PVC-P Geomembranes Behaviour in a Ten-Year Water Laboratory Immersion Test

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ABSTRACT: Changes occur with time in PVC-P properties due to plasticizer loss. A water immersion test in the laboratory was performed on 11 geomembranes during 8 to 10 years. Globally, the behaviour observed is relatively good since plasticizer losses are less than 10%, except for 2 materials. A law relating to plasticizer loss as a function of' time is used to assess the lifetime. The lifetime recorded exceeds - and sometimes significantly - 100 years for 9 out of the 11 materials studied, but is very short (26 years) for one of them. Designers are thus faced with the major problem of criteria selection. Correlations with the results obtained during an accelerated immersion test are not perfect, but the material whose properties proved to be very poor in the long term showed very poor properties during the accelerated test. This therefore highlights the interest of such a test type.

1 - INTRODUCTION

PVC-P geomembranes are commonly used owing to their attractive mechanical properties and their easy welding characteristics. Nevertheless the chemical composition of PVC-P is potentially instable. It generally contents 60 to 70 % of polymeric PVC, 30 to 38% of plasticizer and 2 to 10% of various additives (stabilizers, fillers, lubricants). For common uses, the polymer stability is satisfactory, but the plasticizer, which is generally a small molecule, can migrate outside the material and be released to the environment (water or air). This phenomenon is observed to the detriment of a number of functional properties - in particular flexibility - and it affects the material lifetime. Flexibility prediction for a prescribed environment is a major concern for the designer, in particular in structures where the membrane cannot be accessed for repairs (underground structures waterproofing).

A number of plasticizer loss measurements were performed on geomembranes of in-service structures (Giroud and Tisinger, 1993). This paper assesses the evolution of plasticizer losses in 11 geomembranes immersed in water, in the laboratory, during 8 or 10 years ; the results obtained are extrapolated to 50 years, even 100 years (first results published in 1988 after a 4 year immersion, J.P. Benneton). The results of this plasticizer loss assessment were compared to those of accelerated immersion tests.

2 - EXPERIMENT

2.1 - Geomembranes tested

Table 1 - Presentation of the geomembranes tested

STUDY CODE	PLASTICIZER Type	PLASTICIZER Initial Content Co (%)	Thickness (mm)
P	DIDP + 9/11 linear	37,0	1,9
Q	DOP	37,0	1,9
R	DIDP	36,5	2
S**	DOP	33	2
T	DOP	35	2
U	DOP	33,5	2
V	DOP	37	1,4
W*	linéaire 7/11	32	1,8
X	linéaire 9/11 (92 %) BBP (8 %)	36,9	2,
Y*	0DOP	31,4	1,9
Z	DIDP	32,5	1

* Not especially geomembranes, but materials with a similar formulation ** manufactured by extrusion

2.2 - Experiment modalities

2.2.1 - Immersion conditions

Tap water: temperature 15 to 20° C; renewed every 15 days

15 x 15 cm samples (with no contact between them) for measuring plasticizer losses (from 2 to 3 samples per time periods - 2, 4, 6, 9, 12 months, 2, 3, 4, 6, 8, 10 years); W, X, Y, Z materials were immersed for 10 years, the other ones for 8 years.

20 x 70 cm samples for tensile tests (10-year tests only) on W, X, Y, Z materials.

2.2.2 - Test modalities for characterizing material changes

Plasticizer loss follow-up was performed by gravimetry after a 48 h post-immersion sample drying in an oven at 60°C (French standard NFP 84 509).

Plasticizer chemical analysis was performed by solvent extraction: 48 hours under cold conditions using ethylic ether on samples cut into small pieces.

Density was assessed by hydrostatic measurement (French standard NF 51 063 - method A).

Tensile tests (French standard NFP 84 501): widened dumbbells (25 mm), 50 mm extensometry; 50 mm/min. rate.

3 - DEFINITIONS - MODALITIES FOR CALCULATING AND EXPRESSING THE RESULTS

- M (g) : sample mass
- dM (%): percentage of sample mass loss
- P_L (%): plasticizer loss ; dM as related to plasticizer initial content
- P_{L10} (%): P_L for a 10 year immersion
- C_{PO} (%): Plasticizer initial content
- C_{P10}, C_{P50} (%): Plasticizer content after 10 years, 50 years of immersion. The Giroud definition (1993) was adopted where C_p corresponds to the actual content (C_P = remaining plasticizer as related to the sum (remaining plasticizer + polymer).
- $TP_L(25)$, $TP_L(50)$: Time (in years) after which the plasticizer loss amounts to 25%, 50%. At the end of each exposure period dM was measured and the following was determined:

$$P_L\,(\%) = \frac{dM}{C_P} \times 100 \qquad (1)$$

The study was aimed at following P_L change with time. As an indication, actual plasticizer content C_p can be calculated at the end of a prescribed exposure period given by formula:

$$C_P\,(\%) = \frac{C_{Po} - dM}{100 - dM} \times 100 \qquad (2)$$

This expression is obtained from formula:

$$C_P = \frac{C_{Po}\,(1 - P_L)}{1 - C_{Po}\,P_L} \qquad (3)\ \text{(GIROUD 1993)}$$

where P_L is replaced by its expression given in Formula (1) (adapted for an expression in %).

Average rate of plasticizer loss VP_L: plasticizer loss as related to time unit (%/year).

$$VP_L = \frac{P_L}{T} \qquad (4)$$

As the rate varies with time (Figure 1), the exposure period for which it has been determined must be specified, for example VP_{L10} for 10 years.

Plasticizer migration rate P_M (g/m²/year) (Giroud 1993):

$$P_M = \frac{dM}{A \times T} \qquad (5)$$

; as in the previous case, we consider that the determination period must be specified, for example P_{M10}. It should be noted that this criterion does not allow a direct comparison between several materials with varied thickness.

4 - RESULTS

4.1 - Plasticizer losses P_L as a function of immersion duration.

Plasticizer losses P_L as a function of immersion duration T are shown on Figure 1. To simplify, all the curves obtained have not been plotted, but Table 2 allows comparing P_L for all the materials tested after a 8 year immersion. VP_L rate and P_M migration rate were also determined over the same exposure period.

Table 2 - Plasticizer losses measured after a 8 year immersion (both faces being exposed to the liquid).

	MATERIALS										
Plasticizer loss	P	Q	R	S	T	U	V	W	X	Y	Z
P_L (%)	5,9	2	8,5	20,6	3,6	2,7	1,9	5,7	13,1	2,5	7,7
VP_{L8} (%/an)	0,7	0,25	1,1	2,5	0,5	0,3	0,2	0,7	1,6	0,3	1
P_{M8} (g/m²/an)	6	2,2	10,1	20	4,2	2,9	1,7	4,9	13,3	2,6	4,1

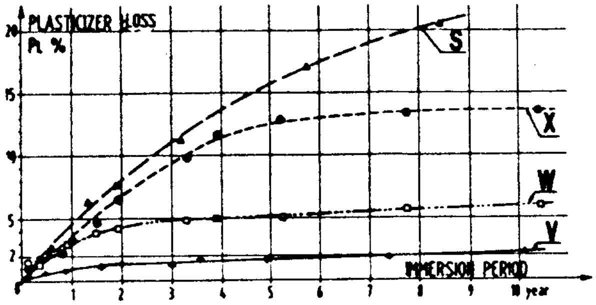

Fig. 1 - Plasticizer losses (P_L) as a function of immersion duration

After a 8 year immersion it can be observed:

A wide spread of the values obtained: for 6 materials, the loss recorded is low (P_L less than 5%), for 3 there is a mean loss (P_L ranging from 5 to 10 %) and for 2 it is high ($P_L \geq 10\%$).

All the curves obtained have a similar shape.

For Material X, a significant curve bending can be observed after 5 years. In this material, the plasticizer contents a mix of a reputedly low migrating product (9/11 linear - 92%) and a highly migrating product (BBP - 8%). The rapid disappearing of the latter has been shown by gas chromatography analysis and explain the significant initial slope of the curve. Therefore this sets the problem of short-term test uses if the chemical composition of the plasticizer is not known (which is generally the case).

4.2 - Plasticizer loss predictions in the long term.

Predicting plasticizer losses in the long term requires to determine the mathematical relation between P_L and immersion duration T over the whole experiment period.
In some cases, the plasticizer loss complies with the following law: (VERDU, 1988).

$$\log P_L = A \text{ lot } T + B \qquad (6)$$

where P_L is in %, T in months.

Using linear regression we were able to actually check this relation over all the materials obtaining very good correlation coefficients r, all exceeding 0.93. Coefficients A and B were thus determined for all the materials studied. Times $TP_L(25)$, $TP_L(50)$ corresponding to plasticizer losses of 30 and 50% and plasticizer losses P_{L10}, P_{L50}, P_{L100} corresponding to immersion durations of 10, 50 and 100 years (Table 3).

Table 3: Calculating plasticizer losses in the very long term.

Caracteristics	A	B	TP_L25 (year)	TP_L50 (year)	P_L10 (%)	P_L50 (%)	P_L100 (%)
P	0,506	-0,207	>100	>100	7	16	23
Q	0,67	-0,93	>100	>100	2,9	8,5	13
R	0,62	-0,24	35	105	11,5	32	49
S	0,77	-0,19	10	24	26	91	100
T	0,60	-0,59	>100	>100	4,7	12	19
U	0,34	-0,30	>100	>100	2,6	4,5	5,7
V	0,35	-0,38	>100	>100	2,2	4	5,1
W	0,41	-0,01	>100	>100	7	14	18
X	0,85	-0,43	12	27	21,5 (*)	85	100
Y	0,34	-0,28	>100	>100	2,7	4,7	6
Z	0,64	-0,33	40	117	10,3	29	46

(*) Note for this material, the great difference with the experimental result (Table 4) which is normal (Par. 4.1.)

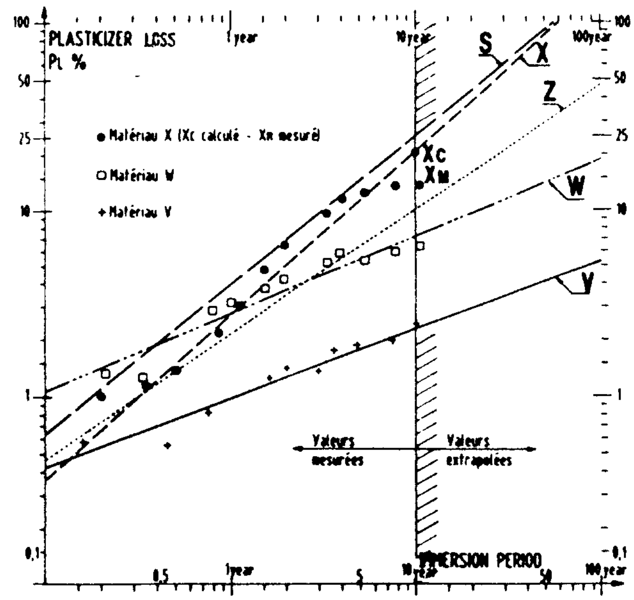

Fig. 2 - Calculating plasticizer losses in the very long term

For a number of very stable materials, the loss of 50% of plasticizer assessed using Relation (6) is observed for durations amounting to several hundred years (even thousands). As a precaution, we limited ourselves to a result > 100 years in the table. Physical laws and mainly rates determined over a 10 year period may not be exactly the same in case of an advanced deterioration of the material. As a conclusion:

- significant behaviour differences can be noted in the materials. After a 50 year exposure period, plasticizer losses range from 4 to 91%.
- the critical percentage of plasticizer required for assessing material lifetime depends on specific in-service conditions. For example, in waterproofing underground structure, it is assumed that the material

is still functional up to a 50% P_L. It is comforting to note that $TP_L(50)$ occurs for duration exceeding > 100 years for most materials, except for Material S for which loss is reached in 24 years, which is a preoccupying factor. The specific case of Material X was explained in section 4.1. It should be noted that under operation condition, only one face of the geomembrane is in contact with water; and therefore the plasticizer loss will be far slower (may be by a factor 2).

4.3 - Studying the content changes

Actual content changes were studied in 4 materials using chemical analysis before and after a 10 year immersion. C_{p10} was compared to that calculated using Formula (2) from actual weight losses.

Table 4: Changes in plasticizer percentage after a 10 year immersion; ponderal determination and extraction.

	Method of determination	MATERIALS W	X	Y	Z
C_{Po} (%)	Extraction	32	36,9	31,4	32,5
C_{P10} (%)	Extraction	29,4	33,1	30	30
dM (%)	Ponderal	1,94	4,95	1,01	2,7
C_{P10} (%) **	Ponderal	30,7	33,6	30,7	30,6
P_{L10} (%) *	Ponderal	6,1	13,4	3,2	8,3

* calculated using Formula 1   ** calculated using Formulae 2 or 3

For the four materials studied a small and allowable deviation is noted between two radically different methods. Ponderal analysis is nevertheless easier to perform and can be more reproducible.

4.4 - Physico-chemical and mechanical changes

As could be assumed, changes in failure characteristics in tensile tests (10 to 15 %) are low, which is a normal phenomenon owing to the low plasticizer losses recorded (7 to 13%) but initial tangent modulus increases greatly for materials X and Z (70 %), weakly for Y and W (21 % and 16 %).

Increases in density (between 0,3 et 1,2 %) are observed.

5 - Accelerated immersion tests

Over the 11 materials tested, only one showed a poor behaviour in long term (excepting Material X).
Comparing the results of an accelerated test (a 10 day immersion at 60°C) with plasticizer losses after 10 years (Table 5) clearly shows that Material S, which demonstrated a poor behaviour during the long term exposure, had also the poorest results during the accelerated tests.

Table 5: Comparing plasticizer losses for a 8 year immersion period with those of an accelerated test.

(en %)	MATERIALS P	Q	R	S	T	U	V	W	X	Y	Z
P_L accelerated	0,34	0	0,7	1,3	0,64	0,47	0	0,29	0,74	0,17	0,04
P_L normal	5,9	2	8,5	21	3,6	2,7	1,9	5,7	13,1	2,5	7,7

6 - CONCLUSIONS

Over a 10 year period, plasticizer losses in water measured on 11 geomembranes used in underground structures are generally low, except in one case. A mathematical relation was highlighted giving a good correlation between plasticizer losses and immersion duration, which allowed predicting the level of plasticizer loss in the long term and to assess the geomembrane lifetime. It exceeds 100 years for all the materials tested, except for one of them. For the designer, this last case stresses the need to have short term qualification tests available, modalities of which can vary. It can be noted that the accelerated test specified in the new French standard (10 days/60°C) allowed predicting the long term behaviour of the two best and the two worse materials

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