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The Effects of Weathering Exposure on the Physical, Mechanical, and Thermal Properties of High-density Polyethylene and Poly (Vinyl Chloride)

***Paulo César Lodi*[a]**, *Benedito de Souza Bueno*[b], *Orencio Monje Vilar*[b]**

[a]*Department of Civil Engineering, São Paulo State University – UNESP, Av. Eng. Luiz Edmundo C. Coube, 14-01, CEP 17033-360, Bauru, SP, Brazil*
[b]*Department of Geotechnical Engineering, São Carlos School Engineering – EESC, University of São Paulo – USP, Av. Trabalhador São-carlense, 400, CEP 13566-970, São Carlos, SP, Brazil*

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This paper presents results describing the physical, mechanical, and thermal properties (melt flow index - MFI and oxidative induction time - OIT) of high density polyethylene and poly (vinyl chloride) after weathering exposure (6, 12, 18, and 30 months). The materials exposed were geomembranes of two thicknesses: 1.0 and 2.0 mm (PVC) and 0.8 and 2.5 mm (HDPE). The climate parameters (average) obtained were 25 °C (temperature), 93 mm (precipitation), 66% (relative humidity), and 19 MJ/m^2.day (intensity of global radiation). Some results showed, for instance, that the behavior of the geomembranes changed after the exposures. A few minor variations in physical properties occurred. The density and thickness, for instance, varied 0.5-1.0% (average) for both the PVC and HDPE geomembranes. The mechanical properties changed as a function of the period of exposure. In general, some decreases were verified by the deformation of PVC. The samples became more rigid. In contrast, HDPE geomembranes became more ductile. Despite the variations in elasticity, some increases in deformability were verified. An MFI test showed some degradation in HDPE geomembranes. OIT tests revealed small values for both intact and exposed samples.

Keywords: *HDPE and PVC geomembranes, weathering exposure, physical and mechanical properties, oxidative degradation*

1. Introduction

Geomembranes (GM) are essentially impermeable membranes (synthetic materials are also called geosynthetics) that are widely used in many civil and environmental applications. Polyethylene (PE) and poly (vinyl chloride) (PVC) are the two most widely used geomembranes for environmental applications. The approximate formulations of PVC and HDPE geomembranes are HDPE (96-98% resin, 2-3% carbon black or pigment, and 0.25-1.0% additives) and PVC (50-70% resin, 25-35% plasticizer, 0-10% filler, 1-12% carbon black or pigment, and 2-5% additives)[1,2]. The GMs should not only have chemical resistance and low permeability but also remain chemically and mechanically stable (durable) over the design life.

Prior field studies and laboratory tests have demonstrated that GMs age with time. The severity of aging depends on the exposure media (e.g., air, water, leachate, hydrocarbons, acid mine drainage) and temperature[2-4]. When used in canals and dams, for instance, the ultraviolet radiation and elevated temperatures are very harmful to all polymers. In high-density polyethylene (HDPE) geomembranes, for instance, oxidation degradation may occur, in which the molecular chains are cut off. If oxidation begins, the molecular chains maintain the degradation process. This process results in a totally changed molecular structure, a decrease in mechanical resistance, and initiation of the stress-cracking phenomenon. The loss of plasticizers and volatiles may occur in PVC geomembranes, resulting in a decrease in elongation and an increase in brittleness. To increase the resistance of the geomembranes, antioxidant (AO) agents and UV stabilizers are added during the manufacturing process. The vital role of AOs in preventing the onset of oxidation degradation is clearly demonstrated by Hsuan et al.[1]. To ensure the proper AOs are being added to geosynthetics, the current practice is to use GRI-GM13[5] and GRI-GM17[6], in which the initial AO amount and AO depletion rate after incubation in forced air ovens and weatherometers are specified in terms of oxidative induction time (OIT) values.

The most important concern when studying oxidation degradation is how it affects the mechanical properties of the material. Tensile tests are often used to assess changes in polymeric materials. Depending on the type of geosynthetic products, appropriate standard tensile test methods should be used. For example, ASTM D 638[7] is used for the evaluation of the tensile properties of geomembranes, and ASTM D 3822[8] is used for testing filaments. The properties that are strongly correlated to degradation are the tensile break strength and the elongation. There should be no change in these mechanical properties until essentially all of the AOs have been depleted[1].

Because many applications must be taken into account, mimicking the duration and intensity of exposure in

*e-mail: plodi@feb.unesp.br

applications such as those involving canals, dams, and reservoirs is very important for evaluating the effects of outdoor exposure[2-4].

This paper presents the results of physical, tensile, puncture, tear, MFI, and OIT tests conducted on HDPE and PVC geomembranes that were exposed to weathering (solar radiation, humidity, wind, rain) for 6, 12, 18, and 30 months.

2. Experimental

Geomembranes of two thicknesses were tested: 1.0 and 2.0 mm (PVC) and 0.8 and 2.5 mm (HDPE). The exposure periods were 6, 12, 18, and 30 months.

The ASTM D 1435[9] was used to conduct the weathering exposure. A panel was built and located along the east-west axis (Figure 1). The samples were fixed to receive direct solar incidence throughout the whole day. The site is located at the following geographical coordinates: 20°22' S latitude and 51°22' W longitude. The altitude is 335m. Monitoring of the climate conditions was conducted with a microdatalogger CR-23X.

Physical and mechanical tests on HDPE and PVC geomembranes were conducted, and the results were compared with fresh samples. OIT and MFI tests were also performed on HDPE geomembranes after the last period to verify the oxidative degradation. These tests are not performed in PVC geomembranes[2,3].

The following ASTM standards were used: ASTM D 5199[10] (Measuring Nominal Thickness of Geotextiles and Geomembranes), ASTM D 3776[11] (Mass Per Unit Area), ASTM D 792[12] (Specific Gravity and Density of Plastics by Displacement), ASTM D 638[7] (Standard Test Method for Tensile Properties of Plastics), ASTM D 4833[13] (Test Method for Index Puncture Resistance of Geotextiles, Geomembranes, and Related Products), ASTM D 1004[14] (Test Method for Initial Tear Resistance of Plastic Film and Sheeting), ASTM D 1238[15] (Test Method for Flow Rates of Thermoplastics by Extrusion Plastometer Endurance of the Geomembrane Under Examination), and ASTM D 3895[16] (Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning).

3. Test Results and Analysis

The climate parameters (average) obtained were 25 °C (temperature), 93 mm (precipitation), 66% (relative humidity), and 19 MJ/m^2.day (intensity of global radiation).

The physical properties showed small variations (increases ≈ 0.5-1.0% - thickness and density) for both PVC and HDPE geomembranes. Table 1 presents the results of physical properties.

The results of the tensile test and tear and puncture resistance tests are presented in Figure 2 and Figure 3, respectively.

Figure 1. HDPE and PVC geomembranes samples exposed to weathering.

Table 1. Results of thickness and density of geomembranes after weathering exposure.

Exposure period (months)	Thickness (mm)				Density			
	HDPE		PVC		HDPE		PVC	
	0.8	2.5	1.0	2.0	0.8	2.5	1.0	2.0
Intact	0.780	2.480	0.990	2.040	0.95	0.95	1.23	1.23
6 months	0.781	2.490	0.993	2.042	0.95	0.95	1.23	1.23
12 months	0.782	2.499	0.993	2.044	0.96	0.96	1.23	1.24
18 months	0.783	2.505	0.994	2.047	0.96	0.96	1.24	1.24
30 months	0.784	2.510	0.995	2.048	0.96	0.96	1.24	1.24

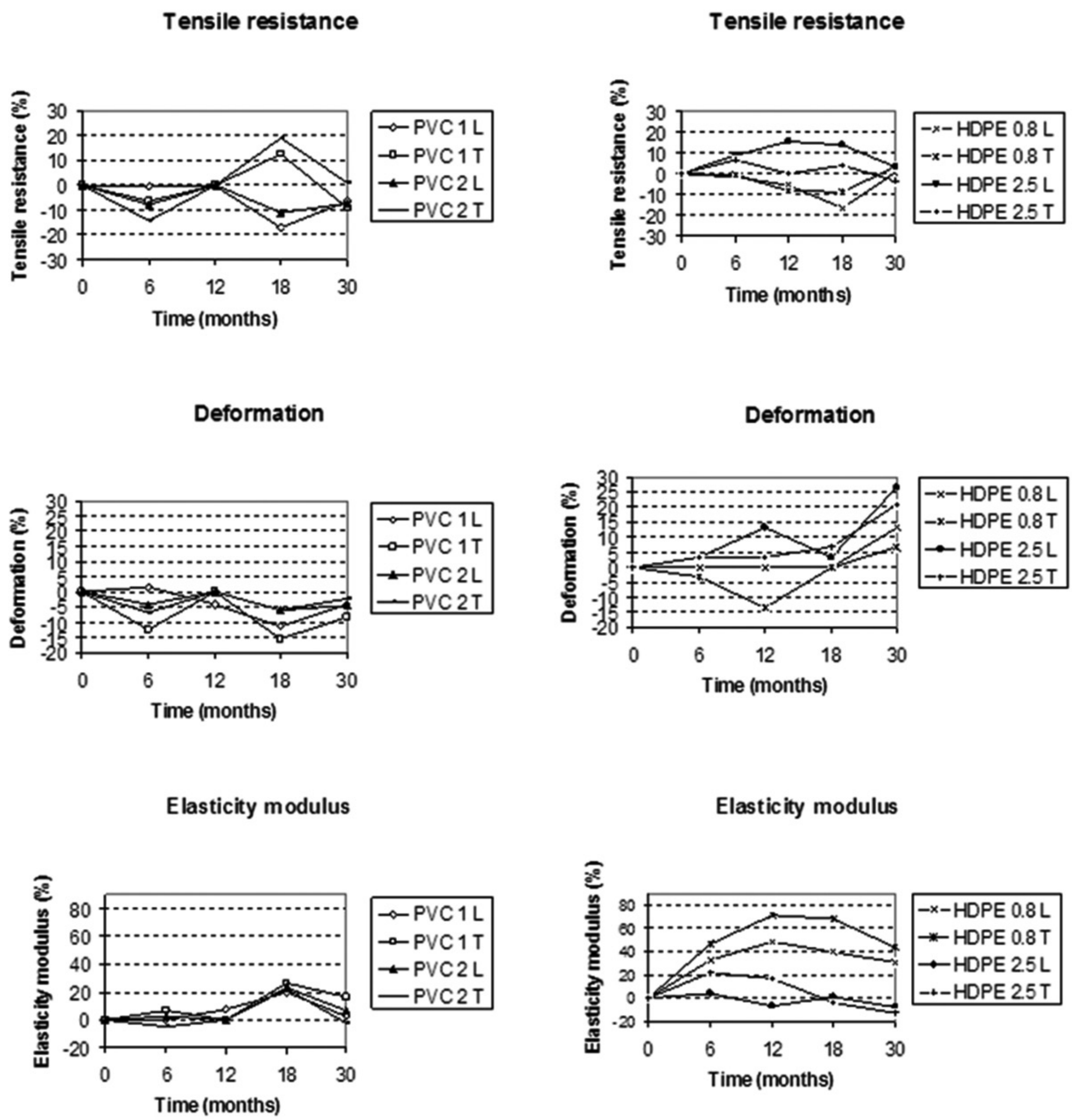

Figure 2. Effects of weathering exposure on mechanical properties after 30 months.

Concerning the tensile properties, the results show some variations for both PVC and HDPE geomembranes after the periods of exposure. After 6 months of exposure, the PVC geomembranes showed alterations in tensile resistance, decreases in deformation, and increases in stiffness. After 18 months, the increases in deformation and elasticity presented the higher variations for the PVC geomembranes (1.0 mm thickness was more affected). The samples became more rigid and stiffer than unexposed samples. Concerning the HDPE geomembranes, more significant variations occurred in the deformation after 30 months (increases in deformation and some variations in elasticity). The behavior was characteristic of a ductile material[3,4].

The tear resistance presented variations for both HDPE and PVC geomembranes. The PVC geomembranes showed a few minor changes for all periods. Increases in tear resistance were verified, but these values were not greater than 20%. For the HDPE geomembranes, the variations were more significant than those observed for PVC. There was an almost 40% increase at 12 months. After 18 months, the samples showed relevant variations, but some decreases occurred in the last period. Interestingly, the larger thickness showed the higher variations.

The puncture resistance did not vary for the HDPE geomembranes after the final exposure period. In contrast, the PVC geomembranes showed significant variations for the smallest thickness. The increases in puncture resistance were greater than 40% after 18 months, and the puncture resistance decreased a small amount in the last period.

The MFI and OIT test results are presented in Tables 2 and 3, respectively.

The MFI test is only performed for polyethylene geomembranes[2,3]. The MFI value for HDPE (0.8 mm) decreased for all the periods. After 6 months of exposure, the decrease was approximately 5.28%. The MFI value for HDPE (0.8 mm) after outdoor exposure for 30 months was

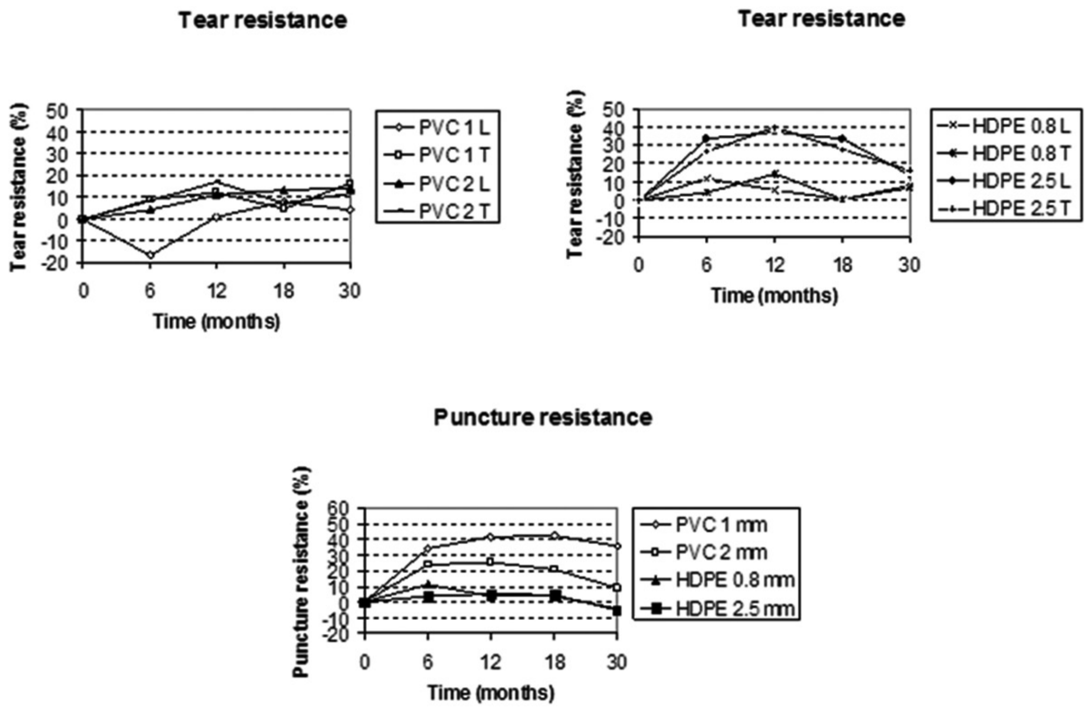

Figure 3. Effects of weathering on tear and puncture resistances after 30 months of outdoor exposure.

Table 2. Results of MFI tests after weathering exposure.

Exposure period (months)	MFI (g/10 min)		Variation (%)		Probably meaning	
	0.8 mm	2.5 mm	0.8 mm	2.5 mm	0.8 mm	2.5 mm
Intact	0.178	0.146	-	-	-	-
6 months	0.168	0.177	(–) 05.28	(+) 21.16	CL	CS
12 months	0.163	0.203	(–) 08.32	(+) 38.69	CL	CS
18 months	0.156	0.213	(–) 12.43	(+) 45.68	CL	CS
30 months	0.150	0.230	(–) 15.64	(+) 57.67	CL	CS

(+) increase; (–) decrease; CS = Chain scission (when increases occurs in MFI value); CL = Crosslink (when decreases occurs in MFI value).

Table 3. Results of OIT tests after weathering exposure.

Exposure period (months)	OIT (min)		Observation	
	0.8 mm	2.5 mm	0.8 mm	2.5 mm
Intact	12.55	10.05	1	1
6 months	11.50	10.04	1	1
12 months	10.20	10.02	1	1
18 months	9.00	10.01	1	1
30 months	8.11	09.97	1	1

[1] shorter than 100 minutes (minimum value).

15.64%. Even though this value is not very significant, it could be considered an indication of crosslinking in the polymer[2,3,5,15,17]. In contrast, the MFI values increased for all the periods of exposure for the HDPE (2.5 mm). After the first period, the value was 21.16%. The values continued to increase over time. After 30 months, a significant increase in the MFI value of 57.67% occurred in HDPE (2.5mm). The MFI results obtained are in agreement with those published in the literature[17,18]. The MFI test is an indirect method to assess molecular weight of the polymer. A high melt index value indicates a low molecular weight, and vice versa. Hence, MFI can be considered as an indicator of oxidation degradation.

The variations in MFI values indicate that some level of degradation occurred in both HDPE geomembranes. The most significant was the HDPE (2.5 mm), which indicates chain scissioning[2,15,17]. When chain scissioning 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. Once sufficient cracks have developed to significantly increase flow through the geomembrane, the geomembrane may be considered to have reached the end of its service life[17,18].

The OIT values for unexposed HDPE geomembranes were 12.55 (0.8 mm) and 10.65 (2.5 mm), respectively. The minimum value expected is 100 minutes[2,5]. OIT tests are unusual for PVC geomembranes. The OIT test results show that the obtained values for both thicknesses are not in agreement with the literature[4,15]. The values indicate that a poor-quality antioxidant package was used in the geomembranes. Antioxidants are introduced for the purposes of oxidation prevention during extrusion and to ensure a long-term service life of the product. There are many types of antioxidants, and each of them behaves differently. Usually, synergistic mixtures of more than one type of antioxidants are used. Although the total amount of antioxidants in the geomembrane is relatively small, their existence is vital to the longevity of the product[2,5,17]. However, the high temperatures employed in the Std-OIT test may bias the test results for certain types of antioxidants, such as HALS antioxidants. HALS antioxidants have a maximum effective temperature of 150 °C[2,3,17,18]. The antioxidant package used in geomembrane presented an amount of 0.5% (hindered phenol and hindered amines – primary antioxidants). However, the detailed antioxidant formulation (i.e., secondary antioxidants) was not provided by the manufacturer. The carbon black used was about 2.5% and 2.0% for HDPE and PVC geomembranes, respectively.

4. Conclusions

The physical, mechanical, and thermal properties in HDPE and PVC geomembranes that were exposed to weathering for 6, 12, 18, and 30 months were presented.

Variations in physical properties were not significant for either PVC or HDPE GMs (increases of 0.5-1.0%). The mechanical properties changed according to the period of exposure. Some decreases in the deformation of PVC were verified (the samples became more rigid). In contrast, HDPE geomembranes became more ductile. Despite the variations in elasticity, some increases in deformability were verified. The results of the puncture and tear tests showed some increases with ageing. The tear resistance of the HDPE geomembranes showed more significant increases than that of the PVC geomembranes. However, the puncture resistance increases more mainly for the smallest thicknesses.

The MFI test showed some levels of degradation in the HDPE geomembranes. The thicker membrane showed an increase in MFI values, which most likely indicates chain scissioning. The MFI test is a qualitative test, but it may be able to indicate when oxidative degradation has already started. The OIT tests revealed small values for both intact and exposed samples. The values presented indicate a poor-quality antioxidant package. However, the Std-OIT test may be unable to evaluate certain antioxidant packages. For this purpose, the HP-OIT (High-Pressure) test is more desirable.

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