les liquides. Ces matériaux doivent être performants durant une longue période de temps. L'étanchéité des cellules de confinement des déchets, des canaux d'irrigation et de navigation, des bassins de retenu d'effluents industriels et des réservoirs d'eau peut être assurée par un système composite de couches très peu perméables incluant des géomembranes. Cette étanchéité doit être performante à court terme pour retenir les effluents liquides entreposés et retenir les eaux de lixiviation extraites des déchets confinés. De plus dans le cas des casiers de confinement, l'étanchéité doit être performante durant une période de temps plus longue que celle nécessaire à la décomposition des déchets confinés. Quelle durée de vie fonctionnelle peut-on espérer d'une géomembrane en fonction des conceptions utilisées, des programmes de contrôle de la qualité mis en oeuvre durant la fabrication, la construction et l'installation de ces matériaux, des conditions atmosphériques, de la nature des sols et des produits en contact?

1. INTRODUCTION

When a geomembrane is used in a civil engineering structure, it is intended to perform a particular function for a minimum expected time, called the design life. A geomembrane is a planar, relatively impermeable, polymeric (synthetic or natural) sheet, used in contact with soil and/or other materials in geotechnical and civil engineering applications. Any application may require one or more functions from the geomembrane such as liquid and gas barrier and puncture resistance. Each function uses one or more functional properties of the geomembrane, such as liquid permeability.

Assessment of the durability of an application using geomembranes requires a study of the effects of time on the functional properties. The polymer structure, the manufacturing process, the physical and chemical environment, the conditions of storage and installation, and the different solicitations supported by the membrane are all parameters which govern its durability. The main task is to assess the evolution of the functional properties for the entire design life of the application.

The durability is related to the change of a property of an installed geomembrane with time. Figure-2 is a schematic representation of the evolution of the available property of a material as a function of time, as represented by the curves on the graph. Along the time axis is indicated the events that happen between manufacture of the product and the end of product life. Each curve represents the changes in the required property during these different and successive events. One can see that after the loading phase, the property required is considered to be constant and equal to the level defined by the design.

The design life is specified on the time axis. It is set by the designer and one of several fixed durations must be determined according to whether the structure is meant for short-term use (typically a few years and not exceeding 5 years), temporary use (around 25 years) or permanent use

(50 to >100 years). The nature of the structure, the environmental risk involved and the consequences of failure may influence this duration: 30 years for a canal and beyond 100 years for landfills.

At the end of the anticipated design life, the designer has to ensure a certain safety level, such that failure is predicted to be well beyond the design life. As shown in Figure-1, the variation of a property with time under condition I is significant but the degradation is not great enough to affect the performance of the application since the long term value is greater than the acceptable limit. On the other hand, the same property degraded faster under condition II to a value lower than the acceptable limit putting in peril the application: the geomembrane cannot perform its function.

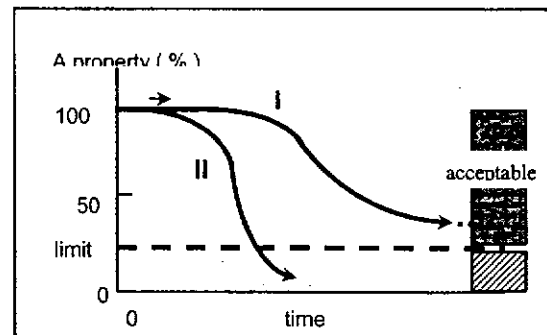


Figure-1 : Functional property variation with time

2. GEOMEMBRANES

Geomembrane sheets are normally produced from thermoplastic polymers. These products are made by extruding a sheet or by melt blown processes. The manufacturing begins with the production of the raw materials which include the polymer resin, various additives, fillers and lubricants. These materials are then

processed into a sheet of various width and thickness in one of the extrusion method. The formulations are feed to one or more extruder containing a rotating continuous screw. It is emerging as a filtered, mixed and molten material into a die. The thickness of sheets varies between 0.75 to 3.0 mm with width varying from 1.8 to a maximal width of 9.5 m.

The drawing process is very important in the production of the different types of polymeric sheets. The mechanical and durability properties of the product depend upon the details of the manufacturing process and the welding of the sheets in panels production. Bonding of geomembrane sheets is done mechanically by thermal (cohesive) bonding using heat with or without pressure, by fusion using heating elements (hot wedges) with pressure, by chemical (adhesive) bonding, or by a combination of these processes.

Any polymer consists of long chain molecules each containing many identical chemical units. Each unit may be composed of one or more monomers, the number of which determines the length of the polymeric chain and resulting molecular weight. Molecular weight can affect physical properties such as the tensile strength and modulus, impact strength, flexibility and heat resistance as well as the durability properties. The mechanical and physical properties of the plastics are also influenced by the bonds within and between chains, chain branching, and the degree of crystallinity.

The orientation of polymers by mechanical drawing to form sheets results in increased orientation and associated higher density leads to higher environmental resistance but also can result in stress cracking phenomenon. Crystallinity has a strong effect on polymer properties, especially the mechanical properties and chemical resistances, because the tightly packed molecules within the crystallites results in dense regions with high intermolecular cohesion and resistance to penetration by chemicals gases and vapors. An increase in the degree of crystallinity leads directly to an increase in rigidity and tensile strength at yield point, hardness and softening point, and to a decrease in permeability and diffusion. These 'tie' molecules are, however, more susceptible to chemical attack.

Durability may also be influenced by sheet thickness and surface exposure. Some means of degradation, such as oxidation and UV-exposure, are dependent on total surface area exposed, while others such as diffusion and absorption are inversely related to thickness. Durability may also be influenced by the nature and quality of the additives and fillers, the carbon black content used in the manufacturing of the geomembrane sheets. The durability of a geomembrane depends upon its polymeric formulation and polymer microstructure, on any additives and fillers compounded with it and their dispersion. The geomembrane should be chemically and biologically resistant if it is to be suitable for long term applications.

All flexible and scrim-reinforced geomembranes like polyvinyl chloride (PVC), flexible polypropylene (fPP) and chloro-sulfonated polyethylene (CSPE) are manufactured by a calendaring method. The polymer formulation is feed to a mixer and the material exits, moves by a conveyor to a roll mill and passes through a set of counter-rotating rollers (calender) to form a final sheet. This type of manufacturing gives rise to multiple plies of laminated geomembranes

with an open-weave fabric (called scrim) between the individual plies. They are named reinforced geomembranes.

The polymers used to manufacture the geomembranes are generally thermoplastic materials and elastomeric materials. The materials used are high density polyethylene (HDPE), linear low density polyethylene (LLDPE), polyvinyl chloride (PVC), flexible polypropylene (fPP), ethylene propylene diene monomer (EPDM), chlorinated polyethylene (CPE) and chlorosulfonated polyethylene (CSPE).

Polyethylene (PE) is one of the simplest organic polymers and it is used in its low density form (LLDPE), which is known for its excellent pliability, ease of processing and good physical properties, or as high density polyethylene (HDPE) which is more rigid and chemically resistant. PE can be stabilized to increase its resistance to weathering.

Flexible polypropylene (FPP) is a newly developed copolymer. It is different from other PP based olefinic polymers in that it is not a blend, but a reactor product using a catalyst. In addition to the significantly higher degree of flexibility, these polymers have a broad melting transition, which allows them to be thermally seamed over a wide range of seaming equipment. These flexible polypropylene based olefins maintain the inherent characteristics of polypropylene.

Polyvinyl chloride (PVC) is the most significant commercial member of the family of vinyl-based resins. PVC is very versatile plastic because its blending capability with plasticizers and other additives allows it to take up a great variety of forms. Plasticizers are used in quantities of up to 35% to create more flexible compounds, the choice of plasticizer being dictated by the properties desired. Conversely, PVC absorbs certain organic liquids which have a similar plasticizing effect. PVC also tends to become brittle and darken when exposed to ultraviolet light or heat-induced degradation. Many PVC formulations, with quite different durability characteristics, are available on the market to suit specific applications.

Ethylene propylene diene monomer (EPDM) is composed principally of saturated polymeric chains constituted of ethylene and propylene molecules. This polymeric material presents a structure increasing ozone resistance and ageing. The presence of a third monomer, Ethylidene Norbornene (ENB), is efficient at providing chemically active cure sites for vulcanisation. Carbon black is added to the formulation to increase the UV resistance and also resistance to tear. Lubricating oils are also added to the formulation prior to the vulcanisation process.

Chlorinated polyethylene (CPE) is a product one step away from PE. On the CPE molecule, chlorine atoms have been introduced along the sides of the PE backbone, replacing hydrogen atoms. The much bulkier chlorine atoms tend to disrupt the formation of any crystallinity. The amount of chlorine that is introduced, and the randomness of their attachment, will determine the extent to which the resulting resin will be non-crystalline, or amorphous. Therefore, CPE will tend to be a more flexible material than polyethylene.

Chlorosulfonated polyethylene (CSPE) is a family of synthetic rubber materials. It was introduced in the early 1950s as a synthetic rubber material with better ageing

characteristics than the natural and styrene-butadiene rubbers. This improved rubber material could be cross-linked to provide elasticity, and which contained a minimum level of crystallinity to provide flexibility while maintaining strength. The basic polymer backbone is the same as polyethylene and because there are no double bonds, the long polymer chains are relatively impervious to attack from degrading agents such as oxygen, ozone or energy in the form of UV light. It is containing chlorine atoms introduced along the side of the PE backbone with a certain number of sulfonyl chloride groups introduced as side chains. Since the sulfonyl chloride groups are larger than the chloride atom, they are more efficient at breaking up the crystallinity and provide chemically active cure sites.

Reworked resin: For HDPE geomembranes, the percent of reworked resin can be found in GRI GM13 document (revision 4, Dec 2000), items 4.3 and 4.4: "The resin shall be virgin with no more than 10 % rework. If rework is used, it must be a similar HDPE as the parent material. No post consumer resin (PCR) of any type shall be added to the formulation". Also no post-industrial recycled polymer shall be added to the geomembrane formulation.

3. SOLICITATIONS ON GEOMEMBRANES

Ageing of exposed geosynthetics is mainly initiated by the ultraviolet (UV) component of solar radiation, heat and oxygen, with contributions from other climatic factors such as humidity, rain, oxides of nitrogen and sulphur, ozone and contained liquids. In most applications geomembranes are exposed to UV light for only a limited time during storage, transport and installation and are subsequently protected by a layer of soil or liquid. On the other hand, *exposed geomembranes, mainly installed at top of slopes of reservoirs, ponds and channels, must resist for a longer time (Figure-2).*



Figure-2 : Photograph of a damaged geomembrane on top of pond slope

The main factors affecting the durability of geomembranes are as follows: particle size distribution of the soils and granular angularity; acidity/alkalinity (pH); chemical composition of the contained liquid; temperature. Chemical degradation of polymers occurs by a variety of processes including oxidation and hydrolysis, depending on the type of polymer and on the acidity or alkalinity of the soil.

chemical attack: As with geotextiles, polypropylene and polyethylene geomembranes are susceptible to oxidation and, similarly, this is retarded by the presence of additives.

PVC geomembranes have a high chemical resistance to the majority of acids, bases, salts and alcohols but the plasticizers can be affected by benzene, trichloro-ethylene and toluene. PVC structure can be attacked by ketones, such as methyl-ethyl-ketone and acetone.

FPP geomembranes can be affected by halogenated aliphatic hydrocarbons (trichloroethylene, methylene chloride, chloroform, chlorinated solvents), aromatics (dichlorobenzene and chlorinated solvents) and by aliphatic hydrocarbons (butane, pentane, hexane, light esters) et aromatics (benzene, toluene, xylene). Care must be ensured when in long term contact with the following chemicals : organic acids (acetic, stearic), volatile organics (ketones, aldehydes, esters, amides, oxygenated solvents), oils and waxes and strong oxidants (potassium permanganate, potassium dichromate, chloride, perchloric acid, peroxides). PECS and EPDM geomembranes can be affected by industrial waste liquids containing high concentration of aromatic and chlorinated organic hydrocarbons

ASTM D5747 is proposed as a test for resistance of geomembranes to chemical attack in landfills while D5322 is a test for the leaching of additives by chemicals, leaving the remaining polymer vulnerable to oxidative attack.

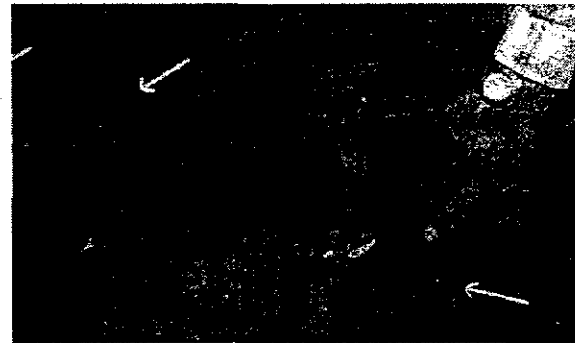


Figure-3: Photograph of a chemically attacked geomembrane

ultraviolet radiation: The energy of ultraviolet radiation is sufficient to initiate rupture of the bonds within the polymer leading to subsequent recombination with, for example, oxygen in the air, or initiating more complex chain reactions. Additives increase resistance to UV radiation in a variety of ways, the most used being the carbon black. Geomembranes protected with an anti-oxidant can resist longer to the attack. The resistance to ultraviolet radiation is affected both by the surface temperature of the sample and by precipitation, for which reason accelerated weathering tests include control of temperature and an intermittent spray cycle. UV radiation in the 400 to 280 nm range is responsible for degradation of geomembrane. The photo-oxidation reaction can break chemical links (C-C or C-H) of the polymer chains and for each type of polymer a wavelength can initiate the reaction.

oxidation : Polypropylene and polyethylene are susceptible to oxidation. This is accelerated by the catalytic effects of transition metal ions in a chemically activated state. Of these the ferric (Fe^{3+}) ion is the most common but copper and manganese have also been shown to be important. However, the sensitivity to oxidation is

dramatically reduced by the inclusion of antioxidant stabilizers or additives. All chemical reactions occur more rapidly at higher temperatures, as described by Arrhenius' Law.

stress cracking: Stress cracking of geomembranes has been studied widely. Although modern grades of polyethylene are very resistant to environmental stress cracking, it is equally necessary to control the presence of residual stresses in a geomembrane introduced during production, installation or welding, and to select material suited to the expected content of the leachate.

Environmental stress cracking, ESC, is the acceleration of low energy "brittle" creep-rupture in unoriented polymers by fluids, particularly those which dissolve in and swell the polymer, enabling the molecules to untangle and separate. The effect is more critical in amorphous polymers such as PVC, where very small fractions of a chemical, often a subsidiary additive to a compound liquid, have been known to cause critical failures. Semi-crystalline polymers such as polyethylene are less susceptible, but not immune, to environmental stress cracking.

Susceptibility to stress cracking can be measured by immersing notched samples under load in a bath of liquid and can be accelerated by raising the load, liquid concentration or temperature. Some fluids are chosen to accelerate crack growth deliberately in testing (ASTM D5397). It is then necessary to carry out longer term tests to establish the degree of acceleration.

Stress cracking is a phenomena observed with HDPE geomembrane and not LLDPE geomembranes. Under stresses, a HDPE geomembrane can become brittle and micro-cracks can appears because of molecular rearrangement of the crystalline structure. This phenomena was also observed at seam edges by Peggs (1994) and Rollin (1993). The stress cracking can be evaluated using the ASTM D5397 standard, the impact test (Rollin, 1993) and the microscopic analysis (Peggs, 1994).

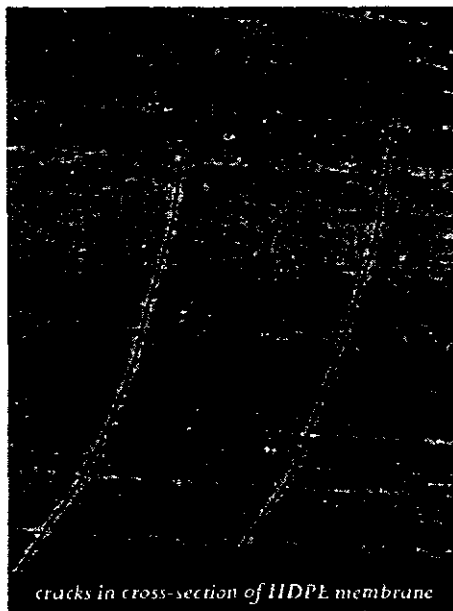


Figure-4: Photographs of micro-cracks HDPE sheet

seaming: For HDPE geomembranes, the manufacturing process and the welding parameters can induced residual stresses in the material leading to a stress crack phenomenon that will lead to a reduction of its service life. The welding techniques used to join geomembrane sheets (such as fusion, glued, adhesive, torched) can also dramatically affect the long term behaviour of the materials.



Figure-5: Photographs of a macro crack on HDPE sheet

carbon black dispersion: Carbon black is added to many polymers to provide long-term resistance to ultraviolet-induced degradation. To achieve this, carbon black should be dispersed and distributed uniformly throughout the as-manufactured geosynthetic material. The ASTM test method D 5596 is used to evaluate the uniformity of carbon black dispersion. Carbon black agglomerates (a cluster of physically bound and entangled particles) should be avoided to prevent crack initiation as shown in Figure-6.

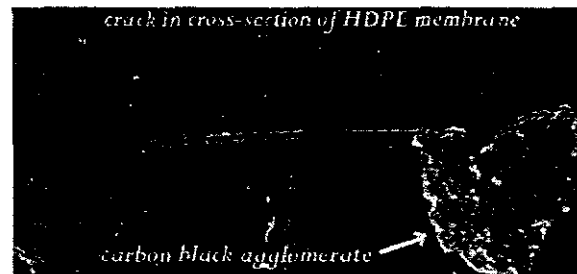


Figure-6: Photograph of a micro-crack initiate by carbon black agglomerate

4. EMPIRICAL EVIDENCE FROM RETRIEVED GEOTEXTILES

Will geomembranes last for 5, 50, 100 years or longer? To answer this question we should start by investigating empirically what has been established over the past 30 years. The use of geomembranes as liner in geotechnical hydraulic applications started in the 1960's while they became extensively used in landfill applications in the 1980's. Many HDPE samples were recovered, principally in landfills (Hsuan (1991), Dullmann (1993), Brady (1994), Rollin (1994) and Rowe (1998)), and PVC samples in dams and canals (Cazzuffi 1987 and Morrison 1993) to assess their functional durability.

Hsuan et al (1991) have recovered HDPE geomembranes from a leachate pond in service for seven years. The HDPE geomembrane was exposed at the top sections of the pond slopes and immersed in leachate at the pond bottom. The macroscopic analysis of the recovered samples from many locations in the pond indicated no detectable changes in the membrane. Only minor variations in the microscopic properties were identified and no stress cracking could be measured in the collected samples.

Dullmann et al (1993) could not observe variation in the mechanical and chemical properties of a HDPE geomembrane recovered from a landfill cell in operation for 8 to 10 years. Brady et al (1994) also analyzed HDPE geomembrane samples collected in many landfills: no detectable variation of their density and water adsorption could be detected. A 50 % reduction in the impact resistance for 30 year old samples and a negligible decrease for 15.5 year old samples was observed. The HDPE samples were found to be more rigid with a decrease in elongation.

Rollin et al (1994) analyzed HDPE geomembrane samples recovered from top, slopes and bottom sections of a 7 year old landfill cell. A minor increase in the yield point resistance and a decrease of the geomembrane elongation at break were noted. The ageing of the samples collected in the cell bottom was slightly more advanced than for the samples collected on the slopes and on the cell roof.

Recently, Rowe et al (1998) recovered HDPE samples from a leachate pond in service for 14 years. For exposed samples, a decrease in elongation, in the stress cracking and in OIT (oxidation induction time) were observed. For samples immersed in the leachate, no OIT variation could be detected.

The U.S. Bureau of Reclamation (USBR) installed in 1957 0.25 mm thick PVC geomembranes to line irrigation canals in Montana, New-Mexico and Wyoming. Since, samples have been collected for evaluation after service life period varying from 2 to 27 years (Morrison & Swihart, 1993). The geomembranes were protected by a soil layer. The samples collected (after 19 years of service) in location under the water level did retain more plasticizer than samples located at the outer edge of the canal slopes: plasticizer loss of 18 to 22 % with elongation at break of 151 to 188 % for samples located under water.

Since 1970, twenty dams located in the Alps have been rehabilitated using 2.0 and 2.5 mm thick PVC geomembranes on their concrete upstream face. These geomembranes have been exposed to the climatic conditions prevailing in high altitude (solar radiation and ice formation). Samples collected at the Lago Miller dam after 9 years of service retain 250 % elongation at break and no structural changes could be observed with an infrared spectrophotometric apparatus (Cazzuffi, 1987). A visit to many of these dams in 1993 supported the fact that the exposed geomembranes were in excellent condition.

5. CONCLUSION

These results and others are some examples giving clear evidence of durability of geomembranes. The minor variations detected in the geomembrane properties during their service life did not modify their function during that period.

6. REFERENCES

- ASTM D5397, Standard Test Method for Evaluation of Stress Crack Resistance of Polyolefin Geomembranes using Notched Constant Tensile Load Test
- ASTM D5322, Standard Practice for Immersion Procedures for Evaluating the Chemical Resistance of Geosynthetics to Liquids
- ASTM D3895, Standard test Method to evaluate the Oxidative induction time
- ASTM D5747, Standard Practice for Tests to Evaluate the Chemical Resistance of Geomembranes to Liquids
- ASTM D 5819 (1998), Standard Guide for Selecting Test Methods for Experimental Evaluation of Geosynthetic Durability
- ASTM D5596, Standard Test Method for Microscopic Evaluation of the Dispersion of Carbon Black in Polyolefin Geosynthetics
- Brady K.C., McMahon W. and Lamming G. 1994. Thirty Year Ageing of Plastics, Transport Research Laboratory, rapport 11, E472A/BG, ISSN 0968-4093
- Cazzuffi, D. 1987. The Use of Geomembranes in Italian Dams, *Int. Water Power & Dams Construction*, vol. 39, n° 3, March, pp 17-21.
- Dullmann O. and Bruno E. 1993. The Analysis of Various Landfill Liners after 10 years Exposure to Leachate, *Geoconfine'93*, Montpellier, volume 1
- Koerner R., Lord A E. and Hsuan Y H 1992, Arrhenius modelling to predict geosynthetic degradation, *Geotextiles and Geomembranes*, Vol 11, No 2, 1992, pp151-183
- Hsuan Y.G., Lord A.E. and Koerner R.M. 1991. Effects of Outdoor Exposure on a High Density Polyethylene Geomembrane, *proceedings Geosynthetics'91*, IFAI, Atlanta, pp 287-302
- ISO 13434 1997. Guide to durability of geosynthetics, under revision
- Morrison, W. R. and Swihart, J. J. 1993. Bureau of Reclamation Experiences with PVC Seams, report U.S. Bureau of Reclamation, Denver, Colorado, pp 63-75.
- Peggs, I. and Rollin, A. L. 1994. Seams in HDPE Geomembranes: The Quality Target, *proceedings Fifth Intl. Conf. on Geotextiles, Geomembranes and Related Products*, IGS, Singapore, September, pp 949-952.
- Rollin, A. L., Marcotte, M., Lafleur, J. and Mlynarek, J. 1993. The Use of Impact Test Procedure to Assess Seams Brittleness, *proceedings Geosynthetics '93*, NAGS, Vancouver, pp 1559-1573.
- Rollin A.L., Mlynarek J., Lafleur J. and Zanesco A. 1994. Performance Changes in Aged In-Situ HDPE Geomembranes, *Landfilling of Wastes: Barriers*, Christensen, Cossu & Stegmann, E & FN Spon, pp 431-443
- Rowe, R.K. 1998. Geosynthetics and the Minimization of Contaminant Migration through Barrier Systems Beneath Solid Waste, *proceedings 6th Int. Conf. on Geosynthetics*, IGS, Atlanta, pp 27-102

GEOSYNTHETICS DURABILITY: A POLYMER CHEMISTRY ISSUE

Dominique Kay, eng., M.Sc.A., CTT Group / SAGEOS, St-Hyacinthe, Quebec, Canada
Eric Blond, eng., M.Sc.A., CTT Group / SAGEOS, St-Hyacinthe, Quebec, Canada
Jacek Mlynarek, D.Sc.A., CTT Group / SAGEOS, St-Hyacinthe, Quebec, Canada

ABSTRACT

Nowadays, polymer applications have reached almost every level of our lives and durability requirements are extremely different from one application to the other. Out of all these polymer applications, geosynthetics remains the most critical as long as it may involve very long-term durability requirements (i.e. over 50 to 100 years service life) and that a failure may be dramatic in terms of costs and potential human injuries. After over 30 years of R&D and lessons learned from failures, the geosynthetic industry has reached a very high level of knowledge with regard to durability concerns and associated material formulation. For each product, the list of degradation mechanisms can be drawn and a specification built.

However, a significant fraction of geotechnical engineers are often not used to consider material aging issues, as long as this is not a concern for most of geotechnical applications, involving relatively inert materials like water and soil. This paper was thus prepared in order to introduce basic elements involved in geosynthetics aging. A review of polymer basic properties is presented in the first section, followed by a description of potential degradation mechanisms of typical geosynthetics polymers. It is believed that the understanding of these elements will help geotechnical engineers gain better acceptance of geosynthetics for long-term applications and help them specify the products with regard to the adequate degradation mechanisms.

RÉSUMÉ

De nos jours, les polymères sont présents à presque tous les niveaux de notre vie, les exigences en termes de durabilité étant très différentes d'une application à l'autre. Parmi ces applications, les géosynthétiques représentent une classe d'application particulière dans la mesure où les durées de vies requises peuvent être extrêmement longues (p.ex. plus de 50 à 100 ans) et que les conséquences d'une rupture peuvent être dramatiques en termes de coûts et de dommages à la santé humaine. Après plus de 30 ans de R&D et d'apprentissages issus de ruptures inattendues, l'industrie des géosynthétiques a atteint un très haut niveau de compréhension des mécanismes de dégradation et de leurs relations avec la formulation des matériaux. Pour chaque produit disponible sur le marché, il est possible de dresser la liste des modes de dégradation potentiels et de construire une spécification de produit en conséquence.

Cependant, la question de dégradation due au vieillissement d'un matériau n'est pas toujours bien maîtrisée par les géotechniciens, qui sont habitués à travailler avec des matériaux relativement inertes comme l'eau et le sol. Aussi, ce document a été préparé afin d'introduire les principaux éléments associés au vieillissement des matériaux géosynthétiques. Une revue des principales propriétés des polymères utilisés est présentée dans une première section, suivie par une description des modes de dégradation potentiels des-dits polymères. Il est présumé qu'une meilleure compréhension de ces éléments permettra de favoriser une meilleure acceptation des géosynthétiques pour des applications à long terme, et permettra de spécifier les produits en tenant compte des modes de dégradation appropriés.

1 INTRODUCTION

Polymers have been used in many industries over decades. They are now part of everybody's life at many different levels ranging from automobile to medical applications, including toys, kitchenware, etc. In terms of volume, geosynthetics represent only a little fraction of the global polymer market.

Geosynthetics applications of polymers differ from other uses because the materials are intended to fulfill their function over a long period of time. In terms of service life, no comparison can be presented between toys requirement (less than one year), house ware (a few years), automotive (5 to 10 year) and geosynthetics (at least 50 years).

Beside this, another issue is the understanding of durability concerns by users of geosynthetics, i.e. geotechnical engineers. Geotechnical engineering is a science dealing with relatively materials with respect to their intrinsic properties (soil, water).

Although some clays may have some aging properties in some specific conditions, most of the situations involving the expertise of a geotechnical engineer will deal with settlement, water seepage, bearing capacity and other concerns associated to a macroscopic behavior of soils, chemistry and microscopic aging being typically not a significant concern.

Although more and more geotechnical engineers begin to understand the durability concerns associated with

geosynthetics, a vast majority still has a misunderstanding approach of geosynthetics:

- either they believe 'it works', and consider only the short term properties involved in the design;
- either they don't trust 'plastic materials', referring to their poor previous experiences with other families of polymers (i.e. toys, automotive), and try to exclude as much as possible utilization of geosynthetics from their design.

As it is for any civil engineering material, geosynthetics are designed to fulfill their function over a given period. It depends on their formulation as well as on the environmental conditions they will experience between their manufacture to their actual service life, including installation. For a similar application, it is possible to purchase a product that will last many decades, as well as to purchase another product, typically cheaper, that will last only a few decades.

Given this background, when time comes to design a project, design guidelines and necessary understanding of a given material are needed. As will be presented in this paper, at least two or three different families of polymers may be used to manufacture a geosynthetic for a specific usage (i.e. polyester, polypropylene or polyethylene for geogrids, polypropylene or polyethylene for geomembranes, polyester or polypropylene for geotextiles...).

Thus, this issue gains complexity given that degradation mechanisms of polymers are as different one from the other as may be their molecular structure and specific formulation (additives, pigments, etc.). Although some aging mechanisms are similar and specific to the application sought (i.e. reinforcement, filtration, waterproofing...), durability design guidelines should thus always be considered as being specific to the polymer used in the fabrication of the geosynthetic.

In this paper, a general description of potential degradation mechanisms of each major category of polymers, as a first introduction to geosynthetics aging chemistry, is given. The different aging processes likely to be met are all described as well, for each category of polymer.

Note that the performance criteria to be considered can typically be provided by geosynthetics manufacturers, as long as they actually have the technical expertise associated to the market they are disserving. After over 30 years of R&D and lessons learned from failures, some of the issues presented below are now well understood and specific design guidance can be provided. Most of them are as simple as safety factors, others require specific performance testing on a project-by-project basis.

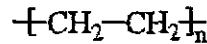
2 POLYMERS USED IN GEOSYNTHETICS

Aging of geosynthetics essentially takes place at the molecular level, or with regard to additives or other components involved in the elaboration of the material. As

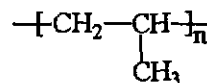
a consequence, the material's first characteristic to consider is its molecular structure.

Polymers are large molecules build through addition (polymerization) of small repetitive molecules called monomers. The molecular structure of the four common polymers used in geosynthetic applications (PE, PP, PVC and PET) is shown in Figure 1.

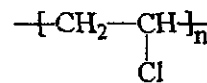
a) polyethylene (PE):



b) polypropylene (PP):



c) poly (vinyl chloride) (PVC):



d) polyester (PET):

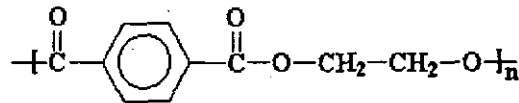


Figure 1: Chemical structure of common polymers used in geosynthetic.

Other types of polymers such as chlorosulphonated polyethylene (CSPE), polyamides and polystyrene are also found in some geosynthetic products. Table 1 listed the most frequent types of polymers used for different types of geosynthetic materials.

Table 1 Polymers used in geosynthetic

Geosynthetic material	Main polymers used
Geomembranes	Polyethylene (HDPE and LLDPE) Plasticized PVC Polypropylene
Geonets	Polyethylenes (HDPE)
Geogrids	Polyethylene (HDPE) Polyesters Polypropylene
Geopipes	Polyethylene (HDPE) PVC
Geotextiles	Polypropylene Polyester

Given that the polymer is a combination of monomers, each molecular group along the polymer chain has its own level of stability. Actual chemical composition of the polymer chain will also control the cohesion of the material. Therefore, the chemical composition of polymer chains will determine the families of physical and chemical degradation mechanisms likely to take place into the material.

Listed below are other important material's characteristics which can influence the finished product's sensitivity:

- polymer chain's structure (level of linearity, branching, cross-linking);
- molecular weight distribution (can be illustrated as the distribution in length of polymer chains in the material);
- morphology (polymer chains relative orientation, crystallinity, etc.)
- irregularities. (structural irregularities, impurities, traces of catalysts, etc.)
- additives (antioxidants, UV stabilizers, pigments, charges, plasticizers, etc.)

If some of these essential polymer properties are influenced by either the selection of raw materials and their quality, some of them will also be influenced by the processing conditions. Thermal and shear stresses sustained by the material during processing can initiate degradation mechanisms (thermal degradation, hydrolysis, etc.), sensitize the material to some other mechanisms (formation of sensitizing structures, degradation or bad mixing of stabilizers, etc.) and control the final morphology of the material (chain orientation, crystallinity, internal stress, etc.).

3 AGING MECHANISMS

During their service life, geosynthetics are exposed to several aging mechanisms, which can influence their properties under some specific conditions. If not properly handled, some environments can have a significant impact on the material properties and eventually reduce its overall durability.

However, every polymer has its own field of sensitivity. Some environments have no significant impact on some polymer, while they can have a high impact on other materials properties. Degradation can also arise in specific exposure conditions only, but not in common fields of practice. Hence, in order to identify the most relevant mechanisms for a given geosynthetic material in a given application, both the material's characteristics and actual exposition level must be considered.

The key parameters to be considered in geosynthetics applications with regard to long-term degradation include temperature, moisture, UV radiation, thermal stress, chemical environment, mechanical stress, microbiological activity and atmospheric pollution. These parameters may – or may not, depending on the type of polymer and presence of synergetic effects – have influence the polymer structure, and eventually the functionality of the product given occurrence of additional synergetic effects.

A description of the degradation mechanisms likely to take place under certain conditions is presented below. These mechanisms have been classified into two categories (physical degradation and chemical degradation). Section 4 will then focus on the identification of the critical issues to be considered for common polymers used in geosynthetic (PE, PP, PVC and PET).

3.1 Physical aging

Physical aging is related to degradations which do not involve a modification in the molecular structure of polymer chains.

Some of these mechanisms involve a mass transfer with the environment surrounding the material (extraction of additive, absorption of solvent, etc.). Others involve a modification of internal chain organization into the material, i.e. a change of morphology (chain orientation, crystallinity, etc.).

The main physical degradation mechanisms likely to influence the performance of geosynthetic materials are described below.

3.1.1 Additive extraction

Different types of additives incorporated in some geosynthetic materials play a key role in the long term performance of the material, i.e. antioxidants, UV stabilizers, pigments, plasticizers, fillers, etc. Some particular exposure conditions can lead to a partial or total extraction of the additives from the material. In example, additives can be leached at the surface of the material by water or any other chemical agent in contact. Some volatile additives can also evaporate, i.e. plasticizers in flexible PVC geomembrane (Figure 2).

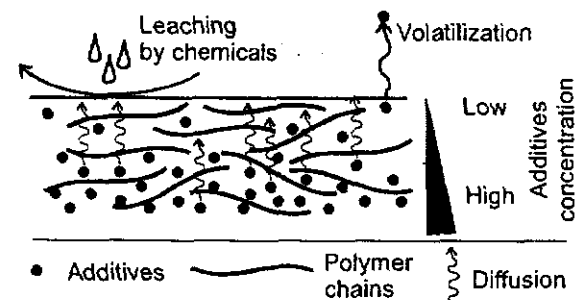


Figure 2: Extraction of additives due to leaching and volatilization.

In addition, additives located close to the surface of the material can be extracted if the level of interaction between the additive and the solvent is higher than between the additive and the polymer. Further extraction requires diffusion of the additives from the bulk of the material to its surface. The diffusion rate of an additive in a given polymer resin is thus governed by the following parameters:

- size of the additive molecule,
- interaction between the additive and the polymer chains (mainly governed by their polarity), compared to the interaction level between the additive and the environment,
- polymer's morphology and chains' mobility.

If the rate of diffusion of the additive from the bulk to the surface is slow compared to the rate of extraction and/or consumption at the surface, the concentration of the

additive at the surface decreases and a concentration profile is built into the material. If this additive is involved in a stabilization process, the level of protection at the surface can be altered, which can eventually lead to the onset of local degradation, even if the concentration of that additive in the bulk remains high (i.e. change of color, micro-cracking, etc.). Analysis of the consequences associated to surface degradation of a geosynthetic should then be considered on a project by project basis, depending on the potential synergistic effects and consequences on the functionality of the product.

Typical examples of additive extractions are loss of plasticizers in a flexible PVC geomembrane and loss of antioxidants of a HDPE geomembrane (non exhaustive).

Extraction and diffusion of additives in geosynthetic materials should be studied in the following cases:

- the material contains additives which have a low level of solubility in the polymer and/or are highly volatile (this issue being typically adequately controlled with modern geosynthetics involved in high sales volume applications);
- the material will be in contact with a solvent susceptible to have a high level of interaction with an additive (project specific);
- the material will be exposed to high temperature (high temperature favoring the migration of additives to the surface by increasing molecular chains' mobility).

In-Lab exposure at different temperatures can be realized to evaluate the resistance of a material to extraction. The evolution of the concentration profile of an additive in the material can be monitored by analyzing the material intrinsic properties at different distances from the surface.

3.1.2 Action of solvent

The interaction between a solvent and a polymer is governed by thermodynamic considerations beyond the purpose of this paper. In resume, polymer chains are linked together by weak inter-chains interactions. In order to avoid alteration of the cohesion of the polymer chains, interaction between the chains must be stronger than between the solvent and the polymer.

The interactions polymer-solvent are usually based on electric polarity. The higher the polarity of the solvent and the polymer, the stronger the interactions between the solvent and the polymer can be. That explains why polymers which have a low level of polarity, such as polyethylene or polypropylene, are well resistant to the majority of chemicals. Some polar polymers can also have a high level of resistance to chemicals if their interactions polymer-polymer are very strong (for example: polyamide).

High interactions solvent-polymer favors the penetration of solvent molecules into the material. These molecules break the interactions between polymer chains, increasing the distance between them and reducing their cohesion, which increases their mobility (Figure 3). This typically leads to an increase in dimensions (swell) and a loss of stiffness.

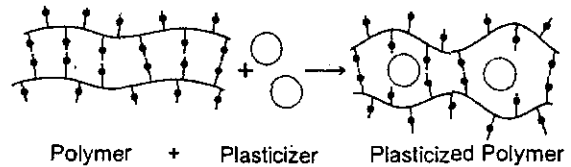


Figure 3 Loss of cohesion in polymer due to the absorption of solvent.

Without significant morphological or chemical modification occurring (i.e. creep, mechanical action...), these changes in the physical structure of the material may be recovered when the solvent is desorbed. But solvent absorption can also lead to irreversible degradation mechanisms such as loss of shorter polymer chains, crazing and hydrolysis.

Even when the extraction is limited to shorter polymer chains, this degradation can affect several properties of the material such as its impact resistance and its glass transition (behavior at low temperature).

In some cases, absorption of a solvent can lead to the formation of cracks by a process called crazing (Figure 4). This mechanism consists in the propagation of a crack associated to the alignment of molecular chains in the stress direction (disentanglement of the chains). This crazing process usually takes place at the tip of a notch. It consists of a small, highly strained, micro voided fibrillar region. Internal stress into the material such as those induced by swelling/shrinking cycles can sometimes be sufficient to enhance the crazing process.

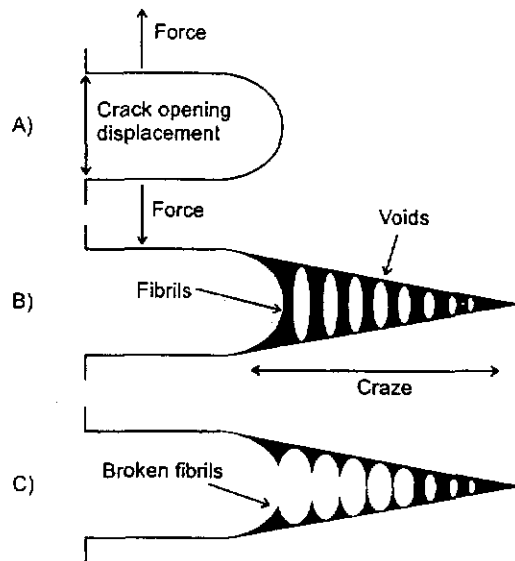


Figure 4 Schematic illustration of the propagation of low stress brittle failure. (a) Preexisting notch subjected to opening force; (b) formation of craze; (c) fracture begins as fibrils break.

Amorphous phases are more vulnerable to solvent penetration than crystalline phases, which are usually considered as impermeable to solvent. Thus, the resistance of a given polymer to a solvent will usually increase with its crystallinity. For semi-crystalline polymers such as PE, PP, swelling of the amorphous phase can lead to the formation of stress at the interface between amorphous and crystalline phases, leading to chain ruptures.

Solvent molecules absorbed by the polymer can also react with the polymer chains to modify its chemical structure. The hydrolysis of polyester by water is an example. That process will be described in section 3.2.4.

Action of solvents on geosynthetic materials should be evaluated specifically when the geosynthetic is likely to be frequently exposed to a harsh chemical listed as a being potentially incompatible with the polymer. Such tables can typically be provided by either geosynthetic manufacturers or polymer engineering literature:

3.1.3 Internal chain reorganization

a) Thermal-induced reorganization

High shear stress sustained by the polymer during the processing induces chain deformations (Figure 5). During the cooling step, which is very fast for most types of processes, the polymer chains freeze in an instable structure – with regard to molecular optimal organization – leading to a combination of amorphous and crystalline molecular arrangement within the material structure. In some cases, residual stress can remain between molecular chain segments.

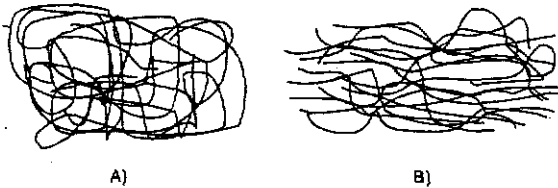


Figure 5 Orientation of polymer chains' segments during processing. (a) Random orientation; (b) oriented melt due to shear stress.

When exposed to heat, the chain mobility is increased and can favor internal chain reorganization in presence of internal stress. Driven by thermodynamic forces, the stressed chain segments tend to move and reorganize themselves in order to reach a more stable state. These movements lead to morphological modifications which can affect the material's properties (dimensions, mechanical resistance, etc.).

An example of internal chain reorganization process is the post-crystallization observed in some semi-crystalline polymers such as polyethylene. Chains being more stable in the crystalline state than in amorphous state, the chain segments surrounding crystals will tend to crystallize when the amorphous phase chains mobility will be increased, i.e. when exposed to an elevated temperature. This will lead to an increase of the overall percentage of

crystallinity of the material and eventually result in an increase of stiffness and a reduction of the material's permeability and elasticity. In a high-density polyethylene, a higher crystallinity will also reduce stress-cracking resistance, as discussed in section 3.1.4.

b) Creep / relaxation

Internal chain reorganization is also another approach to define creep in a polymer. In that case, it does not depend on temperature only but also on applied stress. When exposed to stress, a polymer material responds with an instant elastic deformation, which is reversible, and a slow viscous deformation, which is irreversible. This behavior defines polymers as viscoelastic materials. The irreversible deformation is associated to a slippage between chain segments to release stress. These chain movements are defined as creep when related to an increase of material deformation under constant stress, or relaxation when related to a stress release under a constant deformation.

Figure 6 illustrates creep deformation of a polymer under load. In Figure 6a, the springs schematize an instant elastic strain whereas the dashpots schematize a viscous strain. Based on this model, Figure 6b illustrates the response that the material would have to a stress: creep results in a permanent deformation due to slip between chain segments, schematized by the deformation of dashpot #1.

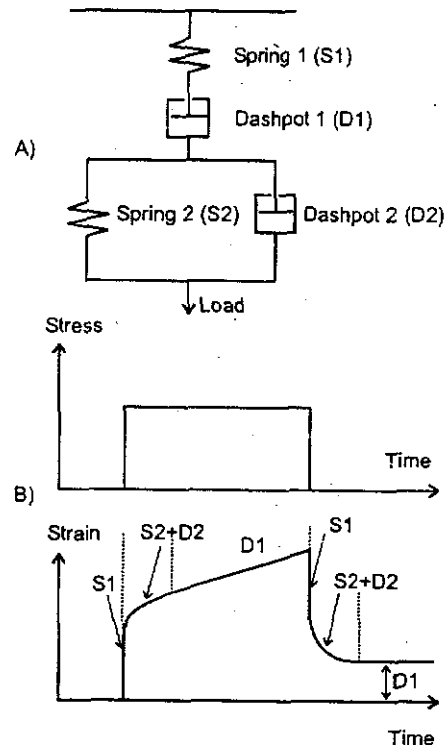


Figure 6 Schematic illustration of creep in polymers. (a) Creep model – combination of springs (elastic strain) and dashpots (viscous strain); (b) response of a material to a stress based on the creep model.

As a secondary consequence, internal chain reorganization typically creates anisotropy in the material, associated to the orientation of chains in the direction of the stress.

Several studies have been conducted in order to improve the knowledge on the relations between the polymer's characteristics (molecular structure, morphology, etc.) and the mechanisms of internal chain reorganization. These mechanisms of degradation (creep, ESC, etc.) can be limited by selecting an appropriated grade of material based on specifications, and by controlling the processing and installation conditions.

When associated to creep, internal chain reorganization is typically well handled by modern geosynthetics manufacturers (i.e. tabulated safety factors). When associated to thermal effects, the key issue will be to define whether or not a change in material property will influence its long-term functionality. As long as common geosynthetics applications do not involve exposition to high temperature, this issue should not be considered critical. When a high temperature can be expected and synergetic actions anticipated, potentially influencing the material integrity, the most effective solution should be to introduce a monitoring program on the project in order to monitor the evolution of the material properties.

3.1.4 Environmental stress cracking

Environmental stress cracking consists of a brittle failure of a stressed sample in the presence of a sensitizing agent. That degradation process concerns geosynthetic materials made of high-density polyethylene.

This type of failure differs from a ductile failure (creep) in the fact that despite the stress is applied on a fairly large area, the deformation only takes place within a thin section and ultimately leads to a complete rupture of the material. In addition, the stress level involved in stress cracking failure is typically less than one-half of the short-term yield stress.

Polyethylene molecular chains are organized in both crystalline and amorphous phases. Some chains have segments in both phases, and act as tie molecules, holding together adjacent crystallites (Figure 7a). The stress applied on the material is thus transmitted between crystallites through these tie molecules, which play a key role in the determination of the mechanical resistance of the material. The stress can also be transmitted by physically entangled molecules extending out of adjacent crystallites.

Stress cracking takes place when a lubrication effect of a sensitizing agent allows tie molecules to become disentangled more easily. Tie molecules then start to slip within the amorphous phase (Figure 7b), and fracture occurs between crystalline regions, involving the amorphous phase only (see Figure 7c). This process takes place without apparent, measurable deformation and leads to a relatively smooth fracture face morphology as long as most of the crystalline molecules were not significantly affected by slippage of the amorphous phase.

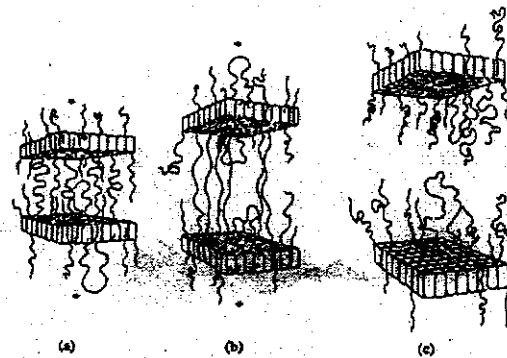


Figure 7 Propagation of brittle-type failure between crystals. (a) Crystal lamellae linked by tie molecules; (b) disentanglement of tie molecules under stress; (c) propagation of failure between lamellae

Hsuan (2000) has evaluated the resistance of several HDPE geomembrane samples in the laboratory according standard test methods (bent strip and NCTL tests) and plotted the average failure time versus applied stress. A typical curve observed from NCTL tests is illustrated in Figure 8. This curve can be divided in two distinct regions having different slopes. When the stress level is relatively high, the specimens fail in a ductile mode, whereas a brittle mode can be observed for low stress levels. The transition between the two failure modes has been observed to be in the range of 20% to 45% of the material yield strength. This transition is the point where the creep rate become lower than the rate of molecular disentanglement of tie molecules at the crack tip. As a consequence, stress-cracking failure can occur only if the stress level is smaller than this transition, higher stresses leading to a ductile failure mode.

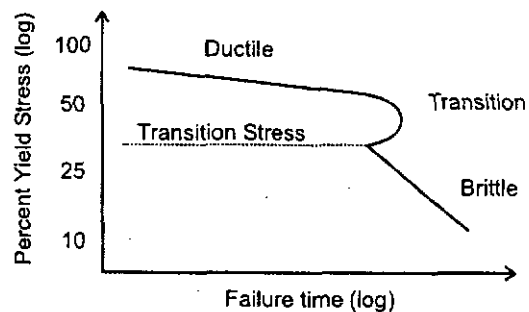


Figure 8 Typical ductile-to-brittle transition in the failure mode of HDPE geomembranes specimens tested according to NCTL test method on a log-log scale (source: Hsuan Y. G., 2000).

Stress cracking is a function of the applied stress, temperature, sensitizing agent properties and molecular parameters (molecular weight distribution, branching, etc.). The stress required to drive the process can be external or internal, cyclic or continued. Although not a

prerequisite for the onset of stress-cracking, a notch, a scratch, or some other type of stress concentrator accelerates the process. As it is for other physical aging processes, stress-cracking is directly related to the chains' mobility and is thus influenced by environments favoring chains' mobility (discussed in 3.1.3) such as high temperature.

Several sensitizing agents can favor stress-cracking. The potency of a sensitizing agent is related to its ability to wet the polymer surface. In general, a sensitizing agent will be critical when its viscosity and surface tension are low and when the difference between the solubility parameter of the sensitizing agent and the polymer is small. Common sensitizing agents can be aqueous solutions of surfactant or pure solvents.

Polymer properties influencing environmental stress-cracking resistance most include crystallinity, molecular-weight distribution, branch length, and lamellar orientation. As a rule of thumb, susceptibility to stress cracking can be defined as related to both density and crystallinity.

Given that ESC can lead to a failure at a stress level far below the short term mechanical resistance of the material, this degradation process should always be considered when high density polyethylene materials are exposed to chemical agents and are exposed to stress.

However, relatively recent research on resins molecular parameter control has reduced the frequency of stress cracking failures. From a design prospective, a material specifications including a resistance to stress cracking higher or equal to the one proposed in GRI GM13 specification for geomembranes (based on ASTM D5397) should be considered as a good basis to avoid occurrence of this problem. Project design and installation procedures reducing the potential occurrence of stress on a polyethylene material shall also be introduced.

Finally, stress-cracking occurrence on HDPE geogrids shall be considered differently than for HDPE geomembranes. Polymers used in geogrids are not comparable to the one used in geomembranes as long as their intended function differs drastically from the one of geomembranes. As an example, average molecular weight is typically far over 10 times higher in geogrids than it is on geomembranes, leading to completely different finished good properties.

3.1.5 Thermal stress

Thermal stress is related to the thermal dilation coefficient of a polymer. Aside from particular chain reorganization processes such as chain relaxation, a temperature increase usually leads to a dilation of the material, while a temperature decrease leads to a contraction. If the material deformation is restrained, thermal stresses are then built.

In monolithic sheet-like geosynthetic materials (i.e. geomembranes), thermal contraction or dilation typically leads to a change in the overall dimension of the panel, creating wrinkles when the temperature increases, or

creating a stress when the temperature decreases. This problem is typically handled at the construction stage by favoring installation and welding of the geomembrane panels at relatively low temperatures, ideally as close as possible from the service temperature to be supported by the material during its service life.

Other materials with a higher wall thickness (i.e. geopipes), when exposed to sudden changes in temperature (i.e. conveying periodically cool or hot liquids) can also be exposed to a temperature gradient within their thickness. Depending on the thermal dilation coefficient of the polymer and its stiffness, this can lead to the introduction of a stress profile in the material. For example, a sudden decrease of temperature will introduce tensile stress at the surface and compression stress in the bulk of the material. Ultimately, when not properly handled, these stresses can influence aging of the material using one of the other degradation processes described above.

Sudden temperature changes can also be problematic for composite materials if the thermal dilation coefficients of the components are different. In that case, thermal stresses are localized at the interface between the matrix and the reinforcement and can lead to a loss of cohesion.

The junction of two different materials (i.e. old / new geomembrane or prefabricated penetration structure / geomembrane) have to be considered as critical locations on a construction project with regard to a thermally induced failure, specially if the materials are expected to be directly exposed to thermal cycles (i.e. weather) on a long term basis. One of the key items to be considered is the coefficient of thermal expansion of both materials.

3.2 Chemical degradation

Chemical aging can be defined as a mechanism involving a modification in the molecular structure of polymer chains.

Some of these mechanisms can lead to chain scission (Figure 9a). As a consequence, the molecular weight of the resin will be globally reduced, affecting the mechanical resistance of the material and leading to embrittlement.

On the other hand, other mechanisms can lead to the creation of molecular bonds between chains by a process called "cross-linking" (Figure 9b). This process reduces the chains mobility and modifies the mechanical behavior of the material, usually increasing its stiffness.

Other chemical mechanisms involving a modification of the chain's composition can also be observed, either by a process of substitution (Figure 9c), i.e. chains oxidation, or a process of elimination (Figure 9d). In example, elimination of HCl can take place in PVC in presence of specific chemical environment. These substitution processes have typically little direct influence on the mechanical properties of the material. However, they can affect their appearance (i.e. color change) and favor occurrence of other degradation mechanisms.

The main chemical degradation mechanisms likely to influence the performance of geosynthetic materials are described below.

3.2.1 Thermal degradation

Thermal degradation is induced by the energy supplied by heat, it involves alteration of molecular bonds along the polymer chains.

A given molecular liaison is characterized by an energy of liaison or bonding energy, which depends on the type of elements involved in that liaison (for example carbon-carbon, carbon-hydrogen, carbon-chlorine, etc.) and the molecular liaisons surrounding that liaison. The higher the bonding energy, the more stable the liaison is. The following table lists the bond energy of some typical liaisons found in common geosynthetic polymers.

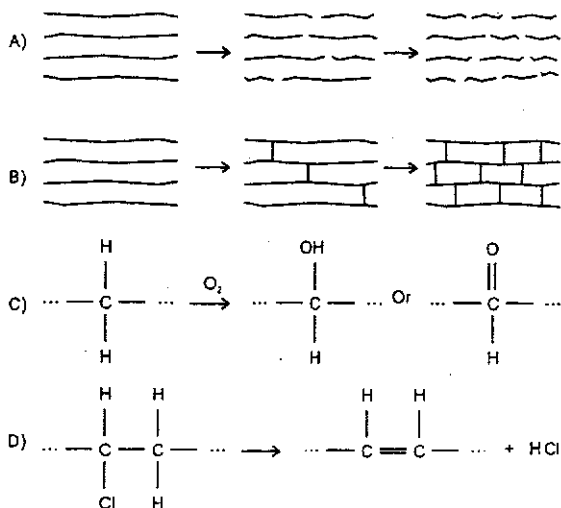


Figure 9 Chemical degradation of polymers. (a) chain scissions; (b) cross-linking; (c) substitution; (d) elimination.

Table 2 Bond energy of typical liaisons found in geosynthetic polymers.

Bond	Bond Energy (Kcal/mol)
C=O	174
C-C (aromatic)	124
C-H (methane)	102
C-Cl (Methyl Chloride)	84
RO-OR (Hydroperoxide)	36

The energy supplied by heat induces vibration at the molecular level. The probability of a bond dissociation increases as the energy of vibration increases and get closer to the energy of liaison. Bond dissociation can lead to chain scission or elimination of molecules such as HCl in the case of PVC. Also, that dissociation results in the formation of free radicals, which can react with surrounding liaisons and propagate the degradation (chain scissions, cross-linking, etc.).

Considering typical geosynthetic applications, thermal degradation is usually not a concern during their service life unless the material is directly exposed to the sun or elevated temperatures. However, this degradation process can occur during the manufacturing process, when the polymer is exposed to high levels of energy (heat) and mechanical stress (shear).

If not properly handled, thermal degradation, which may be induced during the manufacturing process, can have a huge influence on the long term durability of the material. Even if the overall degradation sustained by the material during the manufacturing process is low, the associated structural irregularities can sensitize the material to other degradation mechanisms such as photo-oxidation. In order to reduce occurrence of this problem, thermal stabilizers are added to the resin, in order to avoid occurrence of this problem.

Thermal degradation in presence of oxygen leads to thermo-oxidation of polymer chains. Oxygen sensitizes the material by reducing the temperature for the onset of degradation. The process of thermo-oxidation is complex and involves formation of radical species. This mechanism involves three steps of reactions, which are the initiation, propagation and termination reactions.

Hsuan and Koerner (1998) provide a comprehensive description of thermo-oxidation of HDPE geomembranes. Essentially, it can be summarized as follows:

The initiation step, typically caused by factors such as heat, radiations or chemicals, consists in the formation of a free radical (reaction 1).



Oxygen reacts readily with the free radical to form a very reactive peroxide radical (reaction 2). This reaction is usually faster than any other potential reaction likely to occur.



This newly created radical will then extract a hydrogen atom from the surrounding polymer to form a hydroperoxide and create another free radical (reaction 3). $\text{ROO}\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot$ (3)

This reaction will continue until the free radical species are neutralized whether by coupling reactions or by the action of an antioxidant.

Along with the free radical formed by reaction 3, hydroperoxides, which have weak liaisons (see Table 2) can easily be cleaved, generating radical species $\text{RO}\cdot$ and $\cdot\text{OH}$. These radical species can then extract hydrogen from surrounding chains and increase the rate of degradation.

Hence, propagation reactions generate continuously free radicals, which degrade progressively the polymer chains. These reactions lead to an auto-oxidation cycle.

Hsuan and Koerner (1998) also describe the different stages of oxidation typically observed for polyolefin

material (HDPE geomembrane, PP geotextile, etc.). Essentially, thermo-oxidation usually begins with an induction period where no significant variations can be observed on the physical properties of the material. Then, as oxidation continues, this first stage is followed by an acceleration period where polymer chains react rapidly with oxygen, as illustrated in Figure 10. Mechanical properties remain stable until degradation reaches the acceleration period.

Stabilizers such as antioxidants are incorporated into the resin to increase the duration of the induction period. Several methods can be used to evaluate the performance of antioxidant and specify the level of protection of materials against oxidation. Given that the rate of oxidation at ambient temperature is low, accelerated aging tests such as Oxidation Induction Time (OIT) and Long Term Heat Aging (LTHA) can be used to evaluate the effectiveness of antioxidants. Standard test methods such as ASTM D3895 (oxidative induction time) and ASTM D5885 (high pressure-oxidation induction time) are often used in geosynthetic materials' specifications.

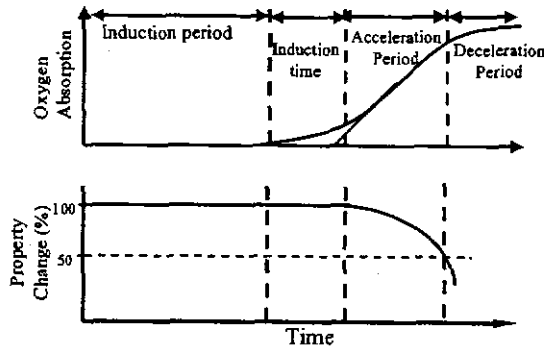


Figure 10: Curves illustrating various stages of oxidation for Stabilized HDPE

3.2.2 Photo degradation

Photo degradation is a process similar to thermal degradation. However, the source of energy is supplied by radiation instead of heat. Molecular liaison can be cleaved by radiation to form free radicals if the energy carried by the radiation is close to the energy of liaison.

The energy carried by a monochromatic ray is inversely proportional to its wavelength. The shorter the wavelength, the higher the potency of bonds cleavage (Figure 11).

The atmosphere and the ozone layer act as a filter and intercept the sunrays of wavelength lower than 295 nm. In Miami (Fl), UV radiations in the range of 295 – 400 nm represent less than 7% of the total energy received from the sun. However, these sunrays wavelengths are the most damageable.

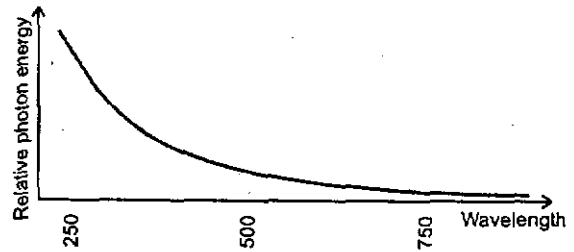


Figure 11 Relative photon energy versus wavelength.

Many variables influence the rate of degradation of polymers by photo-oxidation. The irradiance and the permeability to oxygen are the most important but other factors such as temperature and moisture have also an influence on the rate of degradation.

The solar spectral distribution at the surface of The Earth varies due to the filter effect of the atmosphere and its selective diffusion of short wavelengths. This selective diffusion depends on the relative position of the sun to the horizon. Thus, it varies with the location on Earth (Figure 12), the season and the time of the day, the surface orientation, air pollution, presence of surrounding screening agents such as vegetation, snow, dust accumulation, etc., presence of surrounding reflective agents such as snow, water, etc.



Figure 12 Average annual distribution of UV irradiance on Earth (kLy)

UV stabilizers are widely used in geosynthetics to reduce sensitivity of polymers to photo-oxidation by increasing the duration of the induction period. They can be divided in four types: pigments, UV absorbers, quenchers and free radicals deactivators (such as HALS). Pigments and UV absorbers act as a screen, absorbing UV radiation before they cause damage. Quenchers deactivate excited states, removing the energy from liaisons that have been excited by photons and inhibiting in the say way the formation of free radicals. HALS are primary antioxidant, which have the particularity to involve a cyclic, and regenerative stabilization process. They are very effective to protect polyolefin resins.

Most geosynthetic materials are stabilized with a combination of pigments (mostly carbon black for black

materials), antioxidants and/or HALS. The stabilization of PVC materials is more complex and requires several types of additives.

Many other variables influence the rate of degradation of polymer by photo-oxidation. The permeability to oxygen is one of the most important but other factors such as temperature and moisture have also an influence on the rate of degradation. However, on a practical prospective, given that a certain percentage of anti-oxidants are included in the formulation of a polymer, the thicker a material will be, the longer oxygen will take to travel through it, the higher will be its resistance to photo degradation.

3.2.3 Chemical resistance

The potential physical effects of solvent on polymer materials have been discussed in Section 3.1.2 (swelling, solubilisation, crazing, etc.). In addition, chemical agents in contact with geosynthetic materials can also react with the polymer chains and alter its structure.

Chemicals reactions with polymers follow the laws of organic chemistry. The level of reactivity of a given polymer to a given chemical is directly related to the types of molecular groups along its chains. The chemical resistance of common types of polymer used in geosynthetics applications is discussed in Section 4.

The rate of chemical reactions is mainly controlled by the temperature. For many types of reactions, a 10°C increase typically doubles the reaction rate, and favors the diffusion of chemicals into the material. In some cases, chemical can also neutralize additives such as stabilizers, or react with some pigments to change the material's appearance.

The following section will discuss about the hydrolysis, phenomenon, which is a typical type of chemical degradation process involving reactions between water and some polymers such as polyester.

3.2.4 Hydrolysis

The hydrolysis process involves chemical reactions between water molecules absorbed into the material and some specific types of molecular liaison along the polymer chains.

The main types of chemical liaisons likely to be hydrolyzed by water are amides, imides, urethanes, esters, and ethers. For common geosynthetic materials, the hydrolysis process essentially applies to polyesters fibers (PET) and polyester plasticizers in flexible PVC geomembranes.

In the case of PET, water molecules can react with ester groups on each side of the aromatic ring (Figure 13).

This reaction involves an ionic process in which water molecules are divided in H⁺ and OH⁻ ions. The hydrolysis of PET can be catalyzed either by H⁺ ions (acid environment) or OH⁻ ions (alkaline environment). The

higher the concentration of one of these ions, the higher the potency of hydrolysis reactions.

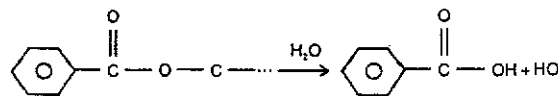


Figure 13 Hydrolysis reaction of ester group in PET fibers.

The concentration of H⁺ ions (or OH⁻ ions) depends on the level of acidity (or alkalinity) of the environment. The higher the acidity (pH<7), the higher the concentration in H⁺ ions and the lower the concentration in OH⁻ ions (and vice-versa). Hence, the hydrolysis potential increases when the environment is either very acid (very low pH) or very alkaline (very high pH).

Doll et al. (1995) have reviewed cases of hydrolysis in PET fibers. In resume, the hydrolysis in neutral or acid environment usually leads to chain scissions (reduction of the average molecular weight) while the process in alkaline environment attacks the fibers' surface, leading to a reduction of its diameter and a loss of weight.

Loss of materials properties in acid environment is usually much slower than in alkaline environment. In addition, hydrolysis may be very rapid at elevated temperature, but becomes a slow process at ambient temperature. High temperatures sustained during the process can lead to important problem of hydrolysis if the material is not dried before.

Hydrolysis is also influenced by the molecular structure of the material such as the percentage of crystallinity. In neutral or acid environment, a high percentage of crystallinity reduces the rate of water diffusion, thus reducing the rate of degradation. In alkaline environment, high level of crystallinity also reduces the rate of surface erosion.

The hydrolysis process lead to a reduction of the molecular weight, which alters the mechanical properties of PET materials and eventually leads to embrittlement. The level of degradation can be monitored by measuring the following parameters:

- intrinsic viscosity;
- carboxyl end group;
- weight loss,
- fibers' diameter.

3.2.5 Microbiological degradation

Degradation of polymer materials by some specific types of microorganisms involves assimilation (metabolization) of short chain segments or components of the geosynthetic material, usually involving hydrolysis or enzymatic oxidation mechanisms. Microbiological degradation can also results from the action of chemicals produced by microorganism metabolism.

Microbiological degradation leads to weight loss and chain scissions. As a consequence, the material may become brittle.

Polymers with molecules including aromatic rings or halogens such as flexible PVC geomembrane are usually not affected by microorganisms. However, those with ester groups such as polyester are more sensitive. The stability of polyolefin geosynthetic material (PE, PP) is essentially related to the molecular weight. As long as microorganisms attacks chain end groups, the potency of microbiological degradation decreases as the molecular weight increases.

Some types of additives can also be altered by microorganisms. Antioxidants and UV stabilizers are usually stable, but some types of plasticizers used in PVC (such as aliphatic polyesters) are particularly sensitive.

Temperature, moisture, UV radiations and visible light are the main factors influencing the microbiological activity. Typically, it is favored in a moist environment and a stable temperature around 30°C. Visible light can favor some types of microorganisms' growth but most of them are destroyed by UV radiations.

Microbiological degradation has little influence for most geosynthetic applications and is typically not a concern with modern resin formulations. However, it could become a concern for applications in tropical environment involving organic soils, with an optimum water supply.

4 ESSENTIAL DEGRADATION MECHANISMS OF COMMON GEOSYNTHETICS

The following sections presents the different types of aging mechanisms, which are the most likely to be met for polymer, used in common geosynthetics.

Note that the actual resistance to the different aging mechanisms presented above is significantly influenced by the molecular structure of the material, i.e. the polymer chain's structure (level of linearity, branching, cross-linking), the molecular weight distribution and the morphology (chain orientation, crystallinity, etc.). Several studies have been conducted over the years to understand the relations between the polymer structure and the degradation mechanisms. As a consequence, significant improvements were already made to material formulation and others are likely to come in the future to continue to improve geosynthetic materials performance and durability.

4.1 Polyethylene (PE)

Polyethylene, HDPE or LDPE, are used in several geosynthetic materials such as geomembranes, geonets, geogrids, and geotextiles.

Polyethylenes have a very simple structure composed of long chains of carbon atoms, with two hydrogen atoms attached to each carbon atom, as illustrated in Figure 1a. Polyethylene is a semi-crystalline polymer so the resin is

composed of an amorphous phase (chains have no specific orientation) and a crystalline phase (chains are organized into well-packed units).

Due to their non-polar nature, polyethylenes are very resistant to chemicals. They present a very low permeability to liquids and gases and are almost insoluble at temperature below 60°C. They are neither attacked by the majority of alkaline and acid agents (except oxidant acid), nor by salt solutions.

The crystalline phase is almost impermeable to chemicals, but the amorphous phase is more sensitive. Halogen hydrocarbons are one of the few types of chemicals which can severely alter the properties of polyethylene. Other chemicals such as mineral oils, aromatic and aliphatic hydrocarbons, and oxidative agents can also affect polyethylene in long-term application. These chemicals can lead to swelling, plasticization and crazing. Oxidative agents can also react with the polymer chains and lead to chain scissions. Diffusion and extraction of additives (in particular small polar additives) can also be a problem in some applications.

Due to its high percentage of crystallinity, HDPE is more resistant to chemicals than LDPE. However, HDPE is sensitive to environmental stress-cracking in presence of sensitizing agents (see Section 3.1.4), which is not the case for LDPE.

Oxidation (thermo-oxidation, photo-oxidation, chemical oxidation) is the main chemical degradation mechanism of polyethylenes. Adequate stabilization with additives such as antioxidants and UV stabilizers is required to ensure the long term performance of the material.

Given that the glass transition of polyethylene is very low, the mobility of polyethylene chains is relatively high. This can lead to internal chain reorganization degradation mechanisms, including post-crystallization, creep and relaxation, especially for LDPE.

In resume, the following durability concerns should be addressed for polyethylene geosynthetics:

- Excellent chemical resistance to several classes of chemicals agents;
- Low microbiological degradation concerns;
- Sensitivity to environmental stress cracking (ESC) in presence of a sensitizing agent;
- Oxidation (specially thermo and photo oxidation) remains the most critical issue and requires material stabilization with antioxidants and UV stabilizers.

Polyethylene geomembranes complying with GRI GM13 specification address most of these issues, as long as this specification is built with regard to these concerns. However, and as specified in the scope of the specification, these values should be considered as minimum values for general applications and could have to be increased when the project is considered to be critical.

It should also be mentioned that polyethylene geogrids are manufactured with very specific resins, the process having

also a drastic influence on the molecular organization and thus on the properties of the finished good. Some of the concerns presented above (i.e. stress-cracking resistance) should be minimized for this family of materials.

4.2 Polypropylene (PP)

Polypropylenes are mainly used as fibers in geotextiles, and some grades of PP are used for geomembranes and geogrids.

PPs have also a structure composed of carbon and hydrogen atoms, as PEs. However, repetitive methyl groups are attached along the backbone chain as illustrated in Figure 1b. These methyl groups limits the chains' mobility, leading to different material behavior.

For example, the glass transition of PPs (homopolymer) is typically in the range of -10°C while it is below -50°C for PEs. Considering that a material becomes brittle and loses its impact resistance when the temperature is under its glass transition, this specific property may become a strong limitation for PP in many applications compared to PE (i.e. material exposed to cold weather). In order to reduce this problem, the structure of PPs is typically modified with copolymers such as ethylene-propylene. These copolymers exhibit low temperature molecular motions, which absorb and dissipate the energy, thereby preventing failure.

Overall, the lower mobility of PP chains reduces internal chain reorganization. Thus, PP are more resistant to creep, relaxation, fatigue and retain their mechanical properties at higher temperature than PEs.

The chemical resistance of PPs is similar or higher than PEs. PPs are not sensitive to environmental stress-cracking, but are more sensitive to oxidation due to the presence of weaker carbon-hydrogen bonds on the tertiary carbon atom. Adequate stabilization against oxidation (thermo and photo oxidation) is required as it is for PEs.

In resume, Polypropylene is globally similar to polyethylene, with the following similarities and differences:

- Both polypropylene and polyethylene have an excellent chemical resistance;
- Polypropylene is not sensitive to environmental stress cracking;
- Polypropylene has a better resistance to internal chain reorganization (creep, etc.) than polyethylene, especially at high temperature.
- Low microbiological degradation concerns, as it is for PE;
- Polypropylene is very sensitive to oxidation and must also be stabilized with pigments, antioxidants and/or UV stabilizers to prevent degradation.

The most critical concern for polypropylene thus appears to be related to its poor oxidation resistance. As a consequence, it is considered that the UV resistance requirement included in many specifications (i.e. AASHTO M288) is appropriate as long as it gives evidences to the purchaser that a minimum treatment against oxidation was

provided to the material (remembering that thermo and photo oxidation typically involve similar degradation mechanisms for polyolefins).

4.3 Polyester

Polyester generally refers to poly (ethylene terephthalate) or 'PET'. This polymer is essentially used in geogrids and sometime in geotextiles, especially when high wettability and/or weight heavier than water are required.

PET fibers usually have a highly oriented semi-crystalline structure in order to reach the desired physical properties. Its chemical structure includes ester groups, which are the important polymeric links in terms of durability.

PET fibers typically have an excellent chemical resistance to many products such as salts, organic solvents and hydrocarbons. However, under certain conditions, they may be sensitive to chemicals such as inorganic acids, halogenated organic acids, inorganic and organic bases, benzyl alcohol and halogenated phenols. PET fibers can also be altered by water if the exposure conditions favors the hydrolysis of ester groups (i.e. high alkalinity environment).

Even if its molecular structure is overall less sensitive to oxidation than PEs and PPs, some chemical bonds of PET can be oxidized under the action of heat (thermo-oxidation) or radiation (photo-oxidation). However, these reactions can be prevented with appropriate stabilizers.

The glass transition of PET is in the range of 70°C . Chain movements at ambient temperature are thus very limited. This gives PET fibers an excellent resistance to creep and other process involving internal chain reorganization.

In resume, the following durability concerns should be addressed for polyester geosynthetics:

- Good chemical resistance to several classes of chemicals;
- Hydrolysis potential in alkaline or acid environments should be considered;
- Excellent resistance to internal chain reorganization (i.e. creep) at typical temperatures up to about 60°C ;
- Microbiological degradation may be a concerns under critical environments;
- Oxidation (specially thermo and photo oxidation) is also a concern, in lesser extend than PP or PE, and also requires material stabilization.

4.4 Poly (vinyl chloride) (PVC)

PVCs are essentially used as flexible geomembrane (plasticized PVC) in geosynthetic applications.

This polymer has a polyhalogenated chain with chlorine atoms covalently linked to atoms of carbon as illustrated in Figure 1c. These chlorine atoms provides many points of dipolar interaction along the chain which leads to strong interactions between chains and consequent rigidity of the polymeric material.

Plasticizing additives are added to reduce these interchain interactions and provide a material with mobility and flexibility characteristics. The glass transition of pure PVC is in the range of 78°C. Plasticizers reduce the glass transition of the material and provide flexibility at low temperature. The higher the plasticizer concentration, the lower the glass transition. Typical PVC geomembranes contain 30 to 35 percent plasticizers per weight. In this range of concentration, the glass transition can be as low as -40°C.

Pure PVCs have an excellent stability to many classes of chemicals such as acids, alkalines, oils, alcohols and aliphatic hydrocarbons. However, they can be swelled and cracked by oxygenated and aromatic solvents such as ketones, esters and toluene. Plasticized PVCs have a slightly lower chemical resistance than rigid PVC due to potential interactions between some chemicals and the plasticizers.

Overall, one of the major durability concerns for flexible PVC geomembranes remains the loss of plasticizers. There are three basic mechanisms for plasticizer loss: volatilization, extraction and microbiological attack:

- Volatilization typically accounts for a large share of plasticizer loss. Direct exposition to the sun heats the geomembrane and favors the volatilization of plasticizers.
- They may also be leached out by chemicals, upon some specific conditions as discussed in 3.1.1.
- Finally, some types of plasticizers such as aliphatic polyesters can be lost due to microbiological degradation as described in Section 3.2.5.

The plasticizer loss rate is a function of plasticizer type (can vary greatly from one type to another), temperature, sheet thickness, environmental conditions and exposition time. As the percentage of plasticizer is reduced, the interactions between polymer chains increase, which reduces the rate of diffusion of plasticizers and eventually locks in the remaining plasticizers.

The effects of plasticizer loss on the physical properties of PVC geomembranes are a loss in total weight, a light reduction in sheet thickness, an increase of tensile modulus, an increase in tensile strength and a reduction in ultimate strain. Plasticizers loss can also lead to visual degradations like crazing and discoloring.

PVCs differ from other polymer materials by their low thermal stability. Thermal degradation lead to HCl emission and thermo-oxidation reactions, these reactions being in competition.

PVCs are also sensitive to thermo-oxidation, which causes discoloration, chain scissions and embrittlement of the material. Addition of heat stabilizers is thus essential to prevent excessive degradation of PVCs during their process and service life.

The resistance of PVC to weathering, light and aging is typically good. However, rigid PVCs typically have better properties than plasticized PVC. High temperature

exposition and UV radiations can cause HCl elimination and oxidation.

Hydrolysis is not a concern for PVC chains, but may affect some types of plasticizers.

In resume, the following durability concerns should be addressed for PVC geosynthetics:

- Good chemical resistance to several classes of chemicals;
- Thermo and photo oxidation are concerns and require material stabilization. Material exposition at high temperature is not recommended.
- Loss of plasticizers is the major concern to be considered. There are three basic mechanisms for plasticizer loss: volatilization, extraction and microbiologic attack. The type of plasticizer and the level of concentration used should be properly selected considering actual exposition, thickness of the geomembrane and the required performance.

5 DISCUSSION

Understanding of polymer long-term behavior has provided the industry an opportunity to develop products with high resistances and a great ability to fulfill their functions in civil enginery applications.

For some products, standard specifications have been developed, with an emphasis on aging properties. As an example, GRI GM13 specification for HDPE geomembranes provides basic requirements, i.e. density and thickness, as well as durability requirements focusing on the most critical degradation mechanisms for this specific material, which are oxidation (photo or thermal) as well as stress-cracking. A purchaser specifying a geomembrane in compliance with GRI GM13 can thus have a high level of confidence regarding the long term efficiency of this material, given that the actual operating conditions will conform to a 'normal' situation, which is understood by authors as being essentially related to the liner temperature, exposition to chemicals and exposition to the sun.

For other polymer membranes, there is no standard specification available to end-user. However, manufacturers of those membranes are in constant research for high quality materials providing better short term properties as well as higher aging properties. For example, polyethylene typically has a higher molecular weight (longer chains, providing higher stress cracking resistance) and includes better antioxidants (providing resistance to photo and thermo degradation) nowadays than it had only one or two decades ago.

It thus seems that a certain level of maturity has been reached by the industry; good products are on the market, and many, if not most of the unknowns regarding functionality, aging and durability have been solved. Authors would like to be cautious with regard to this idea. Despite the industry is actually growing in terms of quality and efficiency, many products still remain specified with only short term properties, like thickness, density, mechanical properties (tensile, tear, puncture and other)

assuming that the durability concerns are not a real issue because the product will come from a well established manufacturer willing to protect its reputation, or without any assumption regarding durability concerns.

At a time when the market is growing out of local borders, assuming that a product will come from a specific manufacturer may be a very wrong idea. Considering that contracts are typically given to lower bids, it is more likely that the installed product will be the cheapest one.

Given that durability and long term efficiency represent a significant share of the total cost of a product, lower cost will typically mean reduced durability. It is thus believed that the lack of long term efficiency requirements provides an opportunity to lower quality manufacturers trying to get shares of the market to sell lower quality products, at a lower cost, without any mean for an engineer to refuse these products.

The question arising thereafter is: in case of problem arising many years after completion of a project, who will be responsible? Fortunately or not, a low quality geosynthetic can still function as expected during a certain time, which may range from, say, 20 to 80 % of what could have been anticipated. As a consequence, the lack of durability requirement in a specification may not even be observed during the time a professional engineer will be held responsible for his design (i.e. a problem could appear after 30 years instead of 120 years, if 120 years is the anticipated design life of the project). In many cases, it drops the durability concerns into an ethical and professionalism field more than toward an actual financial responsibility concern.

6 CONCLUSION

Specification of geosynthetics should always include a chapter focusing on durability, unless the product is dedicated to a short term function. This item should be written to address durability concerns which are specific to the material to be installed on the project, and focus on the service conditions which are likely to be met.

Well established geosynthetic manufacturer typically have data to provide regarding aging and durability of the material they are manufacturing. Despite aging and durability is often a project specific issue, some general specifications can be built, at relatively low cost for the end-user, basing on standard test methods and industry practice. Applicability of these specifications to the project should be reviewed by experienced engineers, in order to guarantee that the relevant degradation mechanisms are considered in the specification.

7 REFERENCES

- Degeimbre R. Rigo J.-M. and Wiertz, Biological Resistance Testing, Geomembranes Identification and Performance Testing, Edited by Rollin A. and Rigo J. M., Chapman and Hall, New York, 1991.

- Doll W. W., Goodrum R., Sprague C. J. (1995), "Alkaline Hydrolysis Testing of Polyester To-Date", Geosynthetics 95, Nashville, Tennessee, USA, Vol. 3, p.975.
- Fay Joseph J. & King III Roswell E. (1994), Antioxidants for Geosynthetic Resins and Applications, Proceedings of 8th GRI Conference, Geosynthetics Resins, Formulations and Mfg., Hsuan & Koerner Editors, IFAI, pp. 77-95.
- Horrocks A. R., D'Souza J. A. (1992), in Handbook of Polymer Degradation, (Hamid, Amin and Maadhah, eds.), Marcel Dekker, New York.
- Hsuan Y. G. (2000), Data Base of Field Incidents Used to Establish HDPE Geomembrane Stress Cracking Resistance Specification, Geotextiles and Geomembranes, Vo.18, pp. 1-22.
- Hsuan Y.G. & Koerner R.M. (1998), Antioxidant Depletion Lifetime in High Density Polyethylene Geomembranes, Journal of Geotechnical and Geoenvironmental Engineering, Vo. 124, No. 6, June, pp. 532-541.
- Koerner R.M. (1989), Durability and Aging of Geosynthetics, Elsevier Applied Science, New York.
- Peacock A.J. (2000), Handbook of Polyethylene; Structures, Properties, and Applications, Marcel Dekker, New York.
- Peggs, I.D., Stress Cracking in HDPE Geomembranes: What It Is and How To Avoid It, Geosynthetics Asia '97, Asian Society for Environmental Geotechnology, New Delhi, India, November 1997, pp 83-90.
- Trotignon J.-P., Verdu J., Piperaud M. & Dobraczynski (1985) A., Précis de matières plastiques; structure-propriétés mise en œuvre et normalisation, 3^e Édition, Association Française de Normalisation, Édition Fernand Nathan.
- Testing Protocols for Oxidation and Hydrolysis of Geosynthetics, U.S. Department of Transportation, Federal Highway Administration, Turner-Fairbank Highway Research Center, Publication No. FHWA-RD-97-144, July 1999.
- Verdu J. (1984), Vieillessement des plastiques, Association Française de Normalisation, Paris.
- Weathering Testing Guidebook, Atlas Material Testing Solutions, Seminar : Principes Fondamentaux du vieillissement, Niveau 1, Montreal, March 2002.
- Weathering of Plastics-Testing to Mirror Real Life Performance, Plastics Design Library, 1999.