LONG-TERM PERFORMANCE AND LIFETIME PREDICTION OF GEOSYNTHETICS

Y. G. Hsuan1, H. F. Schroeder2, K. Rowe3, W. Müller4, J. Greenwood5, D. Cazzuffi6, R.M. Koerner7

1 Drexel University, Philadelphia, Pennsylvania, USA. (e-mail: ghsuan@coe.drexel.edu)
2 BAM, Berlin, Germany (e-mail: hartmut.schroeder@bam.de)
3 Queens University, Kingston, Canada (e-mail: kerry@civil.queensu.ca)
4 BAM, Berlin, Germany (e-mail: Werner.Mueller@bam.de)
5 E.R.A. Technology Limited, United Kingdom (e-mail: John.Greenwood@era.co.uk)
6 CESI SpA, Italy (e-mail: cazzuffi@cesi.it)
7 Geosynthetic Institute, Folsom, Pennsylvania, USA (e-mail: robert.koerner@coe.drexel.edu)

Abstract: To properly understand and assess the long-term behaviour of geosynthetic materials it is necessary to investigate the various types of possible degradation mechanisms. This includes both chemical and mechanical behaviour, and sometimes even their interactions with one another. Clearly, chemical degradation of geosynthetics depends on the polymer type. For example, polyolefins are vulnerable to oxidation; polyesters are susceptible to hydrolysis; and plasticizers can leach from polyvinyl chloride. This paper describes the concept of these three types of degradation, but focuses on the oxidation of polyolefins since the majority of the geosynthetics is made from this type of polymer. The methods used to predict the lifetime of antioxidants and service life of the geosynthetic material will be illustrated. Furthermore, the influence of temperature, pressure, and ultraviolet light on the service life are also demonstrated. Finally, the current specifications targeting the longevity of different geosynthetics are presented.

Regarding mechanical degradation, the paper mainly focuses upon the creep deformation of geogrids and stress crack resistance (SCR) of polyethylene geomembranes and geopipe. The method to assess stress crack resistance is described, and the microscopic mechanisms that lead to such failure are explained. For creep evaluation, different acceleration tests are presented and their applicability with respect to the different types of polymers is illustrated. In addition, the long-term shear behaviour of geocomposites and geosynthetic clay liners is presented.

Keywords: geosynthetic, durability, degradation, antioxidant, weathering.

1. INTRODUCTION

In a recent worldwide assessment of four years of questions to a geosynthetics technical support-service internet hotline, gmatechline@ifai.com, 20% of the questions were specifically on the issue of durability and/or degradation of geosynthetics. An additional 15% were related to long-term mechanical response, and an additional 10% were on the interactive nature of chemical and mechanical behaviour (Koerner and Aho, 2008). Thus, almost one-half of unsolicited questions from regulators, owners, designers, and even manufacturers and installers inquired about the subject area of this keynote paper. As such, its importance cannot be overemphasized.

Upon reviewing the various types of polymers used to manufacture geosynthetics, the main chemical degradation mechanisms are presented. They are as follows:

- Oxidation of polyethylene geosynthetics.
- Migration of plasticizers from polyvinyl chloride geomembranes.
- Hydrolysis of polyester geotextiles and geogrids.

Additionally, the photodegradation of these three polymers when exposed to sunlight is presented along with correlations between outdoor exposure and laboratory weatherometers.

Emphasis then shifts from chemical degradation to the long-term mechanical performance of geosynthetics. These topics are as follows:

- Stress cracking resistance of high density polyethylene.
- Creep behaviour of geosynthetics.
- Long-term shear strength of geosynthetics.

The summary section brings together the three types of chemical degradation, exposed weathering effects, and time-dependent mechanical behaviour on geosynthetics.

2. TYPES OF POLYMERS USED IN GEOSYNTHETICS

The chemical and mechanical behaviour of geosynthetics are highly dependent on the type of polymer used, the additive formulation, the morphology, and the application of the geosynthetic. Table 1 shows the polymers commonly used in the different geosynthetics as well as their approximate formulations.
Table 1. Types of commonly used polymers in geosynthetics

<table>
<thead>
<tr>
<th>Polymer Resin</th>
<th>Geosynthetic</th>
<th>Composition (weight percentage)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Resin</td>
</tr>
<tr>
<td>High density polyethylene (HDPE)</td>
<td>Geomembrane (GM)</td>
<td>96-98</td>
</tr>
<tr>
<td></td>
<td>Geopipe (GP)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Geogrid (GG)</td>
<td></td>
</tr>
<tr>
<td>Linear low density polyethylene (LLDPE)</td>
<td>GM</td>
<td></td>
</tr>
<tr>
<td>Flexible polypropylene (PP)</td>
<td>GM</td>
<td>96-98</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>Geonet (GN)</td>
<td>96-98</td>
</tr>
<tr>
<td></td>
<td>Geopipe (GP)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Geotextile (GT)</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl chloride (PVC)</td>
<td>GM</td>
<td>50-70</td>
</tr>
<tr>
<td>Polyethylene terephthalate (PET)</td>
<td>GG, GT</td>
<td>98-99</td>
</tr>
</tbody>
</table>

* Additives include stabilizers, antioxidants, colorants, and processing aids.

2.1. Polyethylene

Polyethylene (PE) is a polyolefin belonging to the hydrocarbon group as it only contains carbon and hydrogen atoms in its chemical structure. Types of PE used in geosynthetics are mainly linear co-polymers formed by catalytic polymerization under low temperature and pressure (Rodriguez, 1996). The co-monomers become the side chains attaching to the ethylene chain. The types of co-monomers are α-olefins including pentene, hexene, and octene. The type, amount, and distribution of the co-monomers have strong impact on chemical and mechanical properties of the resin. For example, the density of the PE decreases as the concentration of the co-monomer increases. PE is categorized into different classes based on the resin’s density. The three classes commonly used in geosynthetics and their respective densities are provided below (ASTM D 833-2005):

- High density polyethylene (HDPE), \( \rho > 0.940 \text{ g/ml} \)
- Medium density polyethylene (MDPE), \( \rho = 0.926 - 0.940 \text{ g/ml} \)
- Linear low density polyethylene (LLDPE), \( \rho = 0.919 - 0.925 \text{ g/ml} \).

The physical and mechanical properties of PE are highly sensitive to density as illustrated in Figure 1. The selection in the type of PE should be governed by the function of geosynthetic product. For example, MDPE is a more suitable material for geomembranes used as landfill liners in comparison to LLDPE due to its chemical resistance, high strength, and low permeability. It should be noted that most HDPE geomembranes are actually made from MDPE resin. Only by the addition of carbon black and additives does the density become greater than 0.940 g/ml. In this paper we will be consistent with the industry in calling it HDPE. While many manufacturers use MDPE, some do indeed use HDPE resin for their geomembranes.

![Figure 1. Generalized relationships between density of PE and material properties](image)

2.2. Polypropylene

Polypropylene (PP) is another polyolefin formed by catalytic polymerization similar to PE. Geotextiles are made mainly from isotactic PP. For geomembranes, a particular type of PP/PE alloy which is polymerized using a reactor granule technology is used, resulting in more flexible products (Moore, 1998).
2.3. Polyvinyl chloride

Polyvinyl chloride (PVC) is formed by a free radical polymerization. Products made from PVC are rigid and strong and are suitable in building construction for such items as pipes, siders, windows, and door frames. Due to the highly polar nature of the polymer, PVC can be blended with other polar compounds. Adding plasticizers to PVC changes the physical properties of the polymer from a rigid to a flexible material. For PVC used in geomembranes, plasticizers constitute 25 to 35% of the material. These geomembranes are properly referred to as plasticized polyvinyl chloride (p-PVC) which will be the designation used throughout the paper. The type of the plasticizers is critical to the long-performance of the p-PVC geomembrane.

2.4. Polyethylene terephthalate

Polyethylene terephthalate (PET) is a type of polyester formed by the condensation polymerization between terephthalic acid and ethylene glycol. The material properties that affect the chemical resistance of PET include molecular weight, carboxyl end groups (CEG), orientation, crystallinity, content of copolymerized acids and alcohols, moisture content, soil water chemistry, and product design. The relatively high glass transition temperature ($T_g$) of PET affects the mechanical properties (particularly long-term) of the product.

3. OXIDATION OF POLYOLEFIN GEOSYNTHETICS

The oxidation of polyolefins is quite complex, however the basic principles are presented in this paper. For geosynthetics, particularly those designed for geotechnical applications, the oxidation properties depend on the particular polymer resin and its additive formulation. As shown in Table 1, geosynthetics made from polyolefins contain over 95% of polymer with the remainder being carbon black and additives, e.g. processing stabilizers and long-term antioxidants. Furthermore, the material fabrication process, field ambient environment during installation, and environment during service duration can also influence oxidation mechanisms.

3.1. Chemical reactions of oxidation

The oxidation reactions of polyolefins are rather well known. The sequential steps of the oxidation chain reaction include initiation, propagation, chain branching, and finally the termination reactions. Several of the fundamental reactions are highlighted, as follows:

- The initiation reactions, Eqs. (1) to (3), are energized by temperature or radiation. They may also be catalyzed by transition metal ions, catalyst residues from the polymerization processes, or contaminants. A further possibility is the thermal disintegration of initiators present, like peroxides. The precise mechanism is still somewhat controversial (Gugumus, 1989).

$$RH \overset{\text{energy}}{\longrightarrow} R\cdot + H\cdot \quad (1)$$

$$RH + O_2 \overset{\text{energy}}{\longrightarrow} R\cdot + HO_2\cdot \quad (2)$$

$$RH + O_2 + \text{Residual catalysts} \overset{\text{energy}}{\longrightarrow} \text{Free Radicals} \quad (3)$$

- The oxidation cycle is given by Eqs. (4) and (5):

$$R\cdot + O_2 \overset{k_4}{\longrightarrow} RO_2\cdot \quad (4)$$

$$RO_2\cdot + RH \overset{k_5}{\rightarrow} ROOH + R\cdot \quad (5)$$

For reaction (4) the rate constant $k_4$ is very large, on the order of $10^9$ l/mol/sec, and consequently the reaction proceeds rapidly when oxygen is present. On the contrary, reaction (5) proceeds much more slowly since chemical bonds have to be split. The rate constant $k_5$ is in the range of 10 to 60 l/mol/sec.

- Chain branching reactions (also called auto-propagation reactions) are then triggered as expressed in Eqs. (6) to (10).

$$ROOH \longrightarrow RO\cdot + HO\cdot \quad (6)$$

$$ROOH + RH \longrightarrow RO\cdot + R\cdot + H_2O \quad (7)$$

$$2ROOH \longrightarrow RO\cdot + RO_2\cdot + H_2O \quad (8)$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot \quad (9)$$

$$HO\cdot + RH \longrightarrow H_2O + R\cdot \quad (10)$$

The chain branching stage of the oxidation begins when the critical concentrations of both $ROOH$ and $RO_2\cdot$ is reached. The time to build up such critical concentration is defined as the oxidation induction period, and is illustrated in Figure 2.
Termination reactions among free radicals
The chain termination under conditions of sufficient oxygen supply is achieved by recombination of oxygen rich peroxyradicals, is given in Eq. (11):

\[ 2RO_2 \cdot \rightarrow RO + ROH + O_2 \]  

(11)

If there is a lack of oxygen ([R\(\cdot\)] >> [ROO\(\cdot\)]) the terminations take place by combination reactions with other radicals which contain less oxygen (Eqs. 12 to 15). The reaction only occurs if both radicals are not tertiary. (Zweifel, 1997; Zingg, 1998)

\[ R \cdot + ROO \cdot \rightarrow ROOR \]  

(12)

\[ R \cdot + R \cdot \rightarrow RR \]  

(13)

\[ R \cdot + RO \cdot \rightarrow ROR \]  

(14)

Alternatively disproportions are as follows:

\[ 2R \cdot \rightarrow RH + Olefin \]  

(15)

3.2. Material effects on oxidation
The chemical and physical structure of polyolefins can have strong influence on the oxidation. Three major factors are discussed as follows.

3.2.1. Tertiary hydrogen atom

The total energy input of Eq. (1 to 3) depends on the chemical structure of the polymer. The tertiary hydrogen requires lower dissociation energy than the secondary and primary hydrogen atoms to form free radicals as illustrated in Figure 3. Therefore, polymers with greater number of tertiary hydrogen atoms generate more free radicals than those with less tertiary hydrogen atoms. For example, more free radicals can be formed from PP than PE when exposing to the identical condition, since PP possesses tertiary hydrogen in every other carbon atom along the polymer chain.

\[ -C-C-C+H\cdot \]  

Figure 3. Dissociation reaction of the tertiary hydrogen atom
3.2.2. Crystallinity
As indicated in Figure 1, the permeability decreases as density (i.e., crystallinity) of polyethylene increases. Since oxygen diffuses easier into the amorphous phase than the crystalline phase due to its higher solubility, the susceptibility of oxidation increases as density decreases (Rapoport et al., 1975; Ryan and Calvert, 1982).

3.2.3. Orientation (Stretching)
Many geosynthetic products, including GGs and GTs, are formed by orienting the polymer during the manufacturing process. The Peterlin Model (1966) describes the polymer orientation mechanism under tensile stress. It results in a much denser amorphous phase and higher crystallinity, retarding the diffusion of oxygen into the polymer.

3.3. Environmental effects on oxidation
The oxidation degradation of geosynthetic in field conditions is affected by temperature, oxygen partial pressure, and chemical constituents of the surround media, e.g., pH, transition metal ions, etc. Each will be described.

3.3.1. Temperature
Temperature plays the most critical role of all physical and chemical processes. The oxidation mechanism is governed by the transport processes of oxygen and other components involved with chemical processes. Transport processes such as diffusion along with properties including solubility and oxygen permeability are all strongly temperature dependent (Calvert and Billingham, 1979; Billingham, 1989; Crank, 1975; Zweifel, 1997). The oxygen consumption rate at lower temperatures is relatively moderate compared to higher temperatures. As indicated in Eq. 4, the oxygen concentration should be sufficiently high so alkyl free radicals are transformed to peroxynitrogens, leading to [ROO•] greater than [R•]. At an ambient field temperature (20 to 25°C) within permeable soil, the same reactions can surely be prevailing, leading to the accumulation of peroxides in the polymer. At elevated temperatures, which are often used for the accelerated oxidation of polyolefin products, the solubility of oxygen decreases with increasing temperature, while the diffusion rate increases slower than the rate of autoxidation due to its higher activation energy (Ea). Thus, the rate of diffusion often controls the rate of autoxidation. Also the high oxygen consumption rate inside the polymer leads to the condition of [R•] greater than [ROO•], which does not simulate the situation of geosynthetics in permeable soils, but is a reasonable simulation for geosynthetics used in an anaerobic landfill environment. The oxygen diffusion controlled degradation has been observed in many polymer degradation studies. The effect leads to stronger oxidation occurring at the surface (Zweifel, 1997; Viebke and Gedde, 1997 and1998). Maximum incubation temperatures have been suggested for unstabilized PP and PE to be in the range of 80 to 90°C (Viebke et al., 1994; Achimsky, 1997; Gugumus, 1999, Ding, 2001).

3.3.2. Oxygen concentration
The available oxygen concentration in the environment surrounding the geosynthetic is essential to the oxidation degradation. As stated in the previous section, different oxidation reactions can take place based on the available oxygen. However, the reaction rate at ambient temperature is so slow that the evaluation of oxidation degradation becomes impractical to simulate in the laboratory. An alternative test method which will be discussed in the later section of the paper uses high oxygen concentrations to compensate the lower temperature used in this accelerated oxidation test.

3.3.3. Chemistry of the surrounding liquid media
The oxidation of polyolefins can be accelerated by the presence of transition metal ions such as cobalt manganese, copper, and iron (Chan and Allara, 1974; Osawa, 1973; Reich, et al. 1971). The metal ions can promote the breakdown of peroxides via “redox” reactions, as expressed in Eqs. (16) and (17). Wisse (1988) found that the oxidation degradation of a PP geotextile was accelerated by the presence of rusting steel wires. 

\[
ROOH + M^{n+} \rightarrow RO \cdot + M^{(n+1)} + OH^- \quad (16)
\]

\[
ROOH + M^{(n+1)} \rightarrow ROO\cdot + M^{n+} + H^+ \quad (17)
\]

3.4. Additives to minimize oxidation
To prevent complete contact of oxygen with geosynthetics is generally not practical. Therefore manufacturers have developed other methods to minimize the extent or delay the onset of oxidation in polyolefins. As indicated in Table 2, antioxidants (AOs) and carbon black (CB) are incorporated into the polyolefin geosynthetics for this purpose. Antioxidants play the critical role in the durability of geosynthetics that are not exposed to sunlight; they can extend the duration of the induction period delaying the onset of the oxidation, as illustrated in Figure 4. By strategically designing the antioxidant formulation the overall lifetime of the geosynthetic can exceed hundreds of years. Several laboratory durability studies will be presented later part in this paper to demonstrate the durability of antioxidants in different geosynthetics under various environments. For geosynthetics used in exposed environments a combination of AOs and CB is typically required. Alternatives to CB usage (if a black material is not desirable) include adding colorants and/or titanium oxide. Numerous formulations are available in this regard.
3.4.1. Antioxidants

There are many different types of antioxidants (AOs). They mainly belong to four families of chemical compounds. Furthermore, these four families of AOs are categorized into primary and secondary depending on their chemical functions; see Table 2 (Hsuan and Koerner, 1998). Primary AOs stabilize the polymer by trapping or deactivating the free radical species. Some primary AOs function by donating electrons to react with the free radicals \( \text{ROO}^\cdot, \text{RO}^\cdot, \text{and} \cdot\text{OH} \), converting them to \( \text{ROOH}, \text{ROH}, \text{and} \text{H}_2\text{O} \), respectively. Other primary AOs are electron acceptors which convert alkyl free radicals \( \text{R}^\cdot \) to form a stable polymer. Secondary AOs are designed to decompose hydroperoxides \( \text{ROOH} \), preventing them from disintegrating into free radicals. The chemical reactions convert the \( \text{ROOH} \) to a stable alcohol \( \text{ROH} \) (Grassie and Scott, 1988).

<table>
<thead>
<tr>
<th>Chemical Type</th>
<th>Examples of commercially available products</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Primary antioxidants</td>
<td></td>
</tr>
<tr>
<td>Hindered phenols</td>
<td>Irganox® 1076, Irganox® 1010, Irganox® R, Santonox® R, Santowhite Crystals®</td>
</tr>
<tr>
<td>Hindered amines (HALS*)</td>
<td>Various types of Tinuvin®, Chimassorb®</td>
</tr>
<tr>
<td>(b) Secondary antioxidants</td>
<td></td>
</tr>
<tr>
<td>Organic phosphites</td>
<td>Irgafos® 168</td>
</tr>
<tr>
<td>Sulfur compounds (Thiosynergists)</td>
<td>Alkanox® P-24</td>
</tr>
<tr>
<td>Hindered amines (HALS*)</td>
<td>Lowinox Dilauryl thiodipropionate (DLTDP), Lowinox Di-stearyl thiodipropionate (DSTDP)</td>
</tr>
<tr>
<td></td>
<td>Various types of Tinuvin®, Chimassorb®</td>
</tr>
</tbody>
</table>

* HALS = hindered amines light stabilizer

Another factor that should be considered during the selection of AOs is their effective temperature range. Figure 5 shows the effective temperature range of the four groups of AOs (Fay and King 1994). The AO formulation package should protect the product at both the high processing temperature during manufacturing and at the ambient temperature during long-term service. Organic phosphites have an effective temperature range above 150°C and they are used as process stabilizers. On the other hand, hindered phenols have a wide effective temperature range, from ambient to process temperatures. As seen, thiosynergists and hindered amines generally serve as antioxidants to provide long-term service life.

![Figure 5. Effective temperature range of four families of antioxidants](image)
3.4.2. Carbon Black

Carbon black (CB) is widely used as UV stabilizer in polymers; it absorbs UV radiation and dissipates the absorbed energy as heat. Carbon black is produced by the incomplete burning of hydrocarbon gases and oils (Haddad and Gunning, 1994). The product is categorized into different grades based on particle size, surface area, aggregate size, and surface chemistry (Mwila et al., 1994). The optimum function of CB can be achieved by considering:

- **Particle size.** The particle sizes of CB for polyolefin products typically range from 25 to 75 nm. For a constant amount of CB, the UV absorption decreases with increased particle size due to its decreasing surface area. The relationship between both particle size and surface area and morphology of CB is illustrated in Figure 6 (Accorsi, 1995).

- **Residual chemicals.** During the CB manufacturing process, oxidation takes place on the surface of CB, forming different oxygen complexes among which phenolic hydroxyl groups function as radical scavengers and act as mild antioxidants (Hawkins, 1984). Gilroy and Chan (1984) found that CB can enhance the retardation of oxidation of PE when blended with hindered amine, hindered phenol, thiobisphenol, and a sulfur bridged phenol. Thus, CB and AOs can and should be synergistic with one another. However, high concentrations of free sulphur tend to remain in CB with large particle size leading to an antagonistic effect with phenolic antioxidants (Grassie and Scott, 1988).

- **Dispersion.** In order for CB to fully function as UV stabilizer in the polymer, a well dispersed system must be achieved. The dispersion of CB is controlled by the shear force and dwell time of the extrusion process and the compatibility of carrier resin with the polymer in which it is being incorporated. (CB is added to the polymer in a form of master batch which contains up to 25% of CB with carrier resin.) The carrier resin should be the same type of polymer as the intended polymer but with lower viscosity to achieve a good dispersion.

3.5. Laboratory evaluation of the oxidation of polyolefin geosynthetics

Since all geosynthetic products made from polyolefins contain antioxidants, oxidation of the polymer does not begin until nearly all of the antioxidants have been consumed. The laboratory test methods used to assess the oxidation of polyolefins examine both the lifetime of antioxidants in the polymer and the stability of the polymer itself. Figure 7 shows the three consecutive stages in the oxidation process of polyolefin products. Under the same exposure condition, the antioxidant stage, Stage “A” depends on the types and amounts of antioxidants.

![Figure 6. Example of Carbon black morphology](image)

- **Residual chemicals.** During the CB manufacturing process, oxidation takes place on the surface of CB, forming different oxygen complexes among which phenolic hydroxyl groups function as radical scavengers and act as mild antioxidants (Hawkins, 1984). Gilroy and Chan (1984) found that CB can enhance the retardation of oxidation of PE when blended with hindered amine, hindered phenol, thiobisphenol, and a sulfur bridged phenol. Thus, CB and AOs can and should be synergistic with one another. However, high concentrations of free sulphur tend to remain in CB with large particle size leading to an antagonistic effect with phenolic antioxidants (Grassie and Scott, 1988).

- **Dispersion.** In order for CB to fully function as UV stabilizer in the polymer, a well dispersed system must be achieved. The dispersion of CB is controlled by the shear force and dwell time of the extrusion process and the compatibility of carrier resin with the polymer in which it is being incorporated. (CB is added to the polymer in a form of master batch which contains up to 25% of CB with carrier resin.) The carrier resin should be the same type of polymer as the intended polymer but with lower viscosity to achieve a good dispersion.

![Figure 7. Three conceptual stages in oxidation of polyolefin geosynthetics](image)
To evaluate the oxidation of polyolefin in the laboratory, it is necessary to accelerate the rate of reactions so that the oxidation can occur within a reasonable duration. Temperature acceleration is the most common method. Eq. 18 shows the rate of reaction is governed by three parameters (Morrison and Boyd, 1992).

\[
\text{Rate of reaction} = \frac{\text{collision frequency}}{\text{energy factor}} \cdot \text{probability factor}
\]  

(18)

where the collision frequency depends upon the density of particles (i.e., concentration or pressure) and the speed (which depends on the temperature). The energy factor is mainly contributed by temperature. The probability factor is similar for closely related reactions. Thus, temperature has the greatest influence on the rate of reaction, followed by pressure (or concentration).

For stabilized geosynthetics the surrounding medium affects the oxidative process as AOs may be lost by evaporation, extraction, and migration. All of these may be used in the design of an acceleration test.

3.5.1. Temperature acceleration method

Temperature accelerated aging is used almost universally as the method to evaluate oxidation of polyolefins. It is relatively simple to perform while it provides the greatest acceleration to the rate of the reactions as indicated in Eq. 18. One of the basic principles of the thermally accelerated aging studies is that the test temperatures should not be so high that the oxidation mechanism is altered, i.e., similitude of the experiment is required. This principle must be held true for the lifetime prediction assessment. The most common thermal acceleration method is oven aging. Samples of a geosynthetic product are exposed to constantly circulating air by incubation in a forced air oven at an elevated temperature. At different incubation durations, samples are retrieved and tested for their mechanical properties. The failure of the sample is usually defined as a 50% decrease in a specific property which is typically elongation at break. The duration to reach failure is the lifetime of sample at the specific test temperature, i.e. combined duration of Stages A+B+C in Figure 7. For lifetime prediction at a specific site temperature, incubation should be performed at minimum of three elevated temperatures. The lifetime of the sample at each elevated temperature is determined and then analyzed using the Arrhenius equation so that the lifetime at the site temperature (usually at a low temperature) can be extrapolated; see Figure 8. However, the predicted lifetime in an oven aging study only represents geosynthetics that are exposed to a constantly moving air environment. In this regard the oven aging incubation represents an exposed geosynthetics in air (21% of oxygen), but not directly exposed to ultraviolet light. Ideally, the incubation condition should be specially designed to simulate the target field condition in order to appropriately predict the service lifetime of the geosynthetic for that application. For geosynthetics buried in soil like in walls, slopes, or landfill cover applications, the oxygen content is much lower, may be 5 to 15%. Even further at the base of a landfill the oxygen content may even be zero, i.e., anaerobic conditions. These “starved air” incubations are extremely difficult to simulate in a long-term laboratory experiment but are, in reality, the proper method of simulation and will be described in later part of this section. Thus, oven aging represents an extremely worst-case situation for lifetime prediction.

Also it should be emphasized that at a 50% reduction in a mechanical property, i.e., the half-life, the geosynthetic is still intact and generally servicing its desired function. Perhaps a 75 to 90% reduction would be more realistic for lifetime prediction of geosynthetics, but other application (gas pipelines, electrical cable shielding) use 50%.

3.5.2. Pressure and temperature acceleration method

As indicated in Eq. (18), oxidation reaction rates can also be accelerated by the oxygen concentration, i.e. the oxygen pressure. Certainly the pressure should not be so high that the mechanism of oxidation reactions is altered.

A new acceleration method that utilizes both pressure and temperature was developed in the last ten years to evaluate polyolefin geotextiles and geogrids. The test requires sophisticated incubation chambers that can be operated safely at elevated oxygen pressure as well as maintained at a moderately elevated constant temperature. Schroeder, et al. (2000a) developed a autoclave in which test specimens are immersed in an aqueous solution and subjected to
elevated oxygen pressure and temperature to accelerate the oxidation and extract AOs simultaneously. In contrast, Li and Hsuan (2004) incubated test specimens in a pressure cell without liquid while placed inside a forced oven at elevated temperature.

The challenge of the pressure acceleration methods is in the extrapolation of the data to ambient conditions. The pressure effects on the rate of the oxidation reactions must be established. Several European and American research groups are working to develop and verify the pressure model. The summary of these studies will be presented in Section 3.8.

3.6. Tests used to evaluate the property of incubated samples

The duration to reach half-life of properly stabilized polyolefin geosynthetics takes years, particularly at lower incubation temperatures than ~60°C although the depletion of AOs starts immediately after incubation. Thus, the following test methods are used to evaluate both the depletion of antioxidants and oxidation degradation of the polyolefin products.

3.6.1. Test methods to evaluate antioxidants

Identifying the types and amounts of AOs in geosynthetics is a challenging task, since there are many different possible formulations. The precise way is to extract the AOs from the material and then analyze the composition using high performance liquid chromatography (HPLC) (Bart, 2005). This procedure requires an operator who is familiar with analytical chemistry to perform and analyze the results. The alternative test method, oxidative induction time (OIT) test, is more user-friendly. Recently, a new test method was developed by Schroeder, et al. (2002) to evaluate the reaction of HALS by measuring the oxygen consumption of the model oxidation reaction with cumene at 60°C.

The OIT value indicates the amount of AOs but not the type remaining in the test specimen. Many researchers use this method to monitor the depletion of AOs because of its simplicity (Dörner and Lang, 1998 and Lundback et al., 2006 (a), (b)). However, for different AO formulations (types and amount), direct comparison can be misleading. There are two OIT tests, standard OIT (Std-OIT) and high pressure OIT (HP-OIT), which are carried out using a differential scanning calorimeter (DSC) with standard and high pressure cells, respectively. The Std-OIT is performed according to ASTM D3895. The test specimen is subjected to 35 kPa gauge pressure of oxygen at 200°C. The HP-OIT test is performed under 350 kPa gauge pressure of oxygen at 150°C condition according to ASTM D 5885. The determination of the OIT value is illustrated in Figure 9 based on a Std-OIT test. The main application of the HP-OIT test is for antioxidants that have low efficiency temperature range, such as hindered amine types shown in Figure 5 (Thomas and Ancelet, 1993; Hsuan and Guan, 1997).

![Figure 9. Thermal curve from a Std-OIT test](image)

3.6.2. Test methods to evaluate oxidation degradation of the geosynthetics

Once AOs in the geosynthetic are consumed, oxidation degradation starts to occur via either chain scission and/or cross-linking reactions; properties of the polymer will subsequently change. There are three common tests used to detect oxidation degradation:

- **Melt index (MI) test.** Melt index is a qualitative method to assess molecular weight of the polymer. Since the results of oxidation degradation induce molecular weight changes, the MI value of the polymer also changes accordingly and acts as an indicator. The MI value will increase for chain scission reactions and decrease for cross-linking reactions.
- **Fourier Transform Infrared (FTIR).** The chemical compounds, carbonyl and carboxyl groups, produced from the oxidation reaction can be detected by the FTIR. A good correlation has been found between the accumulated carbonyl concentration and tensile break elongation (Tidjani, 2000). The basic advantages of the FTIR analysis include small sample size, non-destructive, and simple to operate. However, the analysis of test data can sometime be challenged.
Tensile properties. Engineering-wise, the most important concern of the oxidation degradation is on the mechanical properties of the material. The tensile test is often used to assess changes of the polymeric materials. Depending on the type of geosynthetic products, appropriate standard tensile test methods should be used. For example, ASTM D 6638 is used for the evaluation of tensile properties of geomembranes and ASTM D 3822 for testing filaments. The properties that are strongly correlated to the degradation are tensile break strength or elongation. That said, there should be no change in these mechanical properties until essentially all of the AOs have been depleted.

3.7. Oxidation degradation of HDPE geomembranes

The durability of HDPE geomembranes has been intensively studied by many researchers. The published results are summarized in this section according to different incubation environments.

3.7.1. Aging in forced air ovens and water baths

Hsuan and Guan (1998) performed an oven aging study on five geomembranes with different AO formulations. The incubation temperatures were 115, 95, 75, and 65°C. The incubated samples were evaluated for OIT, MI, and tensile properties. Although 115°C was beyond the typical upper limit for HDPE aging, the intention was to reach the Stage C of Figure 7 within a reasonable short period of time so that the function of antioxidants in protecting the material properties could be verified. It was found that OIT retained values generally decrease exponentially with incubation time according to a first order reaction, as expressed in Eq. 19. The tensile break properties and MI remained unchanged as long as the OIT value was above one minute, see Figure 10. The decrease in MI value at 115°C indicated that the oxidation was undergoing cross-linking reactions.

\[
\ln(OIT\%) = -kt
\]  

(19)

where “OIT%” is OIT percent retained after incubation time \( t \), “\( t \)" is incubation time (days), and “\( k \)” is a reaction rate constant.

The lifetime of the antioxidants of the geomembranes at 20°C was predicted using Arrhenius equation, as expressed in Eq. 20. One of the Arrhenius curves is shown in Figure 11. A linear relationship was established between \( \ln(k) \) and inverse temperature, and the predicted value at 20°C is 80 years using data from 65 to 95°C.

\[
k = A \exp(-E/RT)
\]  

(20)

where “\( k \)” is the reaction rate constant, “\( E \)” is the activation energy (kJ/mol), “\( R \)” is the universal gas constant (8.314 J/mol-K), “\( T \)” is the incubation temperature (K) and “\( A \)” is a material constant.

Figure 10. Property changes with incubation time at 115°C air incubation (Hsuan and Guan, 1998).
Müller and Jacob (2003) studied the oxidation degradation of nine 2.5mm thick HDPE geomembranes by exposing them to a constant temperature of 80°C in a forced air oven and immersion in a water bath. The incubated samples were periodically tested for OIT and tensile properties. The test data varied due to different AO formulations. Overall, they found that antioxidants depleted significantly faster in water than in air. After 13 years, there was no reduction in tensile properties at 80°C oven aging, while degradation was observed after 5-year in an aqueous environment.

3.7.2. Aging in other liquids (leachate, simulated leachate, and mining leachate)

In addition to using air and water, the effects of leachate on the oxidation of HDPE geomembranes have been studied by Sangam and Rowe (2002); Islam and Rowe (2007(a) and (b)); Rowe, et al., (2008); Rowe and Rimal, (2008a). Also, Gulec et al. (2004) conducted tests on 1.5mm geomembranes immersed in synthetic acid mine drainage (AMD), acidic water having pH of 2, and deionized water at 20, 40, and 60°C. The published data clearly demonstrates the nature of immersion fluid can have a significant impact on the rate of depletion of antioxidants from the geomembrane. Sangam and Rowe’s (2002) tests demonstrated that the antioxidant depletion rate was much faster in synthetic municipal solid water (MSW) leachate than in water, which in turn was much faster than in air. Rowe et al., (2008) examined the effect of the composition of synthetic MSW leachate and showed that there was only a small difference between the activation energies (62.5 and 64.0 kJ/mol) obtained for the four leachates which suggests that the OIT depletion mechanisms were very similar for the four leachates. The simplest leachate which was comprised of only trace metal solutions and surfactants in water was sufficient to simulate a MSW leachate. They also found that the volatile fatty acids and ions typically found in leachate (e.g., Na, Cl, etc) had no significant effect on the time to antioxidant depletion, while the surfactant was the primary component influencing OIT depletion. A relatively little amount of surfactant was sufficient to substantially influence the depletion of antioxidants. For a specific surfactant, Igepal® CA720, there was no further increase in depletion rate once the concentration reached 5mL surfactant per liter of water. They also observed that antioxidants were depleted at a faster rate in relatively acidic or basic immersion mediums (pH 4 and 10) than at more neutral pH (pH = 6 to 8). This is consistent with the finding of Gulec et al. (2004) that antioxidants depleted at a faster rate in acid mining drainage (AMD), followed by acidic water, and then deionized water.

The effect of thickness of the geomembrane on the depletion of antioxidants was investigated by Islam and Rowe (2007b). Three geomembranes with thicknesses of 1.5, 2.0, and 2.5mm were immersed in simulated leachate. They found that geomembrane thickness has a significant impact on the depletion of antioxidants with the thicker geomembrane giving the longest antioxidant depletion time. However, it should be noted that the antioxidant package can also significantly affect OIT depletion rates and hence the conclusion regarding the effect of thickness is only valid for otherwise similar geomembrane formulations.

Based on data for the tests on a 2mm HDPE geomembrane initiated by Sangam and Rowe (2002), Rowe and Rimal (2008b) calculated the depletion rates in water and synthetic leachate at three different temperatures (see Table 3). Also shown are the calculated values for 1.5mm geomembrane in synthetic leachate reported by Sangam and Rowe (2002). It can be clearly seen that immersion in synthetic MSW leachate results in much faster depletion than immersion in water. Comparing the results for 2mm and 1.5 mm geomembranes is more complicated because both the thickness and antioxidants are different. As a consequence at low temperatures the 1.5mm geomembrane has a longer depletion time but at a higher (50°C) temperature the benefit of the extra thickness is only slightly evident. Furthermore, samples of 2mm HDPE geomembrane have been incubated in excess of 8 years. As a consequence the geomembrane has completed Stages A, B, and C at 85°C (Rowe and Rimal, 2008b).
Table 3. Antioxidant depletion time of two geomembrane thicknesses in different exposure conditions

<table>
<thead>
<tr>
<th>GM Thickness (mm)</th>
<th>Test conditions</th>
<th>Estimated antioxidant depletion time (years) at a given temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>In water</td>
<td>95 35 15</td>
<td>Rowe and Rimal (2008a)</td>
</tr>
<tr>
<td>2.0</td>
<td>In syn. MSW leachate</td>
<td>25 10 5</td>
<td>Rowe and Rimal (2008a)</td>
</tr>
<tr>
<td>1.5</td>
<td>In syn. MSW leachate</td>
<td>35 10 4</td>
<td>Rowe and Rimal (2008b)</td>
</tr>
<tr>
<td>1.5</td>
<td>In composite liner</td>
<td>135 40 10</td>
<td>Rowe and Rimal (2008b)</td>
</tr>
</tbody>
</table>

All times greater than ten years have been rounded to nearest five years.

1 Std-OIT_o = 133 minutes; HP-OIT = 380 mins., crystallinity = 44%; based on data from Sangam and Rowe (2002)
2 Std-OIT_o = 135 minutes; HP-OIT = 660 mins, crystallinity = 49%

In the composite liner (GT/GM/geosynthetic clay liner (GCL)), noted in Table 3, where the top surface of the geomembrane was exposed to leachate while the bottom surface is exposed to the hydrated GCL, the OIT values of the geomembrane were about 2.2-4.8 times slower than for the same geomembrane immersed in the same leachate (Rowe and Rimal (2008b)). Rowe and Rimal (2008c) reported results from accelerated ageing tests on geomembranes in composite liners with three different protection layers (GT, GT/GCL and GT/1.5cm sand/GT). Leachate was present in the gravel above the protection layers. The geomembrane rested on a hydrated GCL underlain by damp sand. The OIT results indicated that the antioxidant depletion rates were dependent on the type of protection layer used. With the GT/GCL protection layer the antioxidant depleted at 59 to 66% of the rate for a GT layer alone. Also with the GT/sand/GT the depletion was 72 to 75% of that with a GT layer alone. Extrapolation of the lab tests results indicated that for the geomembrane examined and a liner temperature of 35°C, the antioxidant depletion time was highest for a geomembrane with protection layers of a GT/GCL (65 years) followed by GT/sand/GT (50 years) and lowest for GT alone (40 years). These are much longer than for the same geomembrane immersed in leachate (10 years, see Table 3). Thus, the predictions from simple immersion test in leachate were found to be extremely conservative and this type of simulation does not represent field conditions.

3.7.3. Aging in landfill simulator

In order to determine the lifetime of a geomembrane in a landfill environment, it is important to design the incubation environment of the accelerated aging test as close to field conditions as possible, i.e., simulation is important. The first incubation device used to study the oxidation of HDPE geomembrane as a landfill liner was developed by Hsuan and Koerner (1998). They modified a device suggested by Mitchell and Spanner (1985) to evaluate aging of a geomembrane under compression load, as shown in Figure 12. The geomembrane sample was a HDPE geomembrane with thickness of 1.5mm and it was sandwiched between fully saturated sand above and dry sand beneath. A 300mm head of water was maintained above the geomembrane. Using 10-to-1 mechanical advantage, a static compressive stress of 260 kPa was applied to the HDPE geomembrane sample. Four elevated temperatures, 55, 65, 75, and 85°C, were used and five devices were maintained at each of the temperatures, thus 20 devices in total. After two years of incubation, the mechanical properties of the geomembrane were still unchanged, while depletion of AOs was observed at all four temperatures. The lifetime of AOs in the geomembrane was predicted and to be 200 years at 20°C. The predicted AO lifetime is much longer than the value obtained from the geomembrane in a composite liner configuration shown in Table 3; this is probably due, in large part, to the type of liquid used in the incubation, water versus simulated leachate. Also the presence of the sand above and beneath the geomembrane likely reduced the diffusion gradient of the AOs and oxygen to and from the geomembrane. This may be the same reason that the composite liner consisted of GT/GM/GCL exhibited the longest predicted OIT depletion time than the liquid alone in Table 3.

A new incubation device, geosynthetic landfill liner simulators (GLLS’s), was developed by Brachman et al. (2008), as shown in Figure 13. The devices are capable of simulating the ageing of geomembranes under the combined effects of chemical exposure, elevated temperatures, and applied stresses. They quantified the increase in geomembrane tensile strain with increase in temperature. Experiments are currently underway to provide improved estimates of the service life of geomembranes when used as part of the barrier system in solid waste landfills.
Figure 12. Schematic diagram of incubation device (Hsuan and Koerner, 1998)

Figure 13. Cross-section view of GLLS (redrawn from Figure 1 in Brachman et al. 2008)

3.8. Oxidative degradation of polyolefin geotextiles and geogrids

As with polyolefin geomembranes (HDPE, LLDPE, and fPP), other types of polyolefin geosynthetics like geotextiles, geogrids, geonets, etc., can be degraded in a similar manner. While geomembranes are often considered the most critical, it should be mentioned that walls, slopes, and base reinforcement using these other geosynthetics are often used in the construction of critical infrastructure.

However, caution is required when thermal accelerated aging is used to evaluate the oxidation of highly oriented products such as geogrids. The incubation temperatures must be lower than the drawing temperature to prevent the distortion of the orientation in the amorphous phase which retards the onset the oxidation (Rapoport et al. (1977). Also a “thermal healing” effect was observed in some of the PP filaments by Salman et al. (1998). Furthermore, at highly elevated temperatures the diffusion rate of oxygen into the polymer is slower than the rate of oxygen consumption by the chain reactions at the polymer surface leading to faster oxidation degradation at the surface. This has the effect of protecting the inner bulk material of the polymer (Schroeder et al. 2001). The possible changes in the oxidation mechanism with temperature may lead to over prediction using constant activation energy in the Arrhenius Equation. There is growing evidence for lower activation energies at lower temperature (Ding, 2001; Gugumus, 1999). Hsuan, et al. (2008) detected a nonlinear activation energy between 45 and 105°C for a PP filament with a transition at 65°C, as shown in Figure 14.
Figure 14. Arrhenius plots for different pressures

Another concern regarding temperature accelerated oxidation is in an aqueous environment. The solubility of oxygen in water decreases with rising temperature which could introduce an error in the predicted behaviour at ambient conditions. Also the leachability of AOs increases with temperature. Therefore, the upper limit of the incubation temperature that can be used for an accelerated test has been recommended for different polymers to avoid mechanistic changes (Achimskey and Audouim, 1997). The downside of such limit is the long testing time required to reach the half-life of the test material. Polyolefin geosynthetics that are properly stabilized for long-term application can take over 10 years of incubation, even at a temperature of 80°C (Mueller and Jacob, 2002). In this regard, an alternative acceleration test with a shorter testing time is desired. The industry needs a method that delivers durability results in preferably less than about one year. Otherwise, evolution of new materials can be seriously hampered.

3.8.1. Incubation devices

Any incubation device for high pressure and/or high temperature incubation must be carefully designed for laboratory safety. There are two types of devices. Schroeder et al. (2000a) designed a stirred autoclave vessel for such tests and it has been adopted in EN ISO 13438. The vessel can sustain elevated pressure as well as being heated to the desired elevated temperature, see Figure 15. Test specimens are immersed in aqueous 0.01M NaHCO₃ adjusted to pH 10, under elevated pressure and the liquid is constantly stirred in order to stimulate the equilibration of convective transport of matter and heat. The incubation conditions can be easily modified for other environments. Hsuan and Li (2005) incubated test samples in dry oxygen gas inside pressure cells, as can be seen in Figure 16. The cells were pressurized to the desired level and then placed in a forced oven which was set at the desired test temperature.

Figure 15. Schematic view and photo of the design of autoclaves according to EN ISO 13438
3.8.2. Test data and analysis

Vink and Fontijn (2000) studied the thermal oxidation of a PP geotextile under three oxygen pressures (0.2, 0.6, and 2.1 MPa) at a constant temperature of 100°C. Based on the time to reach 40% retained tensile strength, they concluded that the oxygen pressure significantly increases the oxidation rate. Also the reciprocal oxidation rate is linearly related to the reciprocal oxygen pressure. Similar behaviour was also observed by Richaud, et al (2006) who evaluated an unstabilized PP film at 80°C and oxygen pressures from 0.02 to 5 MPa.

Schroeder, et al. (2000a) investigated the pressure effects on the oxidation of 12 types of polyolefin geosynthetics, including PP geotextiles and HDPE geogrids and HDPE geomembranes. The incubation was according to EN ISO 13438 at a temperature of 80°C under 5 MPa oxygen head pressure. The induction time (time to 80% retained strength) could be reached within 50 days for all 12 geosynthetics. In their recent paper (Schröder, et al., 2006), they propose three pragmatic models to correlate the effects of temperature and pressure with the rate of loss of tensile strength, and the three models are expressed in Eq. (21) to (23). They suggested that Model I seems to be plausible for analyzing the test data of the materials they evaluated.

**Model I:**

\[
\frac{1}{t_{50\%}} = A e^{(B+CP)/T} \]

**Model II:**

\[
\frac{1}{t_{50\%}} = A e^{B/T} \frac{P}{1 + DP} \]

**Model III:**

\[
\frac{1}{t_{50\%}} = A e^{(B+CP)/T} \frac{P}{1 + DP} \]

where \( t_{50\%} \) is half-life period (1/day); \( T \) is the absolute temperature (K); \( P \) is oxygen pressure (MPa); \( A, B, C, \) and \( D \) are constants.

Hsuan and Li (2005) and Li and Hsuan (2006) used OIT to assess the depletion of antioxidants in PP geotextiles and HDPE geogrids at temperatures from 45 to 105°C under oxygen pressures from 0.02 MPa to 6.3 MPa. They found that the antioxidant depletion rate relates to the incubation temperature and oxygen pressure according to Eq. 24 which is similar to the Model I proposed by Schröder, et al. (2000a).

\[
k = C e^{-\frac{E+\alpha P}{RT}} e^{\beta P} \]

where \( k \) is the reaction rate constant; \( E \) is the activation energy (kJ/mol); \( R \) is the universal gas constant (J/mol-K); \( T \) is the incubation temperature (K), \( P \) is the oxygen pressure (MPa), and \( \alpha \) and \( \beta \) are constants.

Based on Eq. 24, the acceleration factors for the AO depletion rate of a PP filament in terms of oxygen pressure and temperature are calculated (see Table 4). Depending on the oxygen pressure, the temperature acceleration factors range from 1.4 to 2.0 for every 10°C rise, while factors ranging from 2.7 to 3.4 can be achieved for every 2 MPa increase in oxygen pressure at different temperature.
Table 4. Acceleration factors in terms of oxygen pressure and temperature

<table>
<thead>
<tr>
<th>$P_{O_2}$ (MPa)</th>
<th>Incubation Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45</td>
</tr>
<tr>
<td>0.02</td>
<td>4.7</td>
</tr>
<tr>
<td>2</td>
<td>12.6</td>
</tr>
<tr>
<td>4</td>
<td>34.7</td>
</tr>
<tr>
<td>6</td>
<td>95</td>
</tr>
</tbody>
</table>

4. MIGRATION OF PLASTICIZERS FROM PVC GEOMEMBRANES

As indicated in Table 1, the p-PVC geomembrane contains 25 to 35% of plasticizers to lower the glass transition temperature and increase its flexibility. The p-PVC geomembrane is susceptible to two processes: (a) desorption of plasticizer and/or sorption of water, and (b) dehydrochlorination (elimination of hydrogen chloride, $HCl$) and oxidation (Gumarglieva, et al., 1996). These two processes may occur simultaneously or separately during the material’s service life. Dehydrochlorination mainly occurs when PVC is subjected to ultraviolet degradation. The mechanism involves the release of gaseous HCl as well as forming conjugated double-bond-containing sequences (polynes) in the polymer chain, as illustrated in Eq. 25. The polynes are highly reactive in absorbing light in the UV and visible regions, resulting in discoloration. In addition, polynes react with oxygen yielding carbonyl products, leading to chain scission and crosslinking in the polymer. Stabilizers are added to the PVC resin to suppress the dehydrochlorination and oxidation reactions (Bacaloglu and Fisch, 1995; Iván, 1996).

\[-CH_2-CHCl-CH_2-CHCl- + h\nu \rightarrow -CH = CH = CH + HCl\]  (25)

where “$-CH_2-CHCl-CH_2-CHCl-$” is the PVC polymer chain; “$h\nu$” is the photon energy, with “$h$” representing Planck’s constant and “$\nu$” representing speed of light divided by wavelength ($c/\lambda$), respectively; “$-CH=CH-CH=CH-$” is the polylene with conjugated double bond and “$HCl$” is hydrogen chloride.

For p-PVC geomembranes that are not exposed to sunlight during their service life, the dehydrochlorination reaction proceeds much slower than the migration of plasticizers. Many case studies on the long-term performance of p-PVC geomembranes have been focused on the loss of plasticizers (Giroud, 1984; Morrison and Starbuck, 1984; Miller, et al. 1991; Hammond, et al. 1993)

4.1. Plasticizers

Plasticizers play an important role in the short- and long-term properties of p-PVC geomembrane. There is a large variety of plasticizers. Rahman and Brazel (2004) present a detailed review of the development of plasticizers. The most common type of plasticizers is the phthalates (92%) in which diisodecyl phthalate (DEHP) accounts for 51% of the phthalates (Murphy, 2001). The major benefits of this plasticizer are its low volatile property at ambient conditions and low cost. The phthalate plasticizers are chemically attracted to the PVC polymer by polarizable benzene nuclei, while the linear portion of the molecules (e.g., disubstituted alkyl esters) affects the volatility and processing. The interactions of plasticizers within p-PVC geomembrane are governed by the properties of the plasticizers which include chemical structure, molecular weight, and functional groups. Plasticizers with shorter chains are easier to process and generally produce products with a higher flexibility; however, they are more volatile than those with longer chains. Other material properties that are considered when choosing the plasticizers for a product include:

- desired thermal and mechanical properties,
- resistance to water, chemicals, UV radiation, microorganisms, and
- volume-cost analysis

The loss of plasticizers can be through leaching and/or migration. In the leaching process, plasticizers are extracted by the surrounding liquid, while migration refers to plasticizers diffusing to the surface of polymer and then dissolving into the surrounding liquid or gas environment. Properties controlling the migration include molecular weight, linearity, and polarity of the plasticizers. Stark et al. (2005) compile a list of commercially available plasticizers and their migration properties. For plasticizers with similar chemical structures, the volatility and diffusion coefficient decreases as molecular weight increases, see Figure 17. The volatility is much more sensitive to the molecular weight of the plasticizer than is water extraction. They also indicate that branched plasticizers exhibited lower migration into an adjacent liquid than linear plasticizers, but they are more volatile than linear plasticizers.

As plasticizers leave the polymer, the flexibility of the p-PVC geomembrane starts to decrease while the density starts to increase. Figure 18 shows the drastic difference in tensile behavior of a p-PVC geomembrane after loss 40% of the plasticizers. The geomembrane no longer behaves as a flexible elastomer but exhibits a pronounced yielding behavior similar to a semi-crystalline material (Miller, et al. 1991). Furthermore, the loss of plasticizers also leads to volume reduction in geomembrane, inducing shrinkage stress that can lead to cracking in p-PVC geomembranes.
4.2. Laboratory study on the aging of p-PVC geomembrane

The large variety of available plasticizers used in any particular formulation is quite a challenge for the evaluation of the long-term performance of p-PVC geomembrane. Instead of performing forensic tests to identify the type and amount of each of the plasticizers, laboratory aging studies generally assess the migration of the plasticizers under an accelerated environment. Frassi ne (2005) and Cazzuffi (2007) performed such an aging study on a p-PVC geomembrane. Samples of 2mm thick p-PVC geomembrane were subjected to ageing in ovens at temperatures of 65°C, 80°C, and 95°C. They were subsequently tested after different incubation times (1, 2, 4, 8, 16, 32 and 96 weeks) to obtain test data required for input of the Arrhenius modelling to predict the lifetime of the geomembrane. These three temperatures were chosen to satisfy the following conditions:

- To be sufficiently different in temperature so as to clearly define variations in properties.
- To be sufficiently high in temperature to observe variations in properties within a reasonable experimental time scale.

Such elevated incubation temperatures accelerate changes in physical properties of the p-PVC geomembrane, particularly the rate of plasticizer loss due to diffusion and the hardening of the material. However, one must also recognize that these elevated temperatures might negatively bias the data in that they are well beyond actual service temperatures. This is a serious consideration and one must always be careful in accelerated aging evaluation of this type.

4.2.1. Analytical tests and data

Four tests were performed on the above mentioned aged samples after different incubation times to assess property changes in the geomembrane.

- The nominal thickness. The thickness was measured according to ASTM D5199 and there were no significant changes under these three elevated temperatures.

- Cold bending. The test method, UNI 8202-15, was used to assess the cold temperature property of the p-PVC geomembrane. A noticeable change in this property was observed at 95°C after 8-weeks of incubation.
• **Plasticizer content.** The plasticizer content of the p-PVC geomembrane was determined according to ISO 6427 using the Soxhlet extraction process. Figure 19 shows that the plasticizer content remained relatively constant for samples aged at 65°C and decreased somewhat at 80°C after 700 days. At 95°C, 40% loss in the plasticizer was detected after 700 days.

![Plasticizer content of the p-PVC geomembrane after aged at different elevated temperatures](image)

**Figure 19.** Plasticizer content of the p-PVC geomembrane after aged at different elevated temperatures

• **Tensile test.** Tensile properties of the p-PVC geomembrane were evaluated using ASTM D638, Type IV. The tensile strength and tensile break elongation of the geomembrane were recorded and analyzed. Figure 20 shows that there is a continuously increase in the tensile strength at all three incubation temperatures. In contrast, the tensile break elongation decreases as aging time increases; see Figure 21.

![Tensile stress of p-PVC geomembrane at difference temperatures](image)

**Figure 20.** Machine direction tensile stress of p-PVC geomembrane at difference temperatures

![Tensile break elongation](image)

**Figure 21.** Machine direction tensile break elongation of p-PVC geomembrane at difference temperatures

4.2.2. **Predicting the lifetime of p-PVC geomembrane**

The Arrhenius equation (Eq. 20) was used to predict reaction rates at lower site specific temperatures by extrapolating the reaction rates at higher laboratory incubated temperatures. Since there is no significant decrease in the plasticizers content at 65 and 80°C after 700 days of incubation, the two mechanical properties just presented are used to analyze the activation energy. The Arrhenius plots are shown in Figure 22, and the average activation energy is 42 kJ/mol.
Field samples of p-PVC geomembrane were retrieved from the upstream face of the Camposecco dam located in Northern Italy after 5 and 10 years of in-situ service. Figure 23 shows a photograph of the dam facing and cross-section of the dam (Cazzuffi, 1998). The retrieved field samples were tested for their tensile properties. The average maximum and minimum field temperatures of p-PVC geomembrane on dams located in Northern Italy are listed in Table 5. An average temperature of 12°C is adopted as the field temperature to be used in the Arrhenius prediction.

The long-term behaviour of the p-PVC geomembrane on the facing of the Camposecco dam was predicted based on the decrease of break elongation with time, as illustrated in Figure 24. The straight line through the test data was constructed based on the average activation energy (42 kJ/mol) obtained from the laboratory accelerated aging tests, as illustrated in Eq. 26. The predicted curve at 12°C matches reasonable well with data obtained from the field samples taken below the water level. The predicted time to reach 50% reduction in tensile break elongation will take about 100 years at 12°C field temperature below the water level. However, for field samples taken above the water level, the greater reduction in the break elongation with time is due to the ultraviolet effects on the p-PVC geomembrane that was not included in the oven aging.

\[
\ln\left(\frac{R_{95oC}}{R_{12oC}}\right) = \frac{E}{R} \left( \frac{1}{T_{12oC}} - \frac{1}{T_{95oC}} \right) = 5080 \times (0.00351 - 0.002717) \quad (26)
\]

The break elongation (%) decreasing rates:
\[ R_{95oC} = 0.14 \text{ /day from lab data} \quad R_{12oC} = 0.0025 \text{ /day} \]

| Table 5. Representative site temperature for p-PVC geomembrane on dams in Northern Italy |
|-----------------------------------|---------------------------------|
|                                   | Above water level | Below water level |
| Maximum temperature               | + 45°C            | + 20°C            |
| Minimum temperature               | - 20°C            | + 4°C             |
Figure 24. Prediction on the decrease of tensile break elongation of p-PVC geomembrane on the facing of the Camposecco dam

Studies like this are extremely important for geosynthetics serving critical functions like waterproofing of dams. It should be recognized, however, that such lifetime prediction is only for the particular formulation that has been evaluated. Transferability of results to other formulations is neither realistic nor appropriate.

5. HYDROLYSIS OF PET GEOTEXTILES AND GEOGRIDS

PET filament and straps are used in a significant number of geotextiles and geogrids. There are several methods to synthesize PET resin using different monomers and/or catalysts. The principle of condensation polymerization to produce PET is expressed in Eq. 27. Products on the market may differ in their additives, and also some impurities and by-products, e.g. diethylene glycol content or modifying components like phthalic acid or other dialcohols, which may have impact on the material’s sensitivity to hydrolysis and other long-term properties, such as oxidation and stress rupture.

\[
\frac{n(HOOC - \phi - COOH) + n(HOCH_2CH_2OH)}{\text{terephthalate acid}} \rightleftharpoons \frac{HO[\text{\(\text{-OC} - \phi - COOCH_2CH_2O\text{-}\)\_n]H + nH_2O}}{\text{ethylene glycol}} \rightleftharpoons \frac{\text{PET}}{\text{water}}
\]

where \(\phi = \text{benzene ring}\)

Since Eq. 27 is a reversible reaction, PET can react with water and revert to compounds with carboxyl (–COOH) or hydroxide (–OH) end groups. This reverse reaction is the hydrolytic reaction which leads to a decrease in molecular weight. There are two types of hydrolytic reactions which run independent of each other. The first kind is often called inner hydrolysis, since it takes place mainly inside the PET product. Inner hydrolysis depends on the presence of water molecules in the PET-product. Thus, even the surrounding medium does not contain water, the presence of water vapour is sufficient to start the reaction. The inner hydrolytic reaction is catalyzed by protons attacking the ester oxygen bond thereby favouring the release of ester alcohol. Thus, cooperation with the simultaneous attack of water-oxygen on the neighbouring carbon atom free acid is formed, as shown in Eq. 28. The availability of protons inside the product is tightly coupled to the presence of carboxyl end groups (CEG) in the polymer if no other permeating acids are present.

For \(\text{pH} \leq 7\), a hydrolysis reaction forms at the end of a polymer chain

\[
\frac{[\text{\(\text{-OC} - \phi - COOCH_2CH_2O\text{-}\)\_n]}H + nH_2O}{\text{PET}} \rightleftharpoons \frac{\text{water}}{\text{terephthalate}} \rightleftharpoons \frac{\text{ethylene glycol}}{\text{-OH}^-}
\]

The second kind of PET-hydrolysis is often called outer or alkaline hydrolysis, since it is a surface reaction leading to pits and holes on the surface. It only takes place in contact of the PET-product to alkaline liquids, as expressed in Eq. 29. The attacking molecular species are \(\text{OH}^-\) anions, which are not able to permeate into the inner PET bulk phase themselves and do not form permeating ion pairs.

For \(\text{pH} > 7\) a reaction within a polymer forms:

\[
\frac{[\text{\(\text{-OC} - \phi - COOCH_2CH_2O\text{-}\)\_n]}2\text{OH}^-}{\text{PET}} \rightleftharpoons \frac{\text{water}}{\text{terephthalate}} \rightleftharpoons \frac{\text{ethylene glycol}}{\text{\(\text{-OC} - \phi - COO^-\)\_n}} + \frac{\text{HO[\text{-CH_2CH_2OOC} - \phi - \text{CO}^-\)]}{\text{water}}
\]
5.1. Material effects on PET’s hydrolysis

The hydrolysis of PET is strongly affected by the chemical and physical structure of the polymeric product. From a chemical aspect, carboxyl end groups (CEG) in the polymer are the most important factors, but comonomers or other chemical modifications, additives and impurities may also be relevant (Zimmermann, 1984). From the physical aspect, molecular weight, and morphology (crystallinity, orientation) can influence the rate of hydrolytic reaction. The reaction is occurring mainly in the amorphous regions.

- **Carboxyl end group.** CEG (−COOH) or hydroxyl groups (−OH) normally are positioned at the end of the PET molecular chain. If each polymer chain contains just one carboxyl end group then the reciprocal of CEG is equal to number average molecular weight $M_n$. The relative concentration of end groups depends on the polymerization process and further chemical treatment. Ravens and Ward (1961) found that the rate of hydrolytic reaction is proportional to the square root of the CEG concentration in neutral water (pH = 7).

- **Molecular weight.** The molecular weight may be directly related to the concentration of CEG as just mentioned. Polymers with high molecular weight contain less CEGs than lower molecular weight polymers. Sprague (1990) found that a PET geotextile with a lower molecular weight degraded faster than one with a high molecular weight in a calcium hydroxide solution at 50°C. Thus it seems to hold for both types of hydrolytic reactions.

- **Morphology.** In neutral and acidic environments, the rate of hydrolytic reaction is based on the diffusion of water into the amorphous phase where the reaction takes place (Golike and Lasoski, 1960; Ballara and Verdu, 1989). For oriented products, such as fibres, the free volume in the amorphous phase of the polymer decreases as orientation increases. McMahon et al. (1959) found that the rate of hydrolysis of oriented PET fibers is much lower than that of films. Therefore, the orientation and crystallinity of PET geosynthetics has a substantial impact on the rate of hydrolysis.

5.2. Evaluation of hydrolytic behaviour of PET geotextiles and geogrids

The chemical degradation of PET geotextiles is associated with the durability behaviour of PET geotextiles in natural soils, which normally range in pH between 4 and 9. Under such soil conditions inner hydrolysis is observed by many researchers (Jailloux, 1996; Schmidt, 1994; Schröder, 1999; Burgoyne, 2007). The standard EN 12447 is an index test to assess PET geotextiles with an expected service lifetime of 25 years. The standard requires the residual tensile strength to be at least 50% after test specimens are immersed in distilled water at 95°C for 28 days. At such high temperature, the material is clearly above its $T_g$, so the product properties may be changed by physical effects, leading to a hydrolytic behaviour different than that in the soil regime. Caution must be applied when interpreting the result of such a short-term test with respect the long-term performance of geotextiles in soil. The kinetics of the hydrolytic reaction of PET in soil which is saturated with water or water vapour is governed by the chemical reaction rate. Since the activation energy of diffusion of water into PET is generally lower than the activation energy of inner hydrolysis, a diffusion limited inner hydrolysis has to be avoided at the high testing temperatures. This change in kinetics is seen by a change of the slope in the respective Arrhenius curve and can easily be avoided by appropriate choice of the temperature range. Another issue that may arise from the high temperature testing is the slow re-crystallization of PET, leading to an increase of tensile strength. Also, the effect of crossing the glass transition temperature ($T_g$) is often neglected, though the impact on extrapolation results is not fully understood.

Some of the test considerations for the hydrolysis test of PET yarns and straps in the laboratory are described as follows:

- **Test specimen preparation.** Test specimens should be cleaned before testing to remove manufacturing processing residuals. Specimens can be dipped into a special solvent in agreement with the manufacturer or just hot water (<50°C) to remove water soluble substances on the surfaces.

- **Test specimen configuration.** For a long-term hydrolytic test of reinforcing PET geotextiles, Schmidt, et al. (1994) suggested to fix the length of the test yarn by winding the yarn around a glass cylinder so that morphological changes at elevated test temperatures can be avoided. This technique was further improved by Schröder (2000), who proposed a simple technique to wind the yarns under constant tension on cylindrical spools manufactured from high grade steel wire mesh, as illustrated in Figure 25.

![Figure 25. Incubation design for PET yarn under fixed length](image-url)
For strap geogrids, the test specimen is also recommended for the same reasons to be tested under conditions of fixed length (relaxation clamps). The primary hydrolytic risk of these materials may arise from junctions which are welded by different methods. At least for biaxial loading a certain tendency to splitting of the straps has to be of concern. Tests for evaluation of the hydrolytic resistance of this style of geogrids are currently ongoing at BAM in Germany.

- Incubation environment. Hydrolysis tests should be performed in a water container equipped with a stirring device at an elevated temperature. The water level in the container must be maintained constant by either a reflux condenser or a water leveller to replenish the lost of evaporated water. Incubation usually requires test series at three to four temperatures so that the test data can be analyzed by the Arrhenius equation (recall Eq. 20). For the evaluation of inner hydrolysis, the liquid can be either deionized water with $4 < \text{pH} < 7$ or an aqueous liquid adapted to the special application. However, Schroeder et al. (2000) pointed out that anions and protons of some strong acids, e.g. sulphuric acid, are generally unable to permeate PET-materials due to the low dielectric constant of PET; hence experiments on inner hydrolysis of geotextiles for low acid concentrations can be conducted in pure water in this case. For outer hydrolysis, liquid with $\text{pH} > 9$ can be used. However, the hydrolysis is governed by both hydroxyl-ions and to a certain degree by cations in the liquid. Figure 26 shows the influence of cations on the tensile strength of PET yarns.

![Figure 26. Different cations influence in chlorides at 0.01 mol on the tensile strength retained of PET yarns after 28 days, at 60°C in a solution containing 0.01 mol NaOH.](image)

### 5.3 Tests for evaluation of hydrolysis of incubated samples

The progress of hydrolysis of incubated PET geosynthetics is commonly monitored by the tensile properties which can be used to predict the long-term field performance of the product, particularly for reinforcement applications.

However, in some cases tensile properties may not be obtainable from retrieved field samples which have been damaged mechanically. Therefore, other material properties that can be correlated to the tensile properties of PET geosynthetics would be beneficial. CEG and molecular weight (or solution viscosity) have been used by some researchers to assess the extent of the hydrolysis in PET geosynthetics (Schoeder, 2005; Elias, et al. 1999; Weidner 1996, 1997; Schmidt, 1994; Merii, 1992). Elias, et al. (1999) observed that the tensile strength decreased with molecular weight while CEG increased. However, to quantitatively correlating changes of tensile strength to molecular weight and CEG may not be easily established, since other parameters like morphology are involved.

### 5.4 Hydrolysis test results and prediction

Laboratory tests have been performed by Elias, et al. (1999) and Schroeder, et al. (2000b) to assess the hydrolysis of different types of PET yarns. The Arrhenius equation was used in both studies to predict the service lifetime at the site-specific lower temperature using test data obtained at elevated temperatures. Table 6 shows the predicted years that would take three PET geosynthetics reaching 50% tensile strength at $20^\circ \text{C}$ in four different pH environments (Elias, et al., 1999). Schroeder, et al. (2000b) used CEG and/or tensile strength to assess the hydrolytic resistance of five PET geosynthetics. Table 7 shows the predicted years for the five tested materials reaching 10% increase in CEG and 50% drop in tensile strength. In these eight PET geosynthetics, the nonwoven geotextile (P-5) with the highest CEGs and relatively low molecular weight exhibited the greatest hydrolytic degradation, particularly at the high pH solution. On the other hand, samples with CEG less than 30 μeq/g will take more than 100 years for the tensile strength to lower to 50% in an alkaline environment with pH of 10. Hsuan and Koerner (2005) evaluated the hydrolytic resistance of eight PET yarns with CEG ranging from 10 to 31. They found that the retained tensile strength after 48 months of incubation in water at $65^\circ \text{C}$ decreases linearly as the initial CEG value increases. Samples with similar CEG values exhibit similar retained tensile strength values. In contrast to these results no unequivocal relationship of CEG and durability at ambient temperatures was found in the five geosynthetic products evaluated by Schroeder et al. (2000b).
The current specification of US Federal Highway Association (FHWA) requires PET geogrids to have CEG less than 30 \( \mu \text{eq/g} \) and number average molecular weight \( (M_n) \) greater than 25,000 g/mol evaluated by GRI-GG7 and GRI-GG8, respectively. In Europe, the approval of reinforcing geosynthetics differs from country to country. It is the common view that the hydrolysis tests should be carried out at three or four appropriate temperatures, ideally below \( T_g \), and the test data should be analyzed by the Arrhenius equation as given in ISO/TS 13434:2007(E). Such test can assess the performance of final product, i.e. including effects of additives, morphology, chemical modifications, by-products, and impurities.

### Table 6. Predicted time (years) for tensile strength to decrease to 50% at 20°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Tensile Strength (kg/mm)</th>
<th>CEG ((\mu \text{eq/g}))</th>
<th>(M_n) ((x10^3))</th>
<th>(\text{H}_2\text{SO}_4) pH = 1</th>
<th>(\text{H}_2\text{O}) pH = 7</th>
<th>(\text{NaOH}) pH = 10</th>
<th>(\text{NaOH}) pH = 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-5</td>
<td>Nonwoven fabric, 540 g/m²</td>
<td>3.7</td>
<td>45-49</td>
<td>18.2</td>
<td>50</td>
<td>161</td>
<td>65</td>
<td>2</td>
</tr>
<tr>
<td>P-6</td>
<td>PVC coated geogrid</td>
<td>18.7</td>
<td>19</td>
<td>30.2</td>
<td>71</td>
<td>1000</td>
<td>294</td>
<td>31</td>
</tr>
<tr>
<td>P-7</td>
<td>Woven fabric</td>
<td>9</td>
<td>18</td>
<td>30.6</td>
<td>238</td>
<td>625</td>
<td>143</td>
<td>12.2</td>
</tr>
</tbody>
</table>

CEG = carboxyl end group

### Table 7. Predicted time (years) for 10% increase in CEG and 50% decrease in tensile strength at 20°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Tensile Strength (N)</th>
<th>CEG ((\mu \text{eq/g}))</th>
<th>DEG %(g/g)</th>
<th>(\text{H}_2\text{O}) pH = 7 (10% CEG)*</th>
<th>Gypsum Solution pH = 10 (50% Strength)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-1</td>
<td>multifilament yarn 1100 dtex, Z 130</td>
<td>80</td>
<td>27.8</td>
<td>0.96</td>
<td>702</td>
<td>871</td>
</tr>
<tr>
<td>Y-2</td>
<td>multifilament yarn 1100 dtex, Z 60</td>
<td>85</td>
<td>12.9</td>
<td>1.09</td>
<td>324</td>
<td>351</td>
</tr>
<tr>
<td>Y-3</td>
<td>multifilament yarn 1100 dtex, F 210</td>
<td>81</td>
<td>25.6</td>
<td>0.86</td>
<td>676</td>
<td>235</td>
</tr>
<tr>
<td>GR1</td>
<td>Single strand of PVC coated geogrid 900 at 70°C</td>
<td>900</td>
<td>24.7</td>
<td>0.85</td>
<td>246</td>
<td></td>
</tr>
<tr>
<td>NW1</td>
<td>Nonwoven fabric 200-300 g/m² 55 dN per 100g/m²</td>
<td>24</td>
<td>0.89</td>
<td>243</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* increase in 10% CEG
** decrease in tensile strength

CEG = carboxyl end group which can be correlated to the molecular weight.

DEG = Di-ethylenglycol-groups which is related to oxidative durability of PET

### 6. EXPOSED WEATHERING OF GEOSYNTHETICS

An added aspect of degradation for exposed geosynthetics is the effect of ultraviolet (UV) light. To greatly varying degrees all polymers are susceptible to sunlight degradation. Within the sunlight spectrum, the energy of the penetrating UV light is sufficient to break chemical bonds within the polymers, with the shorter wavelengths being more severe. Table 8 shows the wavelengths or wavelength ranges that cause photo-degradation of the four types of polymers commonly used in geosynthetics.

### Table 8. Wavelengths for commonly used polymers in geosynthetics

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>330-360^1</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>335-360^2</td>
</tr>
<tr>
<td>Polyvinyl chloride (PVC)</td>
<td>320^3</td>
</tr>
<tr>
<td>Polyethylene terephthalate (PET)</td>
<td>325^4</td>
</tr>
</tbody>
</table>

^1 Hu (1997); ^2 Zhang et al., (1996); ^3 Hirt and Searle (1964)

### 6.1. Photo-degradation mechanisms

The photo-degradation mechanisms of the above four polymers used in geosynthetics are briefly described below:

#### 6.1.1. Polyethylene and Polypropylene (polyolefins)

UV degradation of polyethylene (PE) and polypropylene (PP) is controlled by photo-oxidation via a series of free radical reactions that were shown in Eq. 1 to 3 in the previous section. The energy source in this case is provided by the photon energy which is proportional to the inverse of wavelength. Also the energy required to generate free
radicals in polyolefins is lower than that to breaking a bond; subsequently polyolefins are more susceptible to UV
degradation than other types of polymers.

Appropriate UV stabilization is required for exposed polyolefin geosynthetics. CB is an effective UV absorber or
blocker, and the absorbing efficiency increases as particle size decreases (Cabot, 1990). The particle size of CB used
for UV protection of polyolefin geosynthetics is typically in the range of 22 to 25 nm. Also HALS is a specific group
of antioxidants designed for UV stabilization. The UV degradation of unstabilized and HALS-stabilized polyethylene
and polypropylene has been studied by Gijsman et al. (1994) and Gijsman and Dozeman (1996).

6.1.2. Plasticized Polyvinyl Chloride (p-PVC)
As expressed in Eq. 25, the principle UV degradation mechanism in PVC involves zip-elimination of HCl. The
copolyens are highly reactive in absorbing light in the UV and visible regions, resulting in discoloration and oxidation
degradation. In p-PVC, the plasticizers are also highly susceptible to UV degradation due to their relatively low
molecular weight. Antioxidants are added to suppress the zip-elimination and oxidation reactions (Bacaloglu and

6.1.3. Polyethylene terephthalate (PET)
PET undergoes chain scission forming carboxyl groups from UV exposure at the wavelength indicated in Table 8. Antioxidants are not commonly incorporated into the formulation for PET products since they are less susceptible to
oxidation than other three polymers. Also geosynthetic products made from PET are mainly geotextiles and geogrids
which are generally covered by soil in the majority of applications.

6.2. Exposure methods for weathering resistance
There are two approaches to study the weathering effects on geosynthetics: outdoor natural exposure and exposure in
laboratory weatherometers. Suits and Hsuan (2003) described the commonly used exposure methods in the US. They are summarized as follows:

6.2.1. Outdoor natural exposure methods
This is the most straightforward exposure assuming that time permits. The geosynthetic samples are exposed at a
particular site, according to the guideline provided by ASTM D5970. Due to the variability of the climate from site-
to-site, test data are only applicable for that specific site. Recording the total solar radiant energy and solar UV radiant
energy would be beneficial for potential comparison. However, the effects of temperature, moisture, and the local
environment must also be incorporated into the comparison.

The long testing time of the natural exposure method is often not practical for materials like geomembranes. An
alternative accelerated weathering method uses the Fresnel Solar Concentrator (FSC) exposure technique which
concentrates natural sunlight via specially coated mirrors onto the sample with an intensity of approximately eight
times that of natural sunlight radiation (ASTM G90). Together with other instrumentation necessary to collect the
climatic data, the FSC is an expensive process, and the test is limited to two sites, Arizona and Southern Florida.

6.2.2. Laboratory Weatherometers
Laboratory weatherometers accelerate sunlight degradation in a controlled environment so that more consistent
results can be generated in comparison to outdoor exposure methods. Xenon arc and Ultraviolet (UV)-Fluorescent
Weatherometers are currently used to evaluate the UV degradation of geosynthetics.

- **Xenon arc weatherometer.** This weatherometer generates a solar light irradiance spectrum closely resembling
  natural daylight. In the US, the federal transportation specifications (AASHTO M288) requires geotextiles to
  have 70% retained strength after exposed to 500 hours in a Xenon weatherometer according ASTM D 4355.
  However, a greater than 20% difference in tensile strength retained was found by Searle and Sandri (2001)
  who analyzed the Xenon weathering test results of two nonwoven geotextiles between two laboratories. This
  suggests that the 70% retained strength requirement may be too high for certain types of nonwoven
  geotextiles.

- **UV-fluorescent weatherometer.** The light source of this device only emits a spectrum in the UV region. The
device uses fluorescent lamps targeting different UV light ranges. The UVA-340 lamps generates light
  spectrum from 300 to 400 nm with the maximum peak at 340 nm. In the US, the test is performed according
  to ASTM D 7238 for polyolefin geomembranes. A European standard, EN 12224, for determination the weathering resistance of geotextiles and geotextile-
related produced is also established using a similar weatherometer. The test conditions of these two methods
  are compared in Table 9. The less aggressive conditions used in EN 12224 targets at the GT exposure. The
  European standard also includes a recommendation on the exposure duration which is the time to reach
cumulated energy of 50 MJ/m².
Table 9. Test conditions of ASTM D 7238 and EN 12224 in UV-fluorescent weatherometers

<table>
<thead>
<tr>
<th>Standard (test material)</th>
<th>Irradiance</th>
<th>Dry Cycle</th>
<th>Wet Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature (°C)</td>
<td>Duration (hr)</td>
</tr>
<tr>
<td>EN 12224 (geotextiles)</td>
<td>25.1 W/m² from 320 to 360 nm*</td>
<td>50 ± 3</td>
<td>5</td>
</tr>
<tr>
<td>ASTM D7238 (geomembranes)</td>
<td>0.78 W/m² at 340 nm</td>
<td>75 ± 3</td>
<td>20</td>
</tr>
</tbody>
</table>

* 25.1 W/m² is the accumulated UV irradiance of the entire test duration.

It should be mentioned that for exposed geosynthetic lifetime prediction, incubation times in laboratory weatherometers are extremely long. Often times exceeding five years are necessary depending on the test material, temperature, and UV settings. As such, initial and maintenance costs must be considered. Table 10 shows the costs associated with Xenon and UV-fluorescent devices. Before beginning an exposed lifetime prediction study the choice of the weatherometer should be carefully considered by the parties involved.

Table 10. Comparing costs of Xenon arc and UV-fluorescent weatherometers

<table>
<thead>
<tr>
<th>Item</th>
<th>Xenon</th>
<th>UV-fluorescent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Machine cost</td>
<td>$70-80,000</td>
<td>$10-15,000</td>
</tr>
<tr>
<td>Filter and light source costs</td>
<td>$15,000/year</td>
<td>$300/year</td>
</tr>
<tr>
<td>Power supply costs</td>
<td>$5,000/year</td>
<td>$400/year</td>
</tr>
<tr>
<td>Cooling water costs</td>
<td>$3,000/year</td>
<td>negligible</td>
</tr>
<tr>
<td>Sewer costs</td>
<td>$1,500/year</td>
<td>none</td>
</tr>
</tbody>
</table>

6.3. Correlation of test data between outdoor and weatherometer exposure of geosynthetics

There are very few publications on the correlation between accelerated laboratory weathering tests and outdoor weathering of geosynthetics. The challenge of such correlation lies in the changes of outdoor environment (UV and total solar irradiance, temperature, and humidity) which must be carefully recorded. As such, the correlation is generally assumed to be approximate.

Comer et al., (1998) evaluated the weathering resistance of an experimentally formulated t-PP geomembrane in the UV-Fluorescent weatherometer and exposed in El Paso, Texas. An acceleration factor of 2.6 was obtained by comparing the duration to reach 50% reduction in tensile strength between the weatherometer and outdoors. Baker (1997) correlated the sunlight degradation of three geotextiles by exposing them in a Xenon weatherometer and South Florida outdoor site according to Eq. 30. He cautioned that the large temperature difference between outdoors and the weatherometer was not incorporated into the correlation.

$$ SR = 100 \cdot e^{-af} \tag{30} $$

Where: $SR$ is strength retained (%), $a$ is constant, (material and formulation dependent), and $I$ is total UV radiant of the test (MJ/m²)

The temperature factor also played an important role in a comparison study performed by Koerner, et al., (1998). They compared the weather resistance of seven geotextiles between outdoors (at three sites) and two types of weatherometers (Xenon Arc and UV-fluorescent). By comparing the total UV radiant (TUVR) in MJ/m² to reach 50% tensile strength retained, the energy generated from two weatherometers is much lower than the natural exposure. The accelerated degradation may be partly contributed by the elevated temperatures used in the weatherometers. Most recently, Koerner, et al. (2008) suggested to superimpose temperature into the weathering test so that the temperature effect on the UV degradation can be properly analyzed.

7. LONG-TERM MECHANICAL PERFORMANCE OF GEOSYNTHETICS

For geosynthetics that are subjected to tensile stress during their service lifetime, stress crack resistance (SCR) and creep are two important long-term mechanical properties that should be evaluated carefully. Stress cracking is likely to occur in geosynthetics made from high and medium density polyethylene, while creep deformation or creep rupture can occur in all types of geosynthetics.

7.1. Stress cracking of polyethylene

According to ASTM D 883 “Stress cracking is defined as “an external or internal rupture in a plastic caused by tensile stress less than its short-term mechanical strength.” The phenomenon can occur in crystalline polymers by breaking the interlamellar tie molecules in the amorphous phase (Keith et al., 1971; Lustiger, 1983; Lustiger and Rosenberg, 1988). The number of tie molecules increases with molecular weight, but decreases as the crystallinity increases. Due to the simplicity of its molecular structure, polyethylene can achieve higher crystallinity than other polymers. Thus, geosynthetics made from HDPE and MDPE are more susceptible to stress cracking than products...
made from other polymers. The premature brittle cracking of HDPE products has led to intensive research in the 1980s for HDPE pressure pipes, 1990 for HDPE geomembranes, and recently for HDPE corrugated pipes (Williams, 1987, Hsuan, 1998, Hsuan et al. 2007). Specific tests have been developed and requirements have been implemented for pressure pipes and geomembranes. As a result, new resins with enhanced stress crack resistance (SCR) properties have been developed, and stress cracking in HDPE pressure pipes and geomembranes can be avoided when products are properly specified and formulated accordingly.

7.1.1. Measuring SCR of HDPE geomembranes

A standard test to evaluate SCR of geomembranes was introduced in the 90’s and adopted as ASTM D 5397, the Notched Constant Tensile Load (NCTL) test. The test measures failure times of notched specimens at different applied loads in a liquid environment of 10% Igepal/90% water at 50°C (Hsuan and Koerner, 1995). The test conditions (notching, elevated temperature, and Igepal solution) are specially designed to accelerate crack initiation and propagation. Because of the acceleration property of the Igepal solution on crack propagation, this test is also referred to as the environmental stress cracking test.

The resulting behaviour trend, shown in Figure 27, is obtained by plotting applied stress versus failure time on a log-log scale to generate a ductile-to-brittle curve from which the transition time \( T_t \) and transition stress \( T_\sigma \) are obtained. Materials with low transition stress and long transition time, particularly the latter, indicate a high SCR. A particular value has been set for the transition time to specify SCR of PE geomembranes.

![Figure 27. Ductile-to-brittle transition curve resulting from the NCTL test](image)

7.1.2. Specification of SCR of HDPE geomembranes

In the early 90’s, investigation was carried out to assess the stress cracking behaviour of HDPE geomembranes in the field. Field samples from 16 sites were examined, and NCTL tests were performed on samples from 10 sites where stress cracking had been observed. Based on the resulting test data, a transition time of 100 hours at a transition stress of 35% yield stress was specified to ensure SCR of HDPE geomembranes (Hsuan, 2000).

However, identifying the transition time from the ductile-to-brittle curve requires a minimum of ten applied stresses. The total testing time may be well over 1,000 hours which is too long for a quality control (QC) test. Subsequently, a single point (SP-NCTL) version of the test was developed and is included in ASTM D 5397 as an Appendix. The concept is to select a stress level near, but slightly lower than the transition stress, and specifying the minimum failure time at that stress. By incorporating the slopes of brittle curves obtained from testing 10 field samples, a minimum failure time of 200 hours at 30% yield stress was specified to be the requirement of the SP-NCTL test for HDPE geomembranes. This value has been incorporated into the GRI-GM13 “Specification for HDPE Geomembranes” in 1997. In 2003, the specification was revised by increasing the minimum failure time from 200 hours to 300 hours to further enhance SCR of HDPE geomembranes. There has been no reported stress cracking failure since that time.

7.1.3. Prediction failure time of stress cracking in HDPE geomembrane

The SP-NCTL test is an index QC test to assess the SCR property of a geomembrane under a specific accelerated condition. The specified failure time in GRI-GM13 does not imply the time it takes for a crack to propagate through the thickness of the geomembrane. To predict the stress crack failure time of a HDPE geomembrane in a specific field condition, the test should be performed according to the following guidelines:

- The test should be performed on either un-notched geomembrane specimens or geomembrane seam specimens.
- The test solution should be the same liquid that the geomembrane will be encountered during its service lifetime.
- Tests should be carried out at minimum of two different elevated temperatures between 60 and 80°C.
- A minimum of two applied stresses that are less than 30% of yield stress should be tested at each of the test temperatures.
- The failure time should be recorded accordingly.

The Rate Processing Method (RPM), which is based on the time-temperature superposition principle, is a widely used method to predict the failure time or design stress limit at a site-specific temperature based on test data obtained from elevated temperature tests. The analytical procedure and statistical method to obtain 95% confidence are described in ISO 9080. Eq. 31 shows the most commonly used RPM equation which includes with three constants. Once the three constants are calculated by regression analysis using test data, the failure time corresponding to any applied stress can be predicted at a given temperature. It is expected that the total testing time will be years for a geomembrane that fulfils the GRI-GM13 specification. Furthermore, the prediction of stress crack failure time in the field will still be a challenge, since the in-situ tensile stress of the geomembrane is not well defined, and due to combination of stress relaxation and varying loads the stress probably even changes with time (Lord and Halse, 1989).

\[
\log t = A + B \frac{\log \sigma}{T} + C \frac{\log \sigma}{T}
\] (31)

where:
- \( t \) = time to failure, in hours,
- \( \sigma \) = applied stress, in MPa
- \( T \) = test temperature, in K
- \( A, B, \) and \( C \) = constants

7.2. Creep behaviour of geosynthetics

Tensile creep (elongation or rupture under a constant load) is of primary interest for geosynthetics such as geotextiles and geogrids used in reinforcement of walls, slopes, basal support, bearing capacity and related geotechnical applications. Although substantially less common, compressive creep is of importance to geosynthetics such as drainage composites, geofoam, and geopipe. In addition, stress relaxation of geomembranes and geogrids undoubtedly take place and can be beneficial in reducing the effect of local stresses. However, as these stresses are not well defined, no numerical calculation is attempted here. Creep stresses and rupture are minimised by proper design and correct installation.

7.2.1. Methods of measuring tensile creep

The methods for measurement of tensile creep of geosynthetics, ISO 13431 and ASTM D 5262, are well established. Both methods consist of measuring tensile elongation under a constant load at a set temperature. There is no equivalent test for stress relaxation, it being recognised that measurement is more difficult and that the stress-relaxation behaviour can be derived from creep tests with sufficient accuracy for design. The most significant contribution to the measurement of creep strain over the last ten years has been the stepped isothermal method (SIM) for accelerated testing, i.e., ASTM D 6992. Introduced by Thornton in 1998, SIM has been the subject of numerous papers. The method has been applied to a wide variety of geosynthetics including nonwoven geotextiles (Bueno et al. 2005) and even new fibres such as polymer vinyl alcohol (PVA) and polyethylene naphthalate (PEN) (Lothspeich and Thornton, 2000; Koo et al., 2006). In spite of its wide acceptance, however, it should not be forgotten that to simulate the entire lifetime of a geosynthetic in one overnight test represents a very high level of acceleration, and that the validity of SIM rests on a satisfactory comparison with the results of conventional long-term testing.

A validation of SIM has been presented by Greenwood et al. (2004) who compared the results of SIM creep strain tests with those from conventional tests which had lasted for up to 12 years. They found that three out of the four materials tested exhibited agreement to within 6% between the measured results for the total strain and those predicted by the SIM tests. The outlier was a heavy woven polypropylene geotextile in which the variation widened to 25%. They also obtained a good agreement between the times to rupture for 27 conventional and SIM creep-rupture tests of a polyester fibre reinforced strip. However, the agreement in times to rupture between SIM and conventional creep tests for woven polypropylene geotextiles was less good but within the expected range of variability.

7.2.2. Reduction factors for geosynthetics in soil reinforcement applications

Recently a significant advance has been made in the interpretation and codification of creep rupture, in such a way that it can be used in design, as set out in ISO TR 20432 “Guideline for the Determination of the Long-term Strength of Geosynthetics for Soil Reinforcement”, published in 2007. It is intended that this method will replace the numerous national codes, each of which differs slightly from one another. ISO TR 20432 nevertheless has the status of a guide and does not yet carry the authority of an international standard.

The guide introduces four reduction factors covering the effects of creep, installation damage, weathering and chemical degradation, together with a safety factor, as expressed in Eq. 32.
The characteristic strength of geotextiles $T_{char}$ is generally defined as the mean strength less two standard deviations. This is definition of Minimum Average Roll Value (MARV) for geotextiles as is commonly used in North America. The reduction factors are expressed as numbers greater than unity by which the characteristic strength is divided. Note that they are multiplied by one another as indicative of a worst-case situation. These reduction factors refer to specific site conditions, such as temperature, and are not universal values that can be applied to all situations. The approach is likely to be a very conservative one for design.

The safety factor ($f_s$) accounts for the extrapolation uncertainty. It should also be emphasized that this safety factor does not consider the uncertainties related to soil structure and the calculation of loads, and thus it should not be confused with the “global factor of safety (FS)” used in the conventional geotechnical engineering design. In the context of “load and resistance factor design or LRFD”, it represents the resistance side of the equation (Christopher, 2002). The method of calculating $f_s$ is set out in ISO TR 20432.

Each of the individual reduction factor is calculated according to Eq. 33. In each of the four effects, the percent retained strength at the expected service life, which typically is 75-100 years for reinforcement applications, should be determined.

$$RF = \frac{100}{\text{retained strength} (%)},$$

$RF_{ID}$ is expressed as a ratio of the tensile strength of the geosynthetic before and after a simulated installation damage test. More details will be presented in later part of this section. $RF_w$ is evaluated according to EN 12224. Based on the retained strength after the test, appropriate $RF_w$ value can then be selected from the recommended values provided in the standard. $RF_{CH}$ is determined by an aging test that is governed by the polymer of the geosynthetic product as well as the site environment. The previously described test methods to accelerate the chemical degradation of different types of geosynthetics can be implemented here. $RF_{CR}$ is based on creep-rupture alone and is the focus of this section.

7.2.3. Creep rupture reduction factor

Regarding creep-rupture, the long-term strength is determined by extrapolating the candidate product’s creep-rupture curve to the projected design life, as shown in Figure 28. In this case, the $RF_{CR}$ is $100/52 = 1.92$. The guide allows the inclusion of time-temperature accelerated testing as well as SIM testing. It specifies a minimum of 12 tests, up to six of which can be accelerated, and states the time intervals within which the rupture values should lie. The longest conventional rupture test should have a time to failure in excess of 10000 h. Combination of the conventional and accelerated tests is subject to particular conditions. Guidelines are set out for using results measured on other products in a manufacturer’s range, or otherwise ‘similar’ products. It should be noted that creep rupture analysis is particularly well suited for polymers, such as PET, PVA, and other polymers which have a $T_g$ higher than the service temperature, i.e., they are in a “glassy” state in their service lifetime.

$$T_D = \frac{T_{char}}{RF_{CR} \times RF_{ID} \times RF_w \times RF_{CH} \times f_s}$$

(32)

Where: $T_D$ = Long-term design strength (MPa)
$T_{char}$ = Characteristic tensile strength (MPa)
$RF_{CR}$ = Reduction factor for creep
$RF_{ID}$ = Reduction factor for installation damage
$RF_w$ = Reduction factor for weathering
$RF_{CH}$ = Reduction factor for chemical and biological degradation
$f_s$ = Safety factor
ISO TR 20432 differs from some earlier standards in that it separates creep-rupture from limiting creep strain considerations. A limiting creep strain is probably better suited to polyolefins since their $T_g$ values are lower than the service-life temperature, i.e., they are in the “rubbery” state. The long-term strength based on creep strain is to establish the isochronous curve at the design life with time-temperature shifting if necessary. From the curve, it is possible to read off the maximum load on a geosynthetic to meet a particular strain criterion, which may be a limit on either total or post-construction strain. That said, the predicted creep strains are conservative because part of the load is transmitted to the soil, and strains measured on soil structures are generally well below those assumed in design. The loads applied in practice are generally well below those which, environmental effects aside, would lead to excessive strain and/or rupture within the design life of a soil structure. It has not proved possible to make a general description of the creep strain of the geosynthetic-soil composite such that it can be used for lifetime prediction, and creep tests continue to be performed in air and in isolation because the results are repeatable, conservative, and not restricted to any particular soil environment. The estimated long-term strength based only on creep strain should not be used in Eq. 32 since the effects of weathering, damage, and chemical on strain differ from those on strength.

The procedure described in the US by the Washington State Department of Transportation (WSDoT 925) uses a different methodology in which RFCR may use 10% strain as an alternative failure criterion to creep-rupture. Other methods may also be applied to specific products. Wrigley et al. (2006, 2008) showed that for geogrids made by the drawing of punched extruded sheet there is an abrupt change in creep strain rate at a particular load (55% of tensile strength for the product in question) which is temperature sensitive but independent of time. They recommend the definition of a creep limited strength by this method for HDPE geogrids.

A virtue of the reduction factor approach is its simplicity compared with some other approaches. The fact that the actual strength of the geosynthetic remains constant until shortly before creep-rupture introduces a level of conservatism. Segrestin and Freitag (2006) have made comments regarding the $T_{char}$ and $f_i$. They pointed out that $T_{char}$ should be replaced by the creep rupture strength at 1000 hours obtained from the same curve as Figure 28, and $f_i$ should be a partial safety factor which differs for each of the four reduction factors. In RFCR, the partial safety factor is more logical to apply to the loss of strength in the extrapolation region rather than the residual strength.

7.2.4. Mechanical damage

Mechanical damage caused during installation is not technically a contributor to lifetime prediction, since it results in a single, time-independent reduction in strength. However it must be taken into account in design and is included herein. The method of measurement uses site-specific backfill soil and loading techniques, as set out in ASTM D5818.

The ISO TR 20432 guide includes mechanical damage to identify the resulting factor $RF_{ID}$ in Eq. 32. Identification of $RF_{ID}$ from site damage tests is straightforward and the guide gives advice on how to interpolate a value from tests on other products within a product range, or for a soil whose granularity lies between those of the soils used to derive $RF_{ID}$ from site damage tests. The tests by Hufenus et al (2005) describe results on a wide range of geosynthetics, and the reduction factors they propose could form the basis for a code for use in normal fills, see Table 11. They also report a relatively satisfactory comparison between site tests and the results of ISO 10722 in which damage is simulated on a laboratory scale, but which has so far failed to generate sufficient confidence for it to be adopted. ISO TR 20432 discounts its use for the measurement of $RF_{ID}$.
Table 11. Generic reduction factors for installation damage “RF_{ID}”, Hufenus et al (2005)

<table>
<thead>
<tr>
<th>Type of geosynthetics</th>
<th>Fine-grained soil (clay, silt, sand)</th>
<th>Rounded coarse-grained soil &lt;150 mm</th>
<th>Angular coarse-grained soil &lt;150 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biaxial stretched grid</td>
<td>1.0–1.2</td>
<td>1.0–1.3</td>
<td>1.1–1.5</td>
</tr>
<tr>
<td>Uniaxial stretched grid</td>
<td>1.0–1.2</td>
<td>1.0–1.3</td>
<td>1.1–1.5</td>
</tr>
<tr>
<td>Flat rib grid</td>
<td>1.0–1.2</td>
<td>1.0–1.3</td>
<td>1.1–1.5</td>
</tr>
<tr>
<td>Coated grid</td>
<td>1.1–1.4</td>
<td>1.1–1.5</td>
<td>1.2–1.8</td>
</tr>
<tr>
<td>Slit tape woven fabric</td>
<td>1.1–1.6</td>
<td>1.2–1.7</td>
<td>1.2–1.9</td>
</tr>
<tr>
<td>Woven or knitted fabric</td>
<td>1.3–2.0</td>
<td>1.3–2.1</td>
<td>1.4–2.4</td>
</tr>
<tr>
<td>Yarn reinforced nonwoven</td>
<td>1.2–1.9</td>
<td>1.3–2.0</td>
<td>1.3–2.2</td>
</tr>
<tr>
<td>Needle punched nonwoven</td>
<td>1.1–1.5</td>
<td>1.1–1.5</td>
<td>1.2–1.8</td>
</tr>
<tr>
<td>Heat set nonwoven</td>
<td>1.1–1.6</td>
<td>1.2–1.7</td>
<td>1.2–1.9</td>
</tr>
</tbody>
</table>

An additional reason for including installation damage in a paper addressing long-term degradation issues is that a number of studies have investigated the potential synergy between damage and creep to establish whether or not the long-term strength of a damaged geotextile can be calculated by applying the two reduction factors for creep and installation damage $RF_{CR}$ and $RF_{ID}$, or whether the damage reduces the lifetime under sustained load disproportionately. Results to date have failed to identify any synergy, leaving the design process unchanged.

7.2.5. Creep in compression

Drainage composites consist of two geotextiles separated by a drainage core structure which is often a geonet. Alternatively, there are many other core structures such as columns, cuspsations, stiff webs, etc. Water expelled from the adjacent soil passes through the geotextile filtration layers and then flows laterally within the openwork core structure to an external outlet. Under soil pressure the core structure may compress and reduce the lateral flow. This is further reduced by intrusion of the geotextiles into the core structure. The reduction in flow has been measured as linear with log time (Böttcher 2006) and is accounted for in design by reduction factors for creep and geotextile intrusion similar to the procedure for creep. These factors can be as high as three or more. Of particular concern is the tendency of some apparently rigid core structures to buckle and collapse over time, particularly when shear forces are present which will be described in Section 8.0. A method for measuring creep in compression is well established (EN ISO 25619-1). This has been augmented by the use of the stepped isothermal method to aid long-term prediction, to which shear forces can be added (ASTM D7361, Jeon and Mlynarek 2004, Narejo et al. 2004, Thornton and Sandri 2005, Allen 2005, Yeo and Hsuan 2007, Zanzinger 2008).

A second emerging geosynthetic area where compressive creep is of concern is the use of geofoam as a lightweight fill beneath roadway embankments and behind retaining walls. Conventional creep behaviour of geofoam was evaluated in durations of 1,000 to 10,000 hours (Preber et al., 1994; Horvath, 1995; Duskov 1997; Murphy 1997; and Negussey 1997). Recently SIM was applied to determine the compression creep of geofoam, however this method appears to be limited by a change in material properties at 43°C. A time-temperature-stress-superposition was found to be an appropriate accelerated creep test for geofoam that is sensitive to temperature (Yeo and Hsuan 2006).

8. LONG-TERM SHEAR STRENGTH OF GEOSYNTHETICS

While the subject of shear strength stability of slopes, walls, landfill liners, landfill cover, etc., is usually approached on the basis of short-term interface shear strengths, there are certain geosynthetics where the long-term interface shear strength has been challenged. That said, three types of geosynthetics (textured geomembranes, geocomposite drains, and geosynthetic clay liners) have been evaluated for their long-term performance under the combination of compression and shear stress.

8.1. Long-term shear test device

Seeger et al. (2000) developed an inclined plane test device to evaluate the long-term shear behavior of geosynthetics. The schematic diagram of the test device is shown in Figure 29. The test specimen is mounted between two steel wedges with inclined angle of 21.8° that corresponds to a slope of 2.5(H)-to-1.0(V). The assembly is immersed in a water bath (deionized or tap water) that could be heated to an elevated temperature. A vertical load is exerted onto the specimen holder by way of a force on the upper wedge from the lever mechanism. The vertical and the in-plane displacement of the upper wedge are automatically recorded over the duration of the test via a displacement sensor. The time-to-failure is determined in conjunction with testing conditions.

Incubation in a water bath at an elevated temperature simulates a weaker oxidative environment compared with incubation in forced air ovens for polyolefin geosynthetics. This applies especially for hindered amine stabilized materials (Müller et al., 2003). Oxidative conditions in field situations will generally lie somewhere between water and circulated air conditions.
8.2. Long-term shear test of texture geomembranes

There are four methods for texturing the surface of geomembranes to increase interface friction; coextrusion, spray-on, laminating, and structured (Koerner, 2005). The long-term shear behaviour of two textured geomembranes made from the spray-on method was evaluated by Seeger et al. 2000; Seeger and Müller, 2001. The spray-on coating was made from two types of low density polyethylene resins (labeled as A-chip and B-chip) which have comparable density, melt flow rate and oxidative induction time. Also the same conditions (temperature and pressure) were utilized during the spray-on-process, i.e. a smooth geomembrane at room temperature was slowly moved below a crosswise operating spray gun.

Long-term shear testing was carried in the inclined shear device shown above. The textured geomembrane specimen was mounted on one of the wedges and a PP geotextile (1200 g/cm²) was mounted on the other wedge. A vertical load of 50 kN/m² was applied. The assembly was immersed in a water bath that was heated to a temperature of 80°C. Failure was defined as sudden slippage of the upper wedge as reflected by the abrupt change in vertical displacement.

For geomembrane specimens textured with resin A-chip, the average time-to-failure was only 2 days, while a much longer time-to-failure was obtained for geomembrane textured with resin B-chip, see Table 12. In most tests, no failure was detected for 1.5 years for the B-chips. Slippage, if encountered at all, occurred after long test durations due to embrittlement of the geotextile, causing separation from its fixing mount on the wedge. Slippage due to failure of the geomembrane’s texturing was not observed. Furthermore, one set of specimens (B-259*) was exposed for 1500 hours in a laboratory weatherometer according to EN 12224 with a test temperature of 35°C and relative humidity of 40% prior to the long-term shear test. There was no failure in the subsequent long-term shear test of these samples.

It is unclear which variation in resin properties and/or the fabrication processes caused such large differences in the times-to-failure between the “A” and “B” chips. Failure may be due to ductile fracture of poorly bonded structure particles and stress cracking at the interface between the sprayed chips and the geomembrane. A drastic change in melt index and OIT value of the sprayed chips occurred during the spray-on-process. However, oxidative degradation seems not to be relevant. Figure 30 shows the change in OIT value of the sprayed chips and the smooth geomembrane during incubation in water at 80°C. The materials had been stabilized with phenolic and phosphitic antioxidants. The change in OIT value should therefore reflect the change in the antioxidant content. The increase of OIT values of the sprayed chips after 500 days in oven aging indicates some change in the stabilizer system. One of the possible explanations is that the sprayed chips with lower levels of stabilizers were able to be stabilized by the diffusion of antioxidants from the adjacent smooth geomembrane that contains a higher level of stabilizers. However, no direct experimental evidence for a migration process is available so far.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
<th>Test 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-3</td>
<td>&gt; 395</td>
<td>&gt; 395</td>
<td>399²</td>
<td>404³</td>
</tr>
<tr>
<td>B-4</td>
<td>&gt;698</td>
<td>&gt;620</td>
<td>350³</td>
<td></td>
</tr>
<tr>
<td>B-259*</td>
<td>&gt; 396</td>
<td>&gt;524</td>
<td>&gt;524</td>
<td></td>
</tr>
</tbody>
</table>

*) Textured GM did not fail; geotextile separated from its fixing mount due to brittleness.

*) After 1500 hours of artificial weathering in accordance with EN 12224.
Lastly, it should be pointed out that this study only applies to the spray-on type of texturing geomembranes. For the much more common geomembrane texturing methods of co-extrusion and structuring, the asperities of the texturing process cannot be removed or rubbed-off since they integrated to the core portion of the geomembrane.

8.3. Long-term shear test of geocomposite drains

Geocomposite drains (GCDs) are normally made up of a highly permeable drainage core in between two GT filter layers. Many different drainage cores have been developed. By far, the most common in North America are geonets; either biplanar or triplanar. However, there are many other types as well. For example, there are rigid zig-zag like random arrays of quite thin extruded PP strands, single or double cusped cores, and columnar cores, and others. The geometry and rigidity of the cores vary greatly from product-to-product. The bonding of the core and its two GT filters is accomplished by either heat-bonding the three components, lamination via heat-bonding the geotextiles onto the ribs of a geonet, or by adhesive bonding.

Over time, GCDs can be changed by either physical or chemical processes. Brittle fracture of the core might occur well below the stress and strain limits which were obtained from creep measurements. Unusual failure mechanisms might be possible in a complex structured GCD, which are neither a direct consequence of creep nor that of chemical aging. A collapse or instability may arise in rigid core structures when a certain critical deformation limit is reached during creep deformation (Bronstein and Müller-Rochholz, 2006; Müller, 2007; Yeo and Hsuan, 2007; Zanzinger, 2007). The core structure will then give way to an accelerated deformation resulting in collapse and loss of drainage capacity proportionally.

Müller (2007) evaluated a GCD which consisted of three-dimensional PP strands core. Test samples were subjected to creep compressive tests according to EN 1897 (see Figure 31) at stresses of 400 kPa (Specimen 2), 379 kPa (Specimens 6 and 7), 358 kPa (Specimens 12, 13, and 14), 337 kPa (Specimens 15 and 16), 295 kPa (Specimen 21), 253 kPa (Specimen 24), 210.5 kPa (Specimens 28 and 29). The thickness versus time curves were adjusted along the logarithmic time scale so that the regions of instability roughly overlapped. The diagram shows, that, regardless of the compressive stress, the instability of the core starts when the critical thickness of the GCD reached the range of 5.0 to 5.5 mm. For this product, the initial thickness measured at 2 kPa was about 9 mm. Figure 32 shows creep curves of this GCD which were measured at room temperature under compressive stresses of 20 kPa and 50 kPa as well as under the combined action of compressive stress and shear stress typical of application conditions. An extrapolation of these curves reveals that more than 100 years have to pass until the residual thickness will enter the critical region for instability of the drainage core structure to occur under field conditions. It should be recognized that this shear test program is only for one type of GCD and there are many types that are presently available. The applicability of the critical thickness approach in extrapolating the long-term shear behaviour to other GCDs requires future confirmation.

In addition to the stability of drainage core under long-term shear, the oxidation degradation of the GCD was assessed. Figure 33 shows a stress versus time-to-instability plot for shear tests performed at different temperatures. For tests at 60 and 80°C water, the drainage core was not only flattened but PP strands were broken into fragments as result of oxidation degradation. Thus, for certain types GCDs, careful assessment on their long-term shear performance should be carried out.

![Figure 30. Change in OIT value of texturing chips and the smooth geomembrane during incubation in water at 80°C](image-url)
**Figure 31.** Room temperature creep curves, i.e. thickness versus time, of a GCD under various compressive stresses

**Figure 32.** Creep curve of a GCD, i.e. thickness versus time, at stresses typical for landfill applications

**Figure 33.** "Stress-instability-diagram" for the investigated GCD.
8.4. Long-term internal shear strength of GCLs

Long-term internal shear tests were performed on four types of GCLs in which the bentonite is sandwiched between two geotextiles and reinforced by needle-punching (Müller et al., 2007). The GCLs were manufactured by needling the reinforcing fibers into the carrier geotextile and locking them by either mechanical entanglement or thermal treatment using flame burnishing the backside of the carrier geotextile.

The shear tests were carried out by mounting the upper and lower geotextiles of the GCL test specimen onto the two wedges of the inclined shear device (shown in Figure 29) to challenge the internal shear strength. Two different liquids were used: deionized water and tap water. The test was performed under a shear force of 17 kPa and a normal stress of 45 kPa at 80°C.

The long-term shear behavior of the tested needle punched GCLs strongly depended on the liquid medium. Tap water induced sodium to calcium ion exchange and limited the swelling of the bentonite, thus avoiding the large straining and failure of the reinforcing fibers. No failure was observed even after 3 years of testing at 80°C. Ion-exchange was expected to take place within the bentonite within a few years (Meer and Benson, 2007) which can be beneficial to the long-term shear behavior of the GCL.

With de-ionized water, the sodium bentonite layer was fully hydrated. The high plasticity bentonite was readily deformed under shear, yielding a large elongation of the connecting fibers. Under this condition failure was imminent and the times-to-failure strongly depended on the fiber resin, product design, and temperature. Two failure modes were identified depending on the manufacturing process. GCLs with thermal treatment showed brittle failure by rupture of the fibers near the anchoring points in the carrier geotextile. GCLs, which were not thermal fixed, showed a disentanglement of the fibers from the carrier geotextile, i.e., they pulled out from the carrier geotextile.

The study also found that the short-term bonding strength of needle punched GCLs, which was measured in peel tests, is unrelated to the times-to-failure from the long-term shear test. Surprisingly, GCLs with high short term peel strength yielded a short failure time in the long-term shear test. Therefore, a high strength in peel test is not a reliable indicator for long-term shear behavior in these tests.

9. SUMMARY

Presented herein were the essential aspects of long-term degradation of many types of geosynthetics. Its importance is underscored by the fact that degradation has been, and continuous to be, the most frequently asked question regarding geosynthetics. Obviously, the particular resin types, its additives, and other components in the formulation are of basic importance with respect to the site-specific environment of the particular application. In this context the paper was subdivided into three categories; chemical degradation, exposed weathering, and time-dependent mechanical behavior.

9.1. Chemical degradation

The chemical degradation portion of the paper focused on three types of degradation according to the polymer. They are the oxidation of polyolefin geosynthetics (including geomembranes, geotextiles, and geogrids), plasticizers migration from p-PVC geomembranes, and hydrolysis of PET geotextiles and geogrids.

9.1.1. Oxidation of polyolefins

Since polyolefins are the most widely used polymers in geosynthetics, recall Table 1, the oxidation degradation mechanisms and their prevention are described in detail.

The vital role of AOs in preventing the onset of oxidation degradation is clearly demonstrated. The current practice to ensure proper AOs are being added to geosynthetics is using GRI-GM13 and GRI-GM17 in which the initial AO amount and AO depletion rate after incubation in forced air ovens and weatherometers are specified in terms of OIT values. However, in light of the test results generated from Rowe’s research team, the type of surrounding liquid and adjacent materials above and beneath the HDPE geomembrane can strongly impact the depletion rate of AOs. A chemical compatibility test for AOs of PE geomembranes may be warranted when the longevity of the PE geomembrane at a specific site is considered. Currently the lifetime of PE geomembranes in a landfill environment has not yet been finalized and research is on-going by performing oxidation aging tests in landfill simulators (Rowe et al. 2008). The results of this study should further enhance the confidence in the long-term performance of PE geomembrane, particularly HDPE.

For assessing the oxidation resistance of geotextiles and geogrids that are made from polyolefins, ISO 13438 “Screening test method for determining the resistance to oxidation of geotextiles and geotextile-related products” is available. The test utilizes both temperature and oxygen pressure to accelerate the oxidation process. Samples are immersed in an aqueous solution to challenge the leachability of AOs. A model has been established which relates the incubation temperature and oxygen pressure to the reaction rate. However, a change in activation energy was detected at 65°C and at an oxygen pressure of 6.3 MPa for a PP geotextile. Thus, the validation of the model at lower oxygen pressures is required and research is on-going. Once the model is confirmed, the test can substantially shorten the testing time even at incubation temperatures below 65°C.

9.1.2. Migration of plasticizers from p-PVC geomembranes

The long-term performance of p-PVC geomembranes is primarily governed by the retention property of the plasticizers which is greatly influenced by the molecular weight and molecular structure of the plasticizers. A
minimum molecular weight should be recommended for the plasticizers in p-PVC geomembranes for buried applications, while for the exposed applications, appropriate accelerated weathering testing must be performed to identify the suitable plasticizer. In such cases multiple plasticizers have been used in the formulation for enhanced lifetimes.

9.1.3. Hydrolysis of PET geotextiles and geogrids
Significant research has been performed to assess the hydrolytic susceptibility of PET geosynthetic products. The pH boundary for inner and outer hydrolysis has been defined, and a pH of 9 is the upper limit for using PET geosynthetics for critical applications. The lower limit is about pH = 4, but its value is less certain. In Europe, laboratory index tests (EN 12447) have been established to assess PET geosynthetics for a service life of 25 years. For service longer than 25 years, products should be evaluated by thermal acceleration tests to predict the lifetime using Arrhenius equation. In contrast, the US Federal Highway Administration requires a minimum value CEG of 30 mg/kg and molecular weight of 25,000 for PET geosynthetics used in reinforcement applications with service life typically of 50 to 75 years.

9.2. Weathering
Geosynthetics in exposed conditions represent a greater degradation challenge than when they are covered. In addition to full oxygen of the air environment and high temperatures, there is the aspect of direct UV exposure. In geosynthetics, standards have been developed in both Europe and US for Xenon arc and UV-fluorescent weatherometers to assess the lifetime of exposed geosynthetics. That said, the technical challenge is to predict the natural weathering at a specific site using test data generated from the weatherometer. Current practice is to compare the failure times obtained from the weatherometer and at the field. Additional research is certainly needed in this area and it is presently ongoing (Koerner et al., 2008).

9.3. Time-dependent mechanical properties
Three time-dependent mechanical properties are discussed in this paper. They are stress cracking, creep, and long-term shear strength behavior.

9.3.1. Stress cracking
Stress crack resistance of HDPE geomembranes has been intensively studied since 1990. As a result, a standard test method has been developed and a minimum failure time of 300 hours is specified in GRI-GM13 to ensure SCR of HDPE geomembranes. The result of this test’s implementation is that many HDPE resins have been removed from the market and new resins with higher SCR have become available and are being used. It is anticipated that stress cracking of HDPE geomembranes is no longer an issue.

9.3.2. Creep
Creep is a fundamental material property that must be considered for geosynthetics used in reinforcement applications. The latest accelerated creep test, SIM, has been proven to be acceptable to generate reliable creep data for many types of geosynthetics. The implementation of creep rupture in terms of a reduction factor is presented in ISO TR 20432 in which three other reduction factors, chemical degradation, weathering, and installation damage, are also included. However, the standard does not address a reduction factor for creep deformation which is important for geosynthetics made from polymers with low \( T_g \) values, like the polyolefins. Furthermore, the creep strain measured in the field has been found to be far less than the design values. Additional long-term field strain data will be beneficial to define the appropriate conditions for the various creep tests. In the meantime, creep data obtained from the isolated condition (no lateral stresses) would be likely to provide a conservative design since the contribution of the soil is neglected.

9.4. Long-term shear behavior of geocomposites and GCLs
For geosynthetic composite materials which are factory-formed from multiple layers, the issue of long-term shear strength of the components is important. The general approach of interface shear behavior is a short-term direct shear test. Yet, the long-term behavior might also be important particularly when the applied load is at an inclined angle; thus mobilizing shear stresses. Geosynthetic drainage products (GT/drainage core/GT) and geosynthetic clay liners (GT/bentonite/GT) are certainly susceptible to such multiple stresses during service life.

Certain types of geocomposite drainage products under long-term shear stress was found to exhibit creep deformation, drainage core collapse, or shear failure between two bonded faces. In addition, chemical degradation of the polymer must be evaluated separately to ensure the longevity of the material.

For the long-term shear behavior of GCLs, it is affected by the reinforcing fiber, bentonite, product style, and the surrounding liquid medium. A highly hydrated GCL deforms rapidly under shear stress. The failure mode of the reinforcing fibers can be either brittle rupture for thermal treated products or disentanglement of fibers for products using mechanically entanglement system.
10. CONCLUSIONS

Over the past fifteen years, a significant effort has been made to understand the various degradation mechanisms that are relevant to the geosynthetics. Appropriate laboratory tests have been developed to evaluate the long-term quality of the products. Also a few generic specifications have been established at the regional or international levels to ensure product standards meet these durability criteria.

Perhaps the next phase of the durability research should be to generate data from field-retrieved samples. Geosynthetics have been used for approximately 30 years. Characterizing existing field samples would be useful to confirm the aging process predicted from laboratory acceleration tests. Contrary, it would not be beneficial to characterize a field-retrieved geosynthetic sample in terms of life prediction of new products, if the formulation has been changed or improved. The improvement in resins, and particularly in additive packages, has been meaningful and it is entirely possible that the current generation of geosynthetic products will have far greater durability than older resins and additive packages. Selecting the appropriate laboratory acceleration tests is essential to ascertain the long-term behaviour of these new products.

11. ACKNOWLEDGEMENTS

The research presented in this paper was supported by multiple agencies, including US National Science Foundation (Grant No. CMS 9872285), the US Federal Highway Association (Contract No. DTFH 61-98-R-00043), Fellowship Grants from the Geosynthetic Institute, Deutsches Institut für Bautechnik under AZ: IV 1-5-666/92 Nr.11.40, Federal Highway Research Institute (Project 05.122/2000/CGB), and Natural Sciences and Engineering Research Council of Canada.

Also thank you for Professor Roberto Frassine (Politecnico di Milano) and technical staff at the Geosynthetics Laboratory at CESI for their contribution.

12. REFERENCES


Hsuan, Y.G. and Li, M. 2005. Temperature and pressure effects on the oxidation of high-density polyethylene.


Suits, D.L. and Hsuan, Y.G. 2003 Assessing the photo-degradation of geosynthetics by outdoor exposure and laboratory weatherometer” Geotextiles and Geomembranes, Volume 21, Issue 2, 111-122


