

Characteristics of six PVC-P geomembranes installed in reservoirs in Spanish Mediterranean Basin

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ABSTRACT: This paper presents the results obtained from six polyvinyl chloride geomembranes (PVC-P) reinforced with a synthetic fabric, installed in irrigation reservoirs for a period between 18-31 years. The geomembranes studied are part of the waterproofing system of the following reservoirs - El Hondon de las Nieves, El Rollo, Pla Aceituna, La Caseta de Mira, El Cid-III y El Rabosero, all of them located on the Spanish Mediterranean County of Alicante.

The following experimental tests and interpretation of results are provided: relative values accounting for loss of plasticizer, tensile characteristics, foldability at low temperatures, dynamic impact resistance, puncture resistance, reflected optical microscopy and scanning electron microscopy (SEM). Also, the identification of plasticizers in the geomembrane entails the performance of Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography (GC) and finally, Mass Spectrometry (MS) tests.

For the samples analysed, the loss of plasticizers is significant, ranging from 70.9% to 84.3%. However, the tensile strength results, give evidence of its current regular waterproofing working performance in the reservoirs. The results obtained suggest that the durability of PVC-P geomembranes is function not only of the loss of plasticizers but also the state of the synthetic reinforced fibres.

Keywords: *Geomembranes, reservoirs, durability, PVC-P, waterproofing.*

1 INTRODUCTION

The use of waterproofing in irrigation reservoirs, located in the Mediterranean basin, started in the 1970s when Butyl rubber (IIR) geomembranes were extensively installed. Even nowadays, some field installations are still in good condition and service. However, there was a problem caused by the double bonds of the macromolecule making it vulnerable to attack by ozone (Blanco 2012). In Spain, before the widely used of polymeric geosynthetic barriers, some water works were previously performed such as the Butyl rubber waterproofing of the "Matavacas" weir in 1974 (Cea et al. 2002, Blanco et al. 2010) and in 1968, the thermoplastic chlorinated polyethylene (CPE) geomembrane applied to the "Odiel Perejil" dam (Blanco & Zaragoza 2003, ICOLD 2010).

As early as the 1980s, the waterproofing system of new earthen reservoirs started to replace butyl rubber (IIR) geomembranes by plasticised polyvinyl chloride (PVC) barriers, generally reinforced with synthetic threads.

Thus, the region of Valencia has widely used vinyl barriers and some of those reservoirs maintain the same waterproofing characteristics right up to the present day while in others, there has been a process of re-waterproofing.

This paper exposes the behaviour of six PVC-P geomembranes reinforced with polyester fabric. They are all located in the province of Alicante in the following irrigation reservoirs: El Hondón de las Nieves, El Rollo, Plá Aceituna, La Caseta de Mira, El Cid-III and El Rabosero

2 DURABILITY OF REINFORCED PVC-P GEOMEMBRANES

The durability of geomembranes not only depends on intrinsic factors such as composition and thickness but also, extrinsic factors including stresses and several environmental agents (Cazzuffi 2014).

As can be imagined, regardless of the nature of the resin, all types of geomembranes are affected by environmental agents. Therefore, a process of photo and thermo-oxidation will produce a set of free radicals generating a homolytic chain reaction that degrades the macromolecule. However, some intrinsic factors are particular of each geomembrane.

The service lifetime of a geomembrane can be assessed through the evolution of one or more key characteristics according to the nature of the case (Noval, 2015). Some authors (Hsuan y Koerner, 1998) argue that the service lifetime would be finished when the aforementioned crucial characteristic has been lost 50% of its initial value.

In the particular case of PVC-P, the loss of plasticisers is the key characteristic to follow. Under this theory, the geomembrane should have to be replaced when the loss of plasticisers would be greater than 50%. Nevertheless, it can be found some geomembranes in Spain with contents lower than 15% but which remain fulfilling their function as waterproofing (Noval et al. 2014, Blanco et al. 2013).

3 THE RESERVOIRS

The technical characteristics of the reservoirs are shown in Table 1, included in which are location, capacity, height, elevation, crest perimeter and date of installation.

Table 1. Characteristics of the reservoirs waterproofed with PVC-P

Reservoir	Hondón de las Nieves	El Rollo	Plá Aceituna	Caseta de Mira	Cid-III	El Rabosero
Location	Hondón de las Nieves	Aspe	Agost	Agost	Monforte del Cid	Aspe
Capacity (m ³)	1213,280	536,000	118,132	269,717	531,810	240,772
Elevation (m)	19.50	16.00	8.25	9.00	12.0	12.80
Height of crest (m)	464	399	388	419	404	260
Crest Perimeter (m)	1068	834	535	780	950	691
Slope gradient - Exterior	1.50:1	1.50:1	1.30:1	1.75:1	1.50:1	1.50:1
- Interior	2.50:1	1.50:1	2.50:1	2.00:1	2.50:1	3.00:1
Year of installation of the geomembrane	1990	1987	1994	1997	1984	1994

Meanwhile, Figure 1 shows a partial overview of the water infrastructures. The waterproofing system of all the geomembranes used in the reservoirs into study came from the same commercial company. Also, all of them share a thickness of 1.5 mm being manufactured through the impregnation process.



Casetas de Mira



Hondón de las Nieves



Plá Aceituna



El Rollo



El Cid III



El Rabosero

Figure 1: Overview of the reservoirs into study

4 EXPERIMENT

The experimental method employed was developed by the European regulation (UNE EN 13 361). Static puncture resistance was particularly performed in accordance with the measurement method developed by the authors which is now part of the standards applied by AENOR (Spanish Organization of Normalization and Certification) (Blanco et al. 1996, UNE 104 317).

All samples were extracted from the crest area of the reservoirs on its northern slope. Since such particular area is facing south, it has the highest incidence of solar radiation (Aguiar et al. 2003, Blanco et al. 2003). In the case of the Hondon de las Nieves reservoir, a sample was

also taken from the intermediate area also on the northern slope, where it is sometimes covered by water and sometimes in contact with solar radiation.

4.1 Plasticizers

The contents of plasticisers was assessed according to the Spanish regulation (UNE 104 306). However, extraction with ethyl ether removes all organic products of low molecular weight, which means it does not extract the vinyl macromolecule and the non-organic material but it does extract other additives distinct from the plasticisers, as in the case of UV light absorbents and antioxidants. For this reason, for the calculation of loss of plasticisers, a correction has been made in accordance with the scientific literature (Giroud 1995). The loss of plasticisers in the geomembranes is summarised in Table 2.

Once the plasticisers were isolated, the process of identification began using, firstly, Fourier transform infrared spectroscopy (Ortega & Blanco 1982, Blanco et al. 1989). A significant number of phthalates bands were observed in the analysis.

Subsequently, in order to complete the identification of the additive, the Gas Chromatography technique was used in combination with Mass Spectrometry (GC-MS.). In order to do this, an Agilent 6890N Network Gas Chromatograph was used with a capillary column of phenyl methylpolysiloxane DB%-MS (30 m x 0.25 x 0.25) coupled with an Agilent 5793 MSD quadrupole mass detector system in electron impact mode. The first of these techniques allow us to observe and separate the number of products which make up “the plasticiser” and the second, the identification of elucidated fractions (Crespo, 2011, Blanco et al. 2008, 2009).

The gas chromatography (GC) provided a chromatogram with a single peak at 82.93 min of retention time. When the plasticiser was subjected to mass spectrometry it produced a spectrum with the following fragmentations: MS, m/z(relative intensity): 390(M^+), 279($C_{16}H_{23}O_4^+, 12$), 167($C_8H_7O_4^+, 39$), 149 ($C_8H_5O_3^+, 100$), 113 ($C_8H_1^+, 9$), 57 ($C_4H_9^+, 18$). This was identified as the Bis (2-ethylhexyl) phthalate. Its molecular weight turned out to be 390, lower than the current recommended value for high-durability PVC-P geomembranes, which is 400 (Reservoirs Handbook MARM 2010, PGI 2004)

The low molecular weight of this additive produces great tendency towards migration, fundamentally, to the air (Stark et al. 2005).

Table 2. Loss of plasticisers in the geomembranes

Reservoir	Loss of plasticisers, %	
	Year sample was taken	
	2012	2015
Hondón de las Nieves	66.6	71.6
El Rollo	84.3	84.3
Plá Aceituna	66.4	70.9
Casetas de Mira	78.5	80.0
El Cid-III	--	78.5
El Rabosero	--	71.1

4.2 Technological characteristics

Samples of the materials from the geomembranes considered were subjected to the foldability test at low temperatures (-20°C), for which they were folded on themselves at an angle of 180° after remaining 5 hours in a cold store. For all the studied cases, the materials have not overcome the foldability test.

From the point of view of dynamic impact, all the samples passed the test over the time, since none of them suffer perforation in the impact zone after throwing a 0.5 kg plunger, drop ended in a semispherical ball of 12.7 mm diameter, from a height of 500 mm.

The mechanical characteristics (tensile and puncture resistance) of the original PVC-P geomembranes are summarised in Table 3. Likewise, the results performed for the samples taken in 2015 are given in Table 4 including values for the traction test, elongation at maximum load, puncture resistance and plunger displacement before perforation.

The polyester fabric reinforcement of the geomembranes is responsible for both the higher values of maximum load at break and the low displacement values of the plunger before perforation occurs.

Table 3. Original characteristics of the PVC-P geomembranes

Characteristic	Value
Traction resistance, N/50 mm	
Longitudinal	2208
Transversal	2203
Elongation at maximum strain, %	
Longitudinal	18
Transversal	33
Puncture resistance, N/mm	
External side	430
Internal side	425
Plunger displacement before perforation, mm	
External side	8
Internal side	7

Table 4. Characteristics of the PVC-P geomembranes

Reservoir	Hondón	Plá	El	Casetas	El	El
	de las Nieves	Aceituna	Rollo	de Mira	Cid-III	Rabosero
Traction resistance, N/50 mm						
Longitudinal	3420	3214	3919	2888	2470	2999
Transversal	2121	2333	3977	1943	902	3145
Elongation at maximum load, %						
Longitudinal	16	23	18	21	14	20
Transversal	19	25	34	24	10	33
Puncture resistance, N/mm						
External side	351	472	829	499	560	445
Internal side	320	433	812	386	378	318
Plunger displacement before perforation, mm						
External side	7	5	12	8	11	3
Internal side	5	5	12	7	8	4

4.3 Microscopic analysis

The microscopic evaluation of geomembranes was carried out according to the literature (Soriano et al. 2010, 2012.). Reflection optical microscopy (ROM) was assessed using a LEICA optical microscope; model DMRX, equipped with an automatic photography system. The scanning electron microscopy (SEM) analysis used a ZEISS SEM (model EVO50), equipped with and Oxford Instruments dispersive x-ray spectrometer (Model INCAPENTAFET X3). Since the materials' samples are electrical insulators, they were

metallised by sputtering a 100 to 200 μm layer of gold palladium. Previously, the samples were placed over a dispersion of graphite in isopropanol.

Microphotographs were taken by reflection optical microscopy (ROM) at (x 40) and (x 60) magnifications in order to study both texture and morphology.

Figure 2 shows the external side at (x60) magnifications for the different geomembranes in 2015. In addition, the condition of the aforementioned geomembranes in 2015 has been tested by scanning electron microscopy (SEM) at (x90) and (x900) magnifications. Figure 3 presents the appearance of the external side of the materials at (x90) magnifications.

Both the ROM and the SEM detect on the external side of each of the geomembranes a significant deterioration with surface cracking.

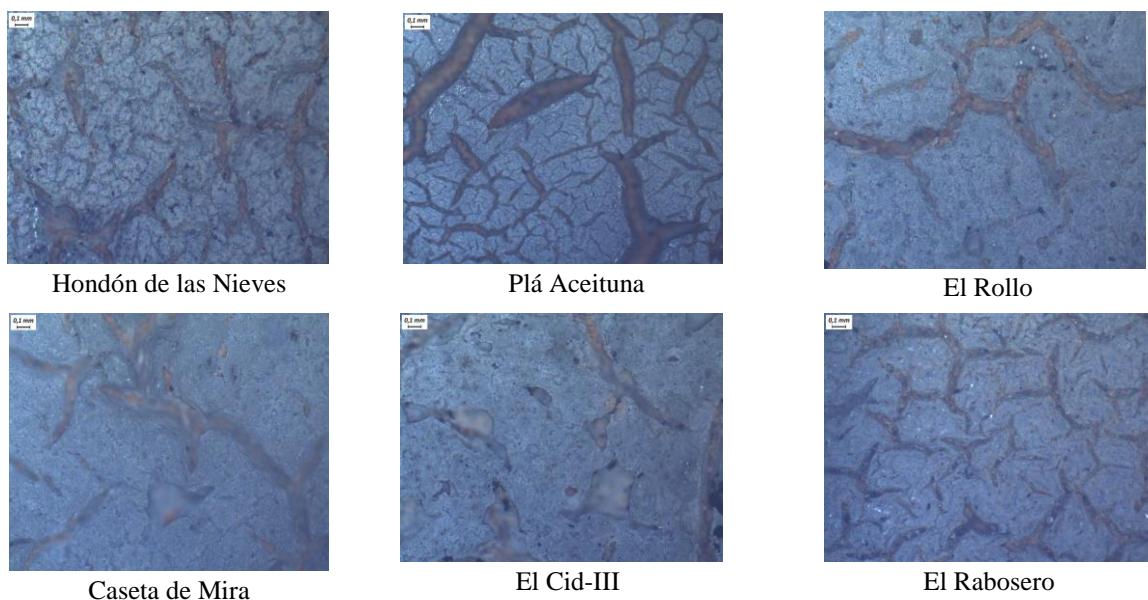


Figure 2. Microphotograph of the external side by ROM at x60 magnifications

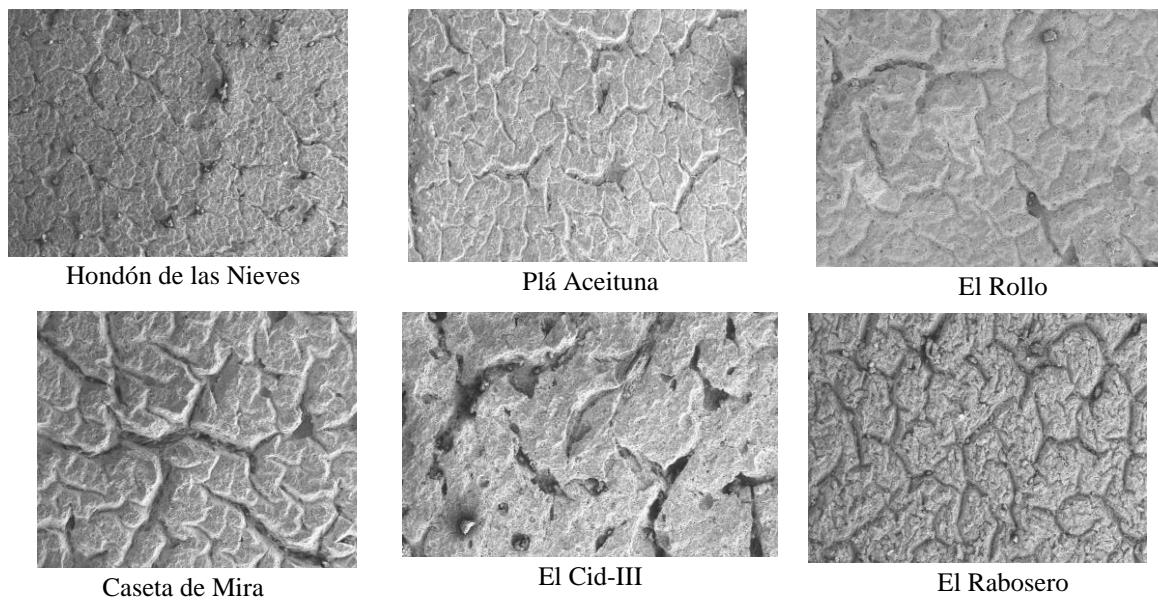


Figure 3. Microphotograph of the external side of the geomembranes by SEM at x90 magnifications

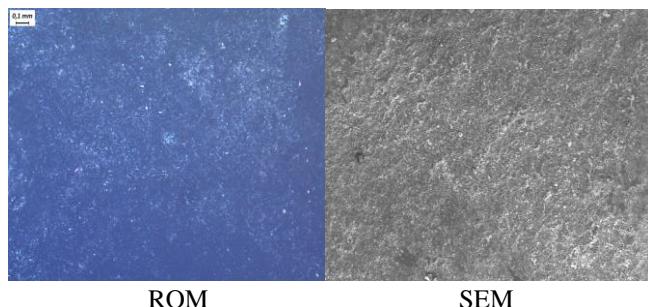


Figure 4. Microphotographs of the internal side of samples from El Cid III reservoir by ROM at x60 magnifications & SEM at x90

Figure 4 shows the microphotographs from the El Cid-III reservoir 31 years after installation, on the internal side, taken using ROM (x60) and SEM (x90) technology. In these, the good condition of the material can be observed. The comparison between the two sides of the tests specimens highlights the effect of UV radiation in the degradation of the organic material.

4.4 *Influence of the sample collection*

Table 5 shows the most significant characteristics of the geomembrane from the Hondón de las Nieves reservoir, 25 years after installation, in samples taken from the Northern slope, in the crest and intermediate areas.

Table 5. Characteristics of the geomembrane at Hondón de las Nieves, 25 years after installation, with reference to the area of the Northern slope from where the samples were taken

	Area from where samples samples were taken	
	Crest	Intermediate
Loss of plasticiser, %	71.6	71.4
Traction resistance, N/50 mm		
Longitudinal	3420	3147
Transversal	2121	2425
Elongation at maximum load, %		
Longitudinal	16	15
Transversal	19	24
Puncture resistance, N/mm		
External side	351	431
Internal side	320	417
Plunger displacement before perforation, mm		
External side	7	8
Internal side	5	9

5 CONCLUSIONS

After the exposition of the most significant findings obtained from the samples of PVC-P geomembranes, some concluding remarks can be established as follow:

1. The mechanical characteristics of these materials are excellent and they have remained well preserved over time. Traction resistance is very high doubling the minimum values required for this type of geomembrane in accordance with the regulations. This issue is

due to the reinforcement geotextile. Only some failures were noticed in the geomembrane installed 31 years ago.

2. The data obtained in the microscopic analysis shows geomembranes whose internal side is in good condition. However, the external side shows severe deterioration, with the presence of surface cracking.
3. The differences between the samples taken at the crest and the intermediate area are not notably significant. But even so, the test specimen from the intermediate area are in better condition as demonstrated by their mechanical and puncture resistance characteristics.
4. Fourier transform infrared techniques, Gas chromatography and mass spectrometry were used to identify the plasticiser forming the geomembrane as Bis(2-ethylhexyl) phthalate, with a molecular weight of 390.
5. The plasticiser has high tendency to migrate to air due to its alkyl radical, which substitutes phthalic acid protons, branched and of a low molecular weight. Thus, leading to the high loss values of this additive.
6. The “impregnation” geomembranes analysed have shown great durability. Basically, due to the right behaviour of the polyester textile of the reinforcement, which being still covered with the vinyl resin has not been affected by solar radiation.
7. Despite the fact that the loss of plasticisers surpasses in each case 70% and in one case 84%, the geomembranes are still installed in the reservoirs and properly fulfilling their function as waterproofing.

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