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Thermal degradation of geomembranes after exposure to heat

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ABSTRACT: HDPE and PVC geomembranes are sensitive to changes in their properties when in contact with high temperatures. The effects of hot temperature on polymeric geomembranes are assessed by the ASTM D794 and ASTM D5721.

This paper brings an analysis of degradation of the Poly Vinyl Chloride (PVC) and High Density Poly Ethylene (HDPE) geomembranes when exposed to conventional and air oven after specific periods.. Mechanical and physical properties were evaluated. OIT tests were also performanced to evaluate the level of oxidation degradation occurred on the HDPE geomembranes. Geomembranes of two thicknesses were tested: 1.0, 2.0 mm (PVC) and 0.8, 2.5 mm (HDPE). The results obtained show, for example, that after the last period of exposure, the PVC geomembranes (1.0, 2.0 mm) were more rigid and stiffer than fresh samples. The HDPE geomembranes, on the other hand, when exposed to heat presented increases in deformation. OIT tests showed efficient to detect some level of degradation on the HDPE geomembranes.

1 INTRODUCTION

Several properties of polymeric geomembranes are sensitive to changes in temperature. Changes in their mechanical and chemical properties can occur in contact with heat or UV radiation. The time and severity of the exposure will determine the degree of those changes (van Zanten, 1986).

This paper brings an analysis of degradation of the Poly Vinyl Chloride (PVC) and High Density Poly Ethylene (HDPE) geomembranes when exposed to conventional oven (after 6, 12, 18 and 30 months) and air oven (after 1, 2, 3, 6 and 14 months). Mechanical and physical properties were evaluated. OIT tests were also performanced to evaluate the level of oxidation degradation occurred on the HDPE geomembranes.

2 HEAT EFFECTS AND EVALUATION

2.1 *Thermal degradation*

Polymeric geomembranes are sensitive to changes in both warm and cold temperatures, each causing its own effects. ASTM D 794 is used to assess the consequences of hot temperature on polymeric geomembranes. Cold temperatures have less critical effects than warm ones, nevertheless the membrane's flexibility decreases and seams are more difficult to make. ASTM D2102 and D2259 characterize the contractions of the membrane, while D1042 and D1204 characterize the expansion and changes of dimensions (Reddy & Butul, 1999).

The rupture due to heat is defined as a change in the appearance, weight, dimensions or other properties that may alter the material to a degree that it is no longer acceptable for the service in question. Increases of material crystallinity associated with an increase of density may occur. In fact, the temperature is an important parameter in the aging process due to its capability to influence mechanical (strength and elongation) and abrasion properties. High temperature can lead to decrease in the bending stiffness, reduction in resistance to chemicals, increase in the speed of creep and increase in process of thermo-oxidation. Temperature affects seaming, embrittlement (low temperature), shrinkage, and softening (high temperature) (van Santvoort, 1994; Reddy & Butul, 1999).

Temperature in the sample may be significantly higher than in the surrounding environment, this is due to the material's thickness and opacity.

Fayoux et al. (1993) carried out tests on the PVC geomembranes to evaluate its durability. The results show that temperature causes the evaporation of plasticizers, which at 40°C is about 0.7 to 3.5 g/m^2/year. Pierson et al. (1993) assessed the thermal behavior of geomembranes exposed to solar radiation, which induces problems (such as wrinkles) and, even flaws at the construction stage, when the geomembrane is still uncovered by waste. Temperatures may reach 80°C in black exposed geomembranes, such temperatures acting on material with high coefficients of thermal expansion cause wrinkles over the entire exposed surface of the geomembrane. It was proven that a white coating applied on the surface of the membrane reduces considerably the overheating of the material and that the use of a geotextile over a black geomembrane only delays the overheating, so this is not an appropriate means to eliminate long-term overheating.

Maia (2001) evaluated the level of degradation of HDPE and PVC geomembranes after 1, 2, 3 and 9 months of exposure to heat in an air oven (75°C). Mechanical and physical properties were evaluated. TGA and DSC were also carried out. Results show that many alterations occurred in geomembranes but was not possible detected a tendency on the behavior of the properties *versus* time.

2.1.1 *Oxidation Time Induction (OIT) tests*

Oxidative degradation is an auto-accelerated process (autoxidation) that increases rapidly after a certain induction period with no significant changes in the polymer properties. The molecular weight distribution is shifted towards lower values, the material becomes brittle and loses finally all mechanical resistance. Since at the beginning the reaction rate at ambient temperatures is very low the induction time is quite large. Depending on the amount of free radical sources and the sensitivity of the polymer to oxidation the induction time might range from a few years to some decades. Antioxidants are mixed into the polymer to protect it from oxidation. Each antioxidant has a temperature range in which it functions most effectively. There are antioxidants which have their effective temperature range at higher temperature and are used as processing stabilizers (phosphites) and there are others which have their most effective temperature range at ambient temperature (HALS) or over a wide range of temperature (hindered phenols) and which are used as long-term stabilizers to provide protection during the low temperature service time (Mueller & Jakob, 2000).

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 method ASTM D3895 (Standard Oxidative Induction Time – Sdt-OIT) 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 200°C at a heating rate of 20°C/min under a nitrogen atmosphere. At 200°C an isothermal condition is maintained for 5 min and the nitrogen gas is changed by the oxygen gas. The test is finished when an exothermal peak occurs (oxidation of material). The minimum OIT value required is 100 minutes.

A complete and great review on the process of oxidative degradation can be found in the papers of Rowe & Sangam (2002) & Hsuan and Koerner (1998).

3 METHODS AND PERFORMANCED TESTS

Geomembranes were exposed to the heat in a conventional oven (after 6, 12, 18 and 30 months at 85°C) and an air oven (after 1, 2, 3, 6 and 14 months at 75°C). The tests were conduced as specified in ASTM D794 and D5721. Geomembranes of two thicknesses were tested: 1.0, 2.0 mm (PVC) and 0.8, 2.5 mm (HDPE). The Standard Specification GM13 (Test Properties, Testing Frequency and Recommended Warranty for High Density Polyethylene (HDPE) Smooth and Textured Geomembranes) recommends the temperature at 85°C to evaluate the OIT after 90 days of exposure under effects of heat. Mechanical and physical properties were evaluated and compared to intact samples. The OIT tests were performanced in accordance to ASTM D3895.

4 TEST RESULTS AND DISCUSSION

The Figure 1 shows the variations of tensile properties for both HDPE and PVC geomembranes. Results of OIT tests are presented in Table 1. These values refer only the last period: 30 months (conventional oven) and 14 months (air oven).

Table 1. Results of OIT tests.

Exposure	HDPE (mm)	OIT (min)
Intact	0,8	12,55
	2,5	10,05
Conventional Oven	0,8	1,68
	2,5	0,96
Air Oven	0,8	1,88
	2,5	0,97

Concerning exposure to conventional oven the PVC geomembranes presented a generalized tendency. Some increase in deformability occurs at the initial periods. However, decreases were verified after the final period. After 18 months, the variations observed were of 30 to 45% (decrease). In spite of reduction at the last period, the variations were 20 to 30%.

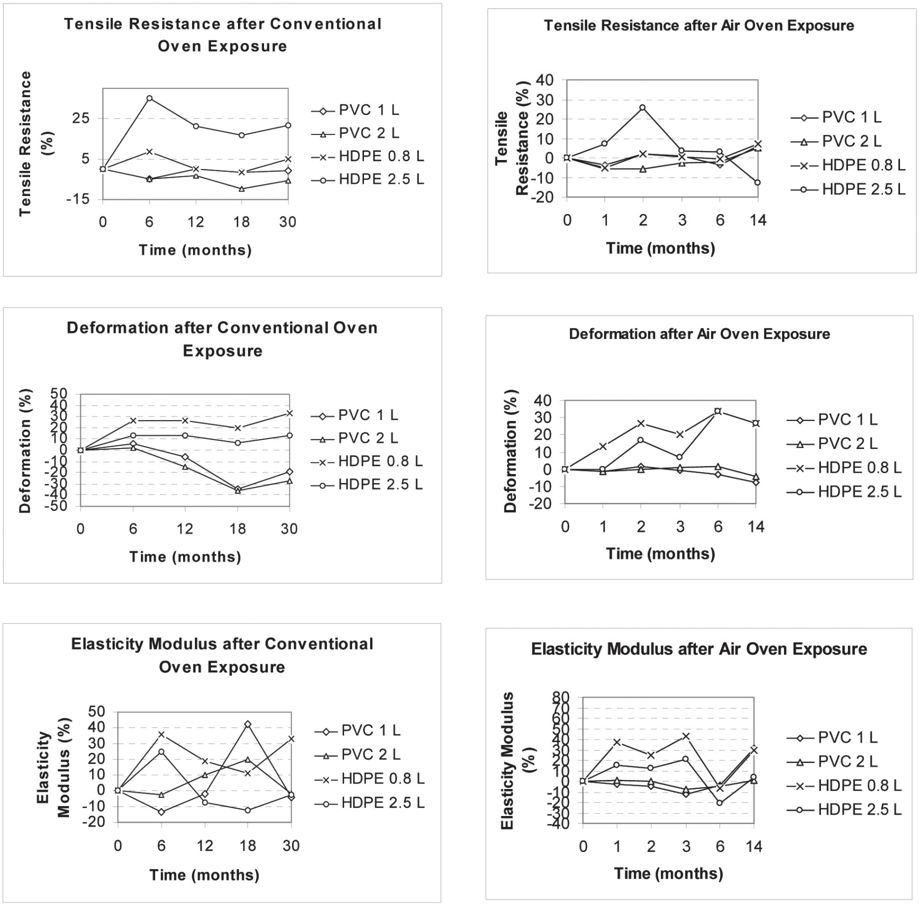

Figure 1. Tensile properties after exposure to heat.

Conversely, the HDPE showed tendency of increase in deformability.

Regarding to stiffness, the PVC geomembranes showed some decrease at the first period but increases were noted until 18 months. At this time the increase reached 40% (PVC 1L). At the last period the values decreases to values nearest to the initial values. HDPE geomembranes (0,8 mm) showed the largest variations. Initially it was observed an increase to all the samples. However, the stiffness shows decreases until the final period. Despite of decreases in stiffness to the HDPE (2,5 mm) after 6 and 18 months, some increases were noted at the final period.

Concerning to the air oven the PVC show some oscillations in tensile resistance (increases *versus* time). At the final period (14 months) the variations were of 5 to 10%. Similarly, the deformability don't show great variations. After 14 months some decreases occurred (5 to 18%). The stiffness shows some oscillations after 3 and 6 months, however, after 6 months a general tendency of increase appears. Is spite of oscillations of stiffness a great variation does not occur considering the time of exposure. The variations in tensile resistance and deformability indicate that the PVC showed some decreases in deformability and increases in stiffness.

The HDPE showed some decreases in deformability after 3 months (0,8 and 2,5 mm). However, the property increased at the final period (20 to 35%). In general, the stiffness showed decreases after the exposure. The HDPE became softer.

The OIT tests presented shorter values (intacts and exposed samples). The HDPE exposed presented OIT values nearest to zero both conventional and air oven. Hsuan & Koerner (1998) explain that the high temperatures employed in the Std-OIT test may bias the test results for certain types of antioxidants, such as HALS antioxidants.

5 CONCLUSIONS

The behaviour of the geomembranes after the exposures to heat showed that both conventional and air oven affects the membranes in the same way. In general, PVC geomembranes showed some decrease in deformability and some increase in tensile resistance and stiffness (especially in the smallest thicknesses). Conversely, HDPE geomembranes presented increase of deformability and decrease of stiffness after the periods of analyses. Considering the time, the air oven exposure affects more severity the membranes.

The OIT values were inexpressive. We must take in account that the Std-OIT test may be unable to evaluate certain antioxidants packages.

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