

GEOSYNTHETICS DURABILITY: A POLYMER CHEMISTRY ISSUE

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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.

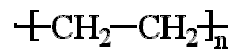
2 POLYMERS USED IN GEOSYNTHETICS

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

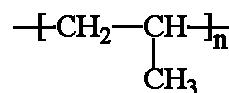
a consequence, the material's first characteristic to consider is its molecular structure.

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.

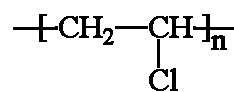
a) polyethylene (PE):



b) polypropylene (PP):



c) poly (vinyl chloride) (PVC):



d) polyester (PET):

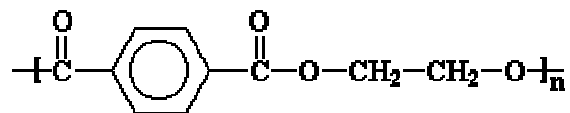


Figure 1: Chemical structure of common polymers used in geosynthetic.

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).

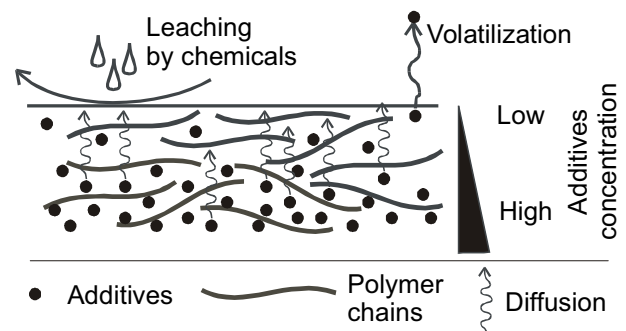


Figure 2: Extraction of additives due to leaching and volatilization.

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 synergetic 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.

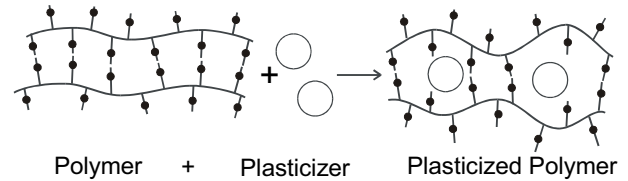


Figure 3 Loss of cohesion in polymer due to the absorption of solvent.

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.

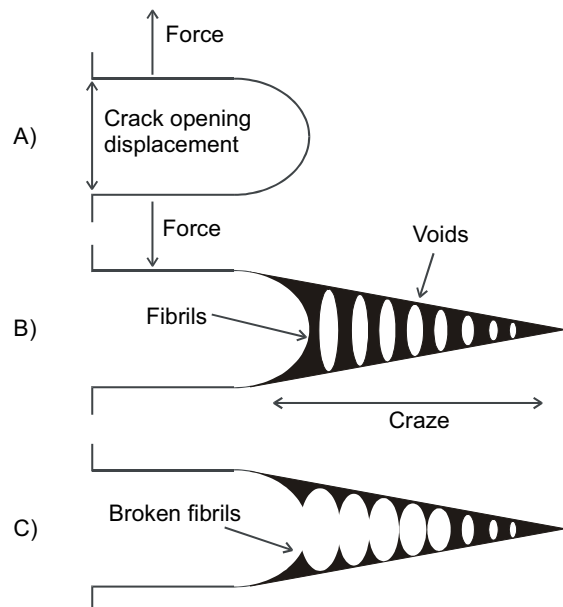


Figure 4 Schematic illustration of the propagation of low stress brittle failure. (a) Preexisting notch subjected to opening force; (b) formation of craze; (c) fracture begins as fibrils break.

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.

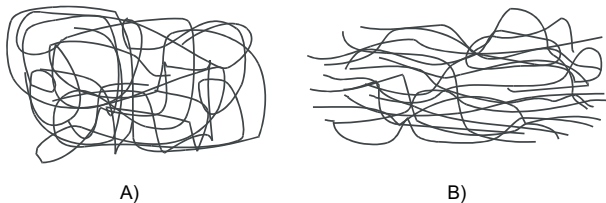


Figure 5 Orientation of polymer chains' segments during processing. (a) Random orientation; (b) oriented melt due to shear stress.

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.

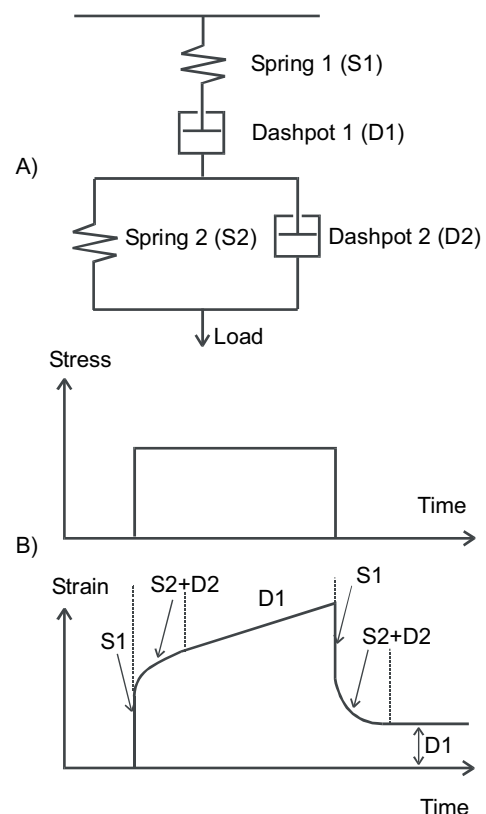


Figure 6 Schematic illustration of creep in polymers. (a) Creep model – combination of springs (elastic strain) and dashpots (viscous strain); (b) response of a material to a stress based on the creep model.

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 geosynthetic 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 geosynthetic 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.

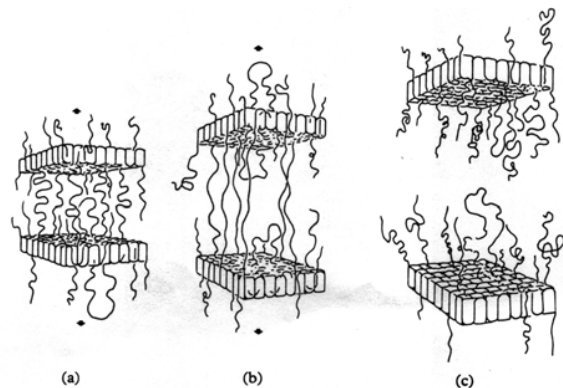


Figure 7 Propagation of brittle-type failure between crystals. (a) Crystal lamellae linked by tie molecules; (b) disentanglement of tie molecules under stress; (c) propagation of failure between lamellae

Hsuan (2000) has evaluated the resistance of several HDPE geomembrane samples in the laboratory according to 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.

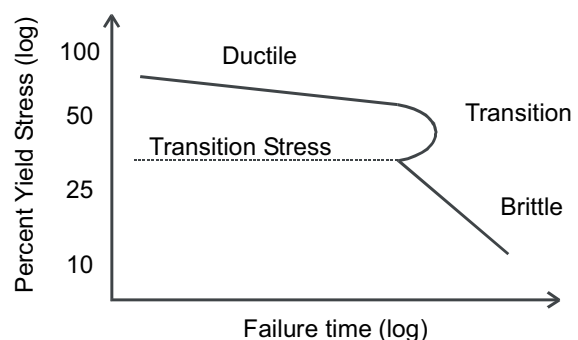


Figure 8 Typical ductile-to-brittle transition in the failure mode of HDPE geomembranes specimens tested according to NCTL test method on a log-log scale (source: Hsuan Y. G., 2000).

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 then 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 then 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.

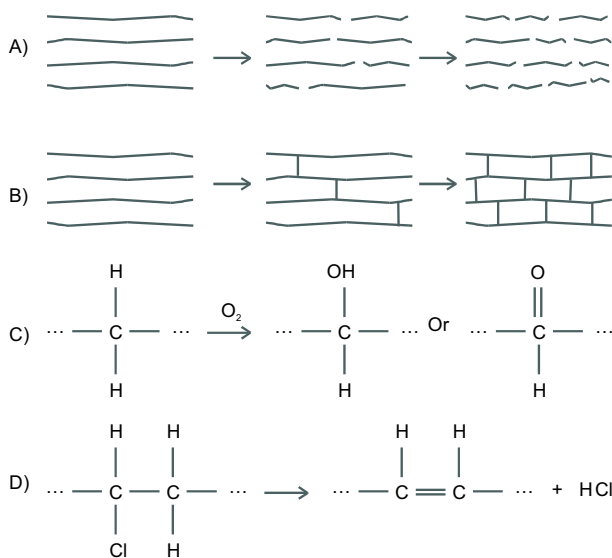


Figure 9 Chemical degradation of polymers. (a) chain scissions; (b) cross-linking; (c) substitution; (d) elimination.

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 sensitized 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.

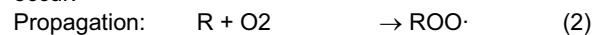
Thermal degradation in presence of oxygen leads to thermo-oxidation of polymer chains. Oxygen sensitizes the material by reducing the temperature for the onset of degradation. The process of thermo-oxidation is complex and involves formation of radical species. This mechanism involves three steps of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

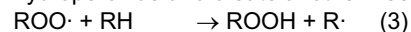
The initiation step, typically caused by factors such as heat, radiations or chemicals, consists in the formation of a free radical (reaction 1).



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).



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.

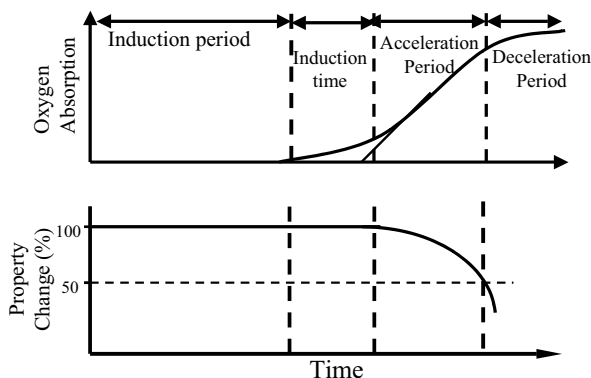


Figure 10: Curves illustrating various stages of oxidation for Stabilized HDPE

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.

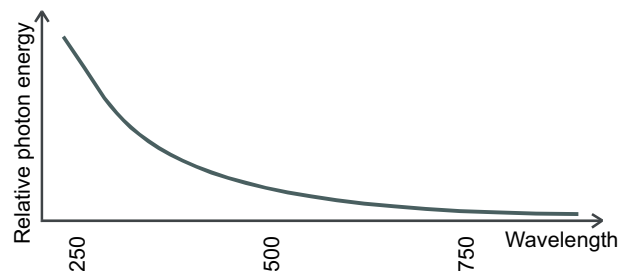


Figure 11 Relative photon energy versus wavelength.

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.

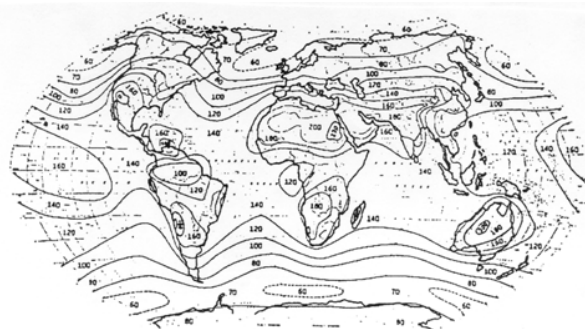


Figure 12 Average annual distribution of UV irradiance on Earth (kLy)

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 10oC 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.

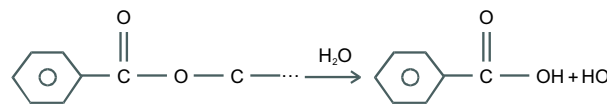


Figure 13 Hydrolysis reaction of ester group in PET fibers.

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 geopipes.

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 enginry 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.

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