ANALYSIS OF DEGRADATION AFTER WEATHERING EXPOSURE USING MFI AND OIT TESTS

Paulo César Lodi[1], Benedito De Souza Bueno[2]

[1] *São Paulo State University (UNESP) at Ilha Solteira. (e-mail: plodi@dec.feis.unesp.br)*
[2] *University of State of São Paulo (USP) at São Carlos. (e-mail: bsbueno@sc.usp.br)*

Abstract: This paper presents MFI and OIT tests in HDPE geomembranes after exposure to weathering agents after 6, 12, 18, 24, 30 and 84 months. HDPE geomembranes of two thicknesses were tested: 0.8 and 2.5 mm. The weathering degradation of geomembranes was evaluated according to ASTM D1435 and D5970. The MFI results show some decrease in values in the HDPE (0.8 mm) after 6, 12, 24, and 30 months. At the last period (84 months), the value showed an increase of 57.67%. Concerning the HDPE (2.5 mm) the results showed increases in values after all the periods. The OIT tests values were very low for all intact and exposed samples.

Keywords: HDPE geomembrane, weathering, degradation, OIT tests.

INTRODUCTION

Natural sunlight contains UV radiation that may degrade all polymers. Moisture, environmental effects and other site-specific phenomena can affect the degradation rates. The susceptibility of geomembranes (GM) to ultraviolet (UV) degradation is an important issue considering that many geomembranes may be exposed to sunlight for short or long periods in many applications. The consequences of long-term exposure include discolouration, surface cracks, brittleness and deterioration in mechanical properties (Rowe & Sangam 2002).

Many authors (e.g. Sharma & Lewis 1994, Suits & Hsuan 2003, and Koerner 1998) report that HDPE geomembranes (GM) are very susceptible to photochemical degradation that is the main factor which causes UV degradation. HDPE GMs are polyolefins and they are more susceptible to UV degradation than other types of polymers. To prevent the degradation process many UV stabilizers are used in polyolefins geomembranes and the service lifetime is initially governed by the consumption of antioxidant stabilizers. Hindered Amines (HALS) are primary antioxidants, which involve a cyclic and regenerative stabilization process.

Suits and Hsuan (2003) described three different groups of UV stabilizers: carbon black, UV screener, and antioxidants. The loading range of carbon black in HDPE geomembranes is typically 2 to 3% (HDPE). Antioxidants are introduced to prevent oxidation during extrusion and to ensure long-term service life of the product (Fayoux et al. 1993, van Santvoort 1994, Sharma & Lewis 1994, Koerner 1998, and Suits & Hsuan 2003). Tests like MFI and OIT are used to detect the oxidative degradation in polyolefins. In practice, a 0.15m soil over the geomembrane would be sufficient to protect it from UV light (Koerner *et al*. 1990).

This paper presents results of MFI and OIT tests in HDPE geomembranes which were exposed to outdoor conditions after 6, 12, 18, 24, 30, and 84 months.

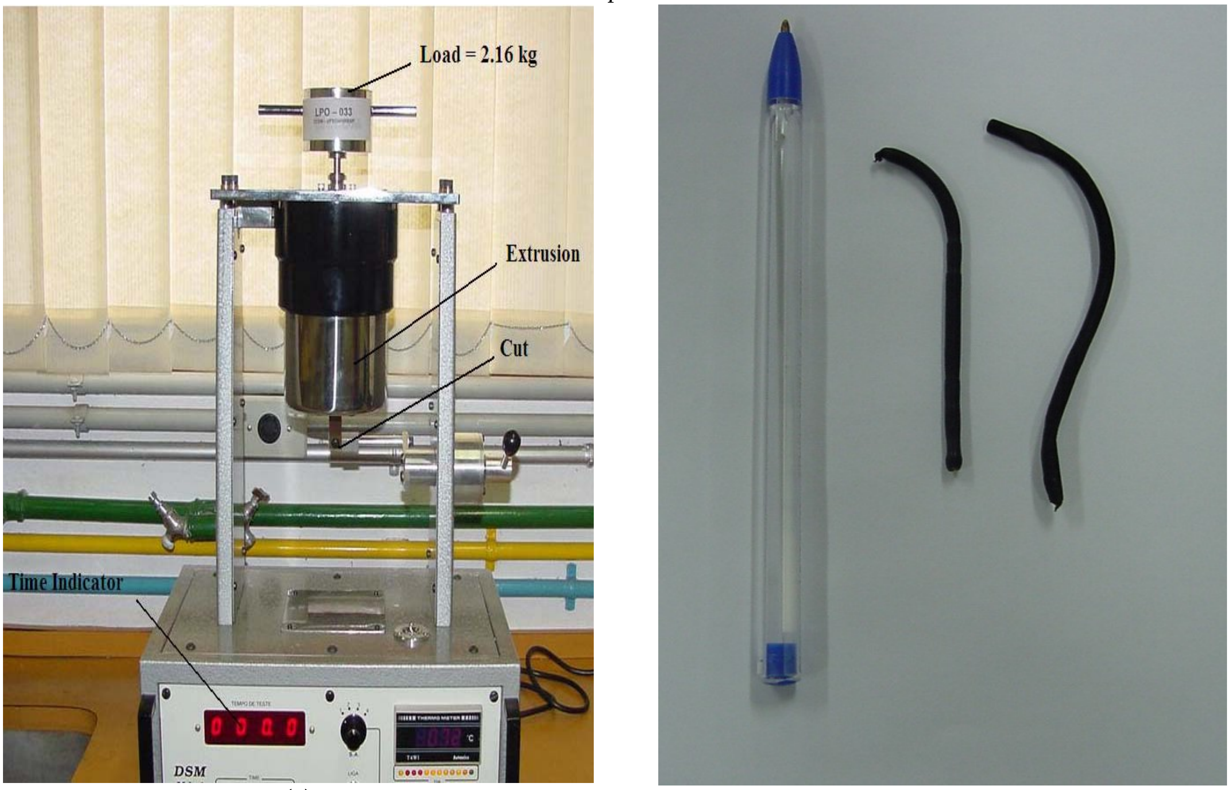
MATERIAL AND METHODS

HDPE geomembranes (0.8 and 2.5 mm thick) were exposed and evaluated after several periods: 6, 12, 18, 24, 30, and 84 months. The outdoor exposure was evaluated according the ASTM D 1435 and D 5970. The samples were exposed on a panel with an inclination of 45 degrees. The aging agents were solar radiation, temperature fluctuations, humidity, wind, and rain after the 6, 12, 18, 24, 30 and 84 month test periods.

Melt flow index (MFI) and oxidative induction time (OIT) tests were evaluated and compared to intact material to assess the oxidative degradation. For this purpose, the ASTM specifications were used: ASTM D1238 (Test Method for Flow Rates of Thermoplastics by Extrusion Plastometer Endurance of the Geomembrane under Examination) and ASTM D3895 (Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning).

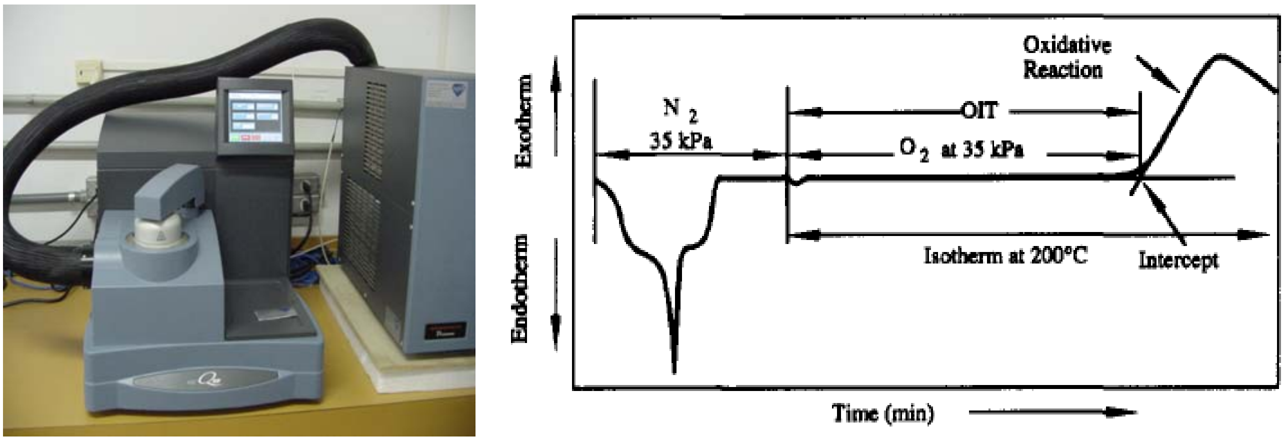
The MFI test measures the amount of molten polymer at 190ºC extruded through an orifice with a defined diameter under a load of 2.16 kg in 10 minutes (ASTM D1238). The apparatus utilized in the MFI test is illustrated in the Figure 1.

The OIT tests were performed in accordance to ASTM D3895 (Standard Oxidative Induction Time – Sdt-OIT) that uses a differential scanning calorimeter (DSC) with a specimen test cell that can sustain a 35 kPa gauge pressure. The specimen is heated from room temperature to 200ºC at a heating rate of 20ºC/min under a nitrogen atmosphere (Figure 2a). At 200ºC an isothermal condition is maintained for 5 min and the nitrogen gas is replaced by oxygen gas. The test is finished when an exothermal peak occurs (oxidation of material). The minimum OIT value required is 100 minutes (GRI – GM13). Figure 2b shows an example thermal curve.



(a) (b)

Figure 1. (a) MFI test equipment (b) extruded samples



(a) (b)

Figure 2. (a) OIT test equipment (b) thermal curve (after Hsuan & Koerner 1998)

RESULTS AND DISCUSSION

MFI and OIT tests results are presented in Tables 1 and 2, respectively. Figure 3 shows the variation of MFI results and the Figure 4 presents the OIT tests results (fresh samples).

The MFI results show some decreases to HDPE (0.8 mm) after 6, 12, 24, and 30 months. At the last period (84 months), the value showed an increase of 57.67%. It seems that the values showed a trend of decrease until 30 months and after that an inverse trend occurred on its behavior. This trend may be visualized in Figure 3. Concerning the HDPE (2.5 mm) the results showed increases in values after all the periods with the highest value being reached at the final period (78.90%). The trend of these values may be observed in Figure 3. Unfortunately, results of MFI tests were not available within the 30-84 months interval.

Table 1. Comparison of MFI tests results

Condition	HDPE (mm)	MFI (g/10 min)	Variation (%)	Probably meaning
Intact	0.8	0.1778	-	-
	2.5	0.1460	-	-
After 6 months	0.8	0.1738	(-) 02.23	CL
	2.5	0.1688	(+) 15.65	CS
After 12 months	0.8	0.1665	(-) 06.34	CL
	2.5	0.1801	(+) 23.34	CS
After 18 months	0.8	0.1622	(-) 08.75	CL
	2.5	0.2010	(+) 37.67	CS
After 24 months	0.8	0.1538	(-) 13.50	CL
	2.5	0.2126	(+) 45.60	CS
After 30 months	0.8	0.1500	(-) 15.64	CL
	2.5	0.2302	(+) 57.67	CS
After 84 months	0.8	0.2515	(+) 41.45	CS
	2.5	0.2612	(+)78.90	CS

(+) increase; (-) decrease; CL = Crosslink; CS = Chain Scission

According the Hsuan & Koerner (1998) the MFI test is a qualitative method to assess the molecular weight of the polymer and may be used like an indicator of oxidation. A high MFI value indicates a low molecular weight, and vice-versa. Hence, the MFI value will decrease to cross-linking reactions and will increase to chain scission reactions. When cross-linking reactions occurs the level of degradation in polymer is superficial but when chain scission occurs it means that the level of degradation may cause severe alterations in tensile properties. According the Rowe & Sangam (2002) when chain scission occurs and as the degradation progresses further, the geomembrane will become increasingly brittle and the tensile properties change to the point that cracking occurs in stressed areas. Stress cracking is important because: (a) even short cracks can allow excessive leachate through the geomembrane that may readily move laterally in areas of poor contact between the geomembrane and the underlying clay; and (b) short cracks can grow with time eventually allowing excessive leakage through the geomembrane even in areas of good contact with the clay. In either case, once the leakage increases substantially, the geomembrane ceases to perform the barrier function for which it was designed as discussed by Rowe et al. (1998). Once sufficient cracks have developed to signicantly increase flow through the geomembrane, the geomembrane may be considered to have reached the end of the service life.

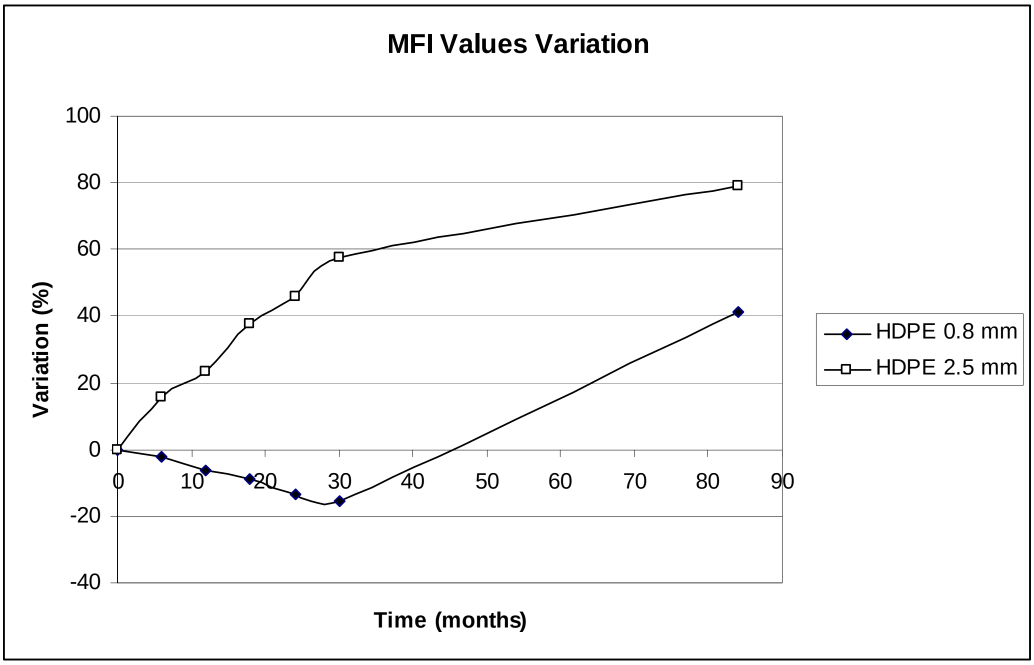


Figure 3. Variation of MFI results

Table 2. OIT tests results

Condition	HDPE (mm)	OIT (min)
Intact	0.8	12.55
	2.5	10.05
After 06 months	0.8	10.10
	2.5	10.00
After 12 months	0.8	9.60
	2.5	9.90
After 18 months	0.8	8.00
	2.5	9.50
After 24 months	0.8	8.60
	2.5	10.00
After 30 months	0.8	8.11
	2.5	11.28
After 84 months	0.8	1.20
	2.5	0.80

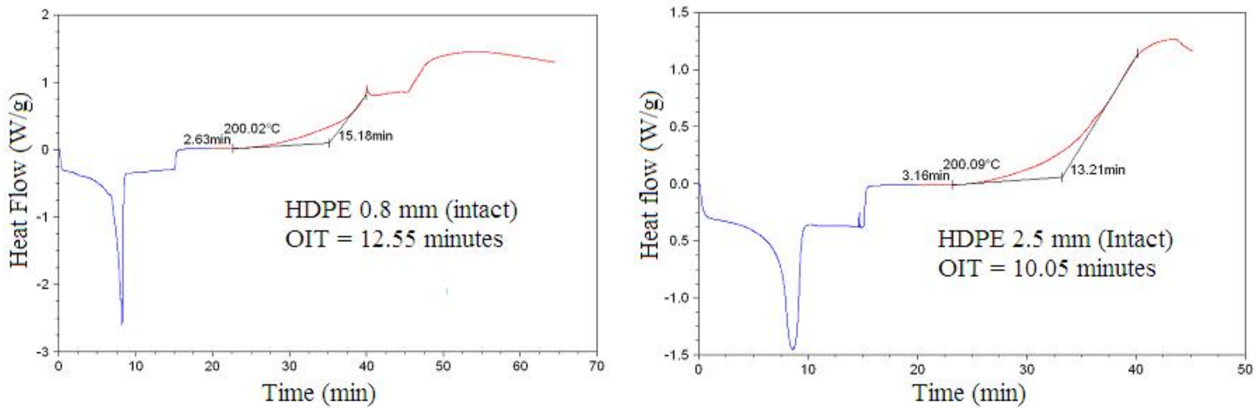


Figure 4. OIT tests results (HDPE) – fresh samples

OIT is the time required for the geomembranes test specimen to be oxidized under a specific pressure and temperature. Since the antioxidants protect the geomembrane from oxidation, the OIT value indicates the amount of antioxidant remaining in the test specimen (Hsuan & Koerner 1998).

The OIT tests values were very low for all intacts and exposed samples. The minimum value required (100 minutes, GRI Test Method GM13, 2006) was not achieved. After the last period the OIT values were practically negligible: 1.20 minutes (HDPE 0.8 mm) and 0.80 minutes (HDPE 2.5 mm).

The 200°C employed in Std-OIT test is unable to evaluate the stabilization effect of Hindered Amine (HALS) antioxidants because the maximum effective temperature of the HALS is below 150°C. Thus, at 200°C HALS molecules may quickly volatize from the geomembrane losing, therefore, their intended effect at in-situ temperatures. To address this concern, the HP-OIT (High Pressure) test may be used. In this test the 150°C isothermal temperature is specified because HDPE GMs reaches complete melting at approximately 140°C which is the highest temperature that should be considered to minimize the degradation of the HALS. However, the HP-OIT is not a common test, is expensive, has a longer testing time (up to 300 minutes), a special testing cell and set up are required, and it is specific for some OIT values (it can’t detect short OIT values). Hsuan & Koerner (1998) report that the major differences between the two OIT tests are oxygen pressure and isothermal temperature. Their differences create somewhat of a dilemma insofar as the selection of a preferred test method for OIT.

CONCLUSIONS

MFI and OIT tests were used to evaluate the oxidative degradation on the HDPE geomembranes after outdoor exposure.

Results of MFI tests showed that some levels of superficial degradation occurred in HDPE 0.8 mm until 30 months of exposure. After that test duration , the MFI value showed that chain scission had started. Chain scission was verified for the HDPE 2.5 mm after all the test periods.

The OIT tests results were very low for both fresh and exposed samples. In spite that the Std-OIT test may be unable to evaluate certain antioxidants packages, a comparison with MFI values show that the material had incurred some level of oxidative degradation.

Corresponding author: Prof Paulo César Lodi, São Paulo State University (UNESP) at Ilha Solteira, Alameda Bahia, 550 - Centro, Ilha Solteira, São Paulo, 15385000, Brazil. Tel: (+55) 18 3743 1217. Email: plodi@dec.feis.unesp.br.

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