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GEOMEMBRANE STRESS CRACKING RESISTANCE USING VARIOUS POLYMERS

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ABSTRACT

This paper aims to link the influence of the HDPE polymer used in the manufacture of geomembranes to the stress cracking resistance of specific geomembranes.
For this, several characteristics will be analyzed such as density (directly related to the crystallinity of the polymer), the melt flow index (linked to the molecular weight of the polymer) and the molecular weight distribution of the polymer.

1. INTRODUCTION

Geomembranes used during the mining process are placed on the base of Heap Leach Pads, Pregnant solutions ponds and Tailing Dams, for metal rich leachates collection. These leachates are acid solutions (e.g., sulfuric acid or sodium cyanide, depending on the metal to be leached); therefore it is necessary to have a geomembrane with a very high resistance to stress cracking in a surface-active situation. This paper therefore studies those specific characteristics of the polymer which will give high durability to the geomembrane in an acid and abrasive situation.

An important factor to evaluate the resistance is the Single Point Notch Constant Tensile Load (SP-NCTL) according to the ASTM D 5397 standard. This paper explains the relevance of this document and how some parameters of the polymer can influence either high or low resistance to stress cracking and therefore a higher or lower durability of the geomembrane.

Medium-density polyethylene (MDPE) and High-density Polyethylene (HDPE) are widely used resins for the manufacturing of geomembranes. They offer two major advantages: high chemical resistance and low permeability. It is important to mention that geomembranes called HDPE actually come from MDPE; however, by adding the corresponding carbon black percentage, the resulting geomembrane density is within the range of HDPE.

The relatively high crystallinity that HDPE exhibits is a risk for stress cracking rupture. The stress cracking is defined as an internal or external cracking in a plastic sheet caused by tensile stress below the short-term mechanical strength of the material. This cracking might be accelerated because of high temperatures and the presence of surfactants in the environment of the geomembrane.

The phenomenon of stress cracking in polyethylene sheets manufactured with semicrystalline polymers such as polyethylene is widely noted in the literature and occurs because of breaks and failure in the amorphous regions of the polymer (see Figure 1), when the sheet is submitted to tensions in the presence of chemical agents.

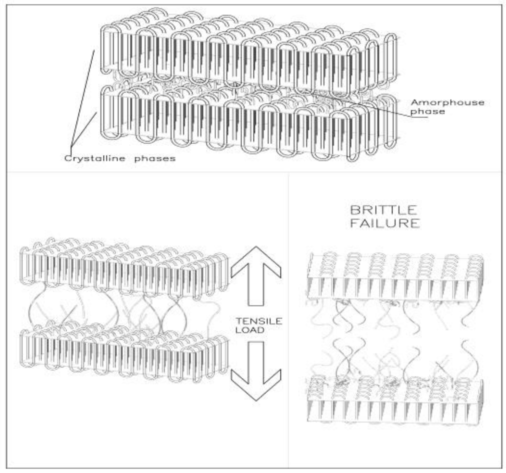

Figure 1: Stress Crack Phenomenon

The stress cracking resistance of a geomembrane depends largely on the polymer's characteristics among which are crystallinity (density), molecular weight, and molecular weight distribution.

This parameter (the stress cracking resistance) is also influenced by the manufacturing process of the geomembrane, the installation process of the liner, and the quality of the welding while seaming the sheets. In general, for the same density, a polyethylene with a high molecular weight distribution has a lower crack resistance under environmental tension. Polyethylenes with a low melting index under 1.0g/10min (190ºC – 2.16kg) exhibit good stress crack environmental resistance.

One way to quantify the stress crack resistance of a geomembrane is the Notched Constant Tensile Load (NCTL) (see Figure 2)

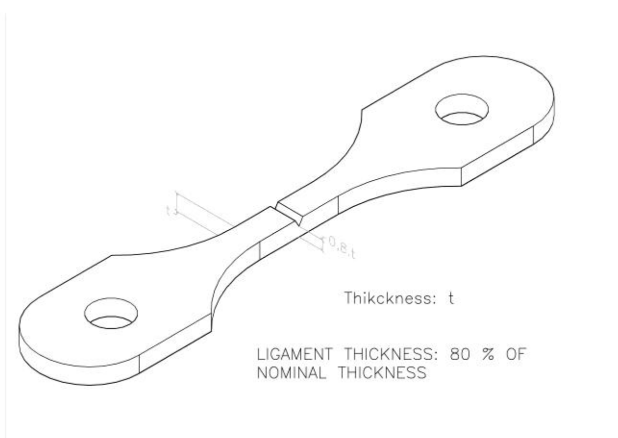

Figure 2: View of the Notched Test Specimen of the NCTL Test

This test has two variations: the entire curve test and the single point-notched constant tensile load test in which the specimens are subjected to 30 per cent of measured yield stress of the material at a temperature of 50ºC and the time of deterioration is registered. In this study, the stress cracking resistance's tests have been developed according to the SP-NCTL.

2. POLYMERS USED

2.1 Density and Crystallinity

Polymers submitted to testing in this study were commercial polyethylenes of different densities and different degrees of crystallinity. The density was quantified following EN-ISO 1183 (UNE-EN ISO 1183-2:2005) and the degree of crystallinity was quantified by differential scanning calorimetry (DSC). Crystallinity was obtained by dividing the heat of fusion of the polymer by the heat of fusion of the polymer which would be obtained if it was 100 per cent crystalline. Results are shown in Table 1.

Table 1: Density and Crystallinity of the Polymers Used

Polymer	Density (g/cm^3)	Crystallinity %
POLYETHYL.1 (PE-1)	0.932	51.2
POLYETHYL.2 (PE-2)	0.934	49.9
POLYETHYL.3 (PE-3)	0.936	56.8
POLYETHYL.4 (PE-4)	0.937	53.4
POLYETHYL.5 (PE-5)	0.938	54.5
POLYETHYL.6 (PE-6)	0.940	59.0
POLYETHYL.7 (PE-7)	0.941	49.4

2.2 Melt Index and Melt Flow Ratio (MFR)

The melt index or melt viscosity is an indirect way of measuring the molecular weight of the polymer. In general, high melt index values are related to low molecular weights and vice versa.

The melt index was quantified following EN-ISO 1133 (UNE-EN ISO 1133-1:2012), obtaining the value with the three possible loads (2.16kg, 5.0kg and 21.6kg). Results are shown in Table 2.

Table 2: Melt Flow Index (MFI) and Melt Flow Ratio (MFR) of the polymers

Polymer	MFI g/10 min (190ºC/2.16kg)	MFI g/10 min (190ºC/5.0kg)	MFI g/10 min (190ºC/2.16kg)	MFR
PE-1	0.78	2.19	19.76	25.33
PE-2	0.15	0.63	16.59	110.60
PE-3	0.93	2.65	23.54	25.31
PE-4	0.23	0.95	19.84	86.26
PE-5	0.23	1.00	18.95	82.39
PE-6	0.95	2.78	25.92	27.28
PE-7	0.12	0.57	11.67	97.25

The MFR is an indicator of the molecular weight distribution when two MFI similar polymers are compared, and in practice, a polymer with a wide molecular weight distribution will show a lower viscosity.

2.3 Molecular weight distribution

The molecular weight distribution was measured by Gel Permeation Chromatography (GPC) with double detector: refractive index (Conventional) and light scattering (giving absolute values). Values obtained in both ways are shown in Table 3 and the curves are shown in Figure 4.

Table 3: Molecular weight distribution

Polymer	Conventional GPC				Absolute GPC			
	Molecular Number (Mn)	Molecular Weight (Mw)	Centrifugal Molecular Weight (Mz)	Mw/Mn	Mn	Mw	Mz (abs)	Mw/Mn
PE-1	33,836	123,073	360,010	3.6	36,303	139,072	552,017	3.8
PE-2	13,695	213,069	1,136,889	15.6	12,147	179,555	603,578	14.8
PE-3	33,745	118,428	348,000	3.5	34,242	125,125	550,115	3.7
PE-4	15,984	158,834	922,274	9.9	13,402	132,019	467,779	9.9
PE-5	17,947	188,819	1,390,405	10.5	14,701	136,672	418,528	9.3
PE-6	33,646	114,261	311,081	3.4	31,073	110,818	280,464	3.6
PE-7	19,989	211,101	1,054,881	10.6	23,141	270,407	1,966,035	11.7

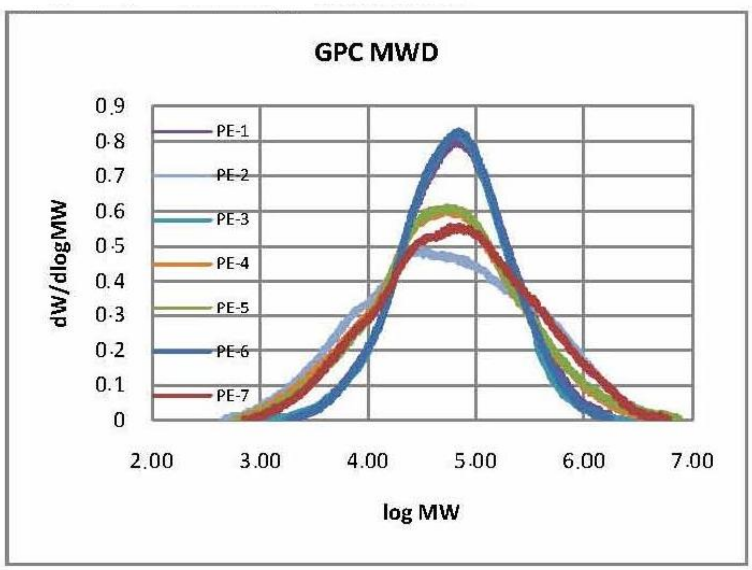

Figure 4. Molecular weight distribution curves

3. PROCESSING OF GEOMEMBRANES

Each of the polymers analyzed was transformed into a polyethylene sheet following this general formulation:

Base Polymer + Carbon Black + Antioxidants + UV stabilizers

In this way as many geomembrane samples as polymers analyzed were obtained. The manufacture was completed by a flat-die cast co-extrusion system. In all cases, the geomembrane was 7.5 m wide and 1.5mm thick.

4. STRESS CRACKING RESISTANCE (SCR) TEST

The manufactured geomembranes were submitted to a stress cracking test according to ASTM D 3597 by the SP-NCTL test. Results are shown in Table 4.

Table 4: Stress Cracking Resistance

Sheet	Polymer	Stress-Cracking (hours)
GEO-1	PE-1	>1200
GEO-2	PE-2	>1600
GEO-3	PE-3	246
GEO-4	PE-4	840
GEO-5	PE-5	647
GEO-6	PE-6	35
GEO-7	PE-7	180

5. DATA ANALYSIS

Geomembrane GEO-6 exhibits the lowest SCR resistance (thirty-five hours) due to the fact that the polymer from which it was manufactured is the one with the highest density (0.940g/cm^3) and one of the three with lowest MFR, and because of that a narrow weight distribution, as seen in Figure 4.

If density was the only or the most influential parameter in the SCR values, we could not claim that GEO-7, manufactured with a 0.941 g/cm^3 density polymer had a SCR resistance value of 180 hours higher than that of GEO-6. The main reason for this result is that the molecular weight distribution is significantly wider for polymer PE-7.

Polymers PE-1, PE-3 and PE-6 have a very similar weight distribution however the Stress Cracking Resistance is very different. The reason is that the density of PE-6 is higher than the density of PE-3, and this higher than density of PE-1, respectively. So for narrow molecular weights distribution the density limit has to be around 0,935 g/cm3, so the stress cracking resistance could be near 300 hours.

Polymer with higher densities could improve SCR if the molecular weight distribution is wider as GEO-4 (d=0,937 g/cm3) and GEO-5 (d=0,938 g/cm^3).

Maybe the best situation if for PE-2 with a density of 0,934 g/cm^3 and the second wider molecular weight distribution, presents a SCR more than 1000 hours.

6. CONCLUSIONS

There is no direct relationship between the polymer density and stress crack resistance.

Also, there is no evidence of relationship between the molecular weight distribution and its stress crack resistance.

Polyethylenes with higher density but a wider molecular weight distribution, improve the stress crack resistance values.

Polyethylenes with a narrow molecular weight distribution but lower density, improve their performance in terms of stress crack resistance.

One of the worst situations occurs for polyethylenes with densities ≥0.940 g/cm3 and narrow molecular weight distribution.

The best situation will be found in lower-density polyethylene and wider molecular weight distribution until the own process allows it or the mechanical or chemical geomembrane's properties.

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