LONG TERM PERFORMANCE OF POLYMERIC GEOMEMBRANES

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

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

1. INTRODUCTION

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

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

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

The design life is specified on the time axis. It is set by the designer and one of several fixed durations must be determine according to whether the structure is meant for short-term use (typically a few years and not exceeding 5 years), temporary use (around 25 years) or permanent use (50 to >100 years). The nature of the structure, the environmental risk involved and the consequences of failure may influence this duration: 30 years for a canal and beyond 100 years for landfills.

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

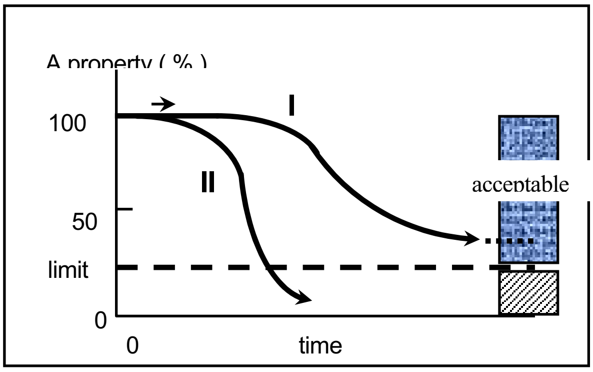

Figure-1 : Functional property variation with time

2. GEOMEMBRANES

Geomembrane sheets are normally produced from thermoplastic polymers. These products are made by extruding a sheet or by melt blown processes. The manufacturing begins with the production of the raw materials which include the polymer resin, various additives, fillers and lubricants. These materials are then processed into a sheet of various width and thickness in one of the extrusion method. The formulations are feed to one or more extruder containing a rotating continuous screw. It is emerging as a filtered, mixed and molten material into a die. The thickness of sheets varies between 0.75 to 3.0 mm with width varying from 1.8 to a maximal width of 9.5 m.

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

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

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

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

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

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

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

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

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

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

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

Chlorosulfonated polyethylene (CSPE) is a family of synthetic rubber materials. It was introduce in the early 1950s as a synthetic rubber material with better ageing characteristics than the natural and styrene-butadiene rubbers. This improved rubber material could be cross-linked to provide elasticity, and which contained a minimum level of crystallinity to provide flexibility while maintaining strength. The basic polymer backbone is the same as polyethylene and because there are no double bonds, the long polymer chains are relatively impervious to attack from degrading agents such as oxygen, ozone or energy in the form of UV light. It is containing chlorine atoms introduce along the side of the PE backbone with a certain number of sulfonyl chloride groups introduced as side chains. Since the sylfonyl chloride groups are larger than the chloride atom, they are more efficient at breaking up the crystallinity and provide chemically active cure sites.

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

3. SOLLICITATIONS ON GEOMEMBRANES

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

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

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

chemical attack: As with geotextiles, polypropylene and polyethylene geomembranes are susceptible to oxidation and, similarly, this is retarded by the presence of additives. PVC geomembranes have a high chemical resistance to the majority of acids, bases, salts and alcools but the plasticizers can be affected by benzene, trichloro-ethylene and toluene. PVC structure can be attack by ketones, such as methyl-ethyl-ketone and acetone.

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

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

Figure-3: Photograph of an chemically attacked geomembrane

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

oxidation : Polypropylene and polyethylene are susceptible to oxidation. This is accelerated by the catalytic effects of transition metal ions in a chemically activated state. Of these the ferric (Fe^{3+}) ion is the most common but copper and manganese have also been shown to be important. However, the sensitivity to oxidation is dramatically reduced by the inclusion of antioxidant stabilizers or additives. All chemical reactions occur more rapidly at higher temperatures, as described by Arrhenius' Law.

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

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

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

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

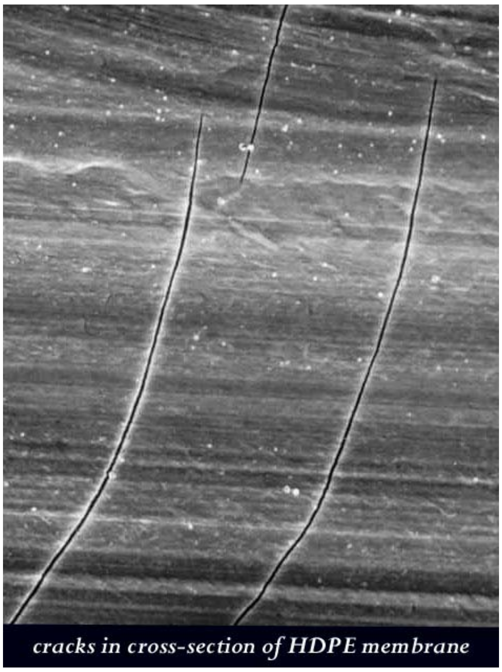

Figure-4: Photographs of micro-cracks HDPE sheet

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

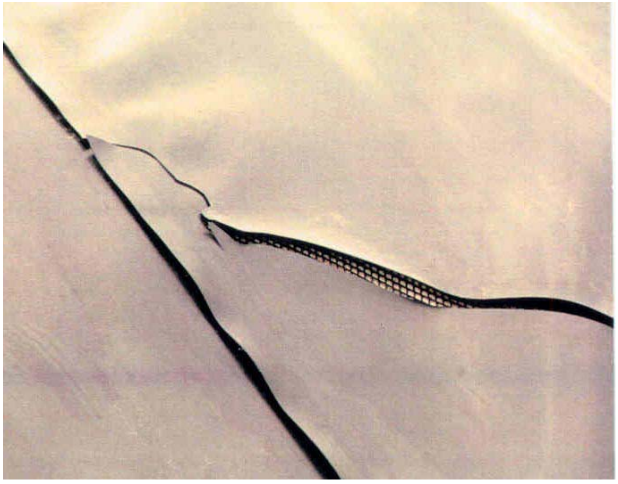

Figure-5: Photographs of a macro crack on HDPE sheet

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

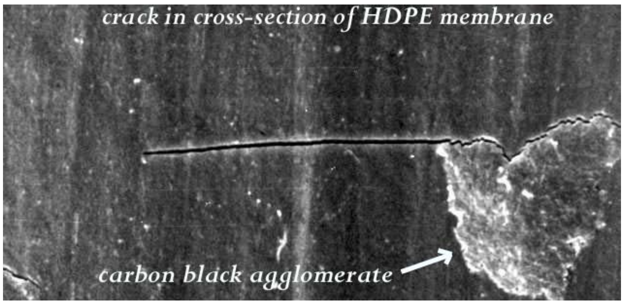

Figure-6: Photograph of a micro-crack initiate by carbon black agglomerate

4. EMPIRICAL EVIDENCE FROM RETRIEVED GEOTEXTILES

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

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

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

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

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

The U.S. Bureau of Reclamation (USBR) installed in 1957 0.25 mm thick PVC geomembranes to line irrigation canals in Montana, New-Mexico and Wyoming. Since, samples have been collected for evaluation after service life period varying from 2 to 27 years (Morrison & Swihart, 1993). The geomembranes were protected by a soil layer. The samples collected (after 19 years of service) in location under the water level did retain more plasticizer than samples located at the outer edge of the canal slopes: plasticizer loss of 18 to 22 % with elongation at break of 151 et 188 % for samples located under water.
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Since 1970, twenty dams located in the Alps have been rehabilitated using 2.0 and 2.5 mm thick PVC geomembranes on their concrete upstream face. These geomembranes have been exposed to the climatic conditions prevailing in high altitude (solar radiation and ice formation). Samples collected at the Lago Miller dam after 9 years of service retain 250 % elongation at break and no structural changes could be observed with a infrared spectrophotometric apparatus (Cazzuffi, 1987). A visit to many of these dams in 1993 supported the fact that the exposed geomembranes were in excellent condition.

5. CONCLUSION

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

6. REFERENCES

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ASTM D3895, Standard test Method to evaluate the Oxidative induction time

ASTM D5747, Standard Practice for Tests to Evaluate the Chemical Resistance of Geomembranes to Liquids

ASTM D 5819 (1998), Standard Guide for Selecting Test Methods for Experimental Evaluation of Geosynthetic Durability

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