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Long-term durability assessment of PVC-P waterproofing geomembranes through laboratory tests

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ABSTRACT

Waterproofing heavily influences the operation and maintenance costs of underground structures. Currently, the most commonly used technology for tunnel waterproofing is plasticized polyvinyl chloride (PVC-P) geomembranes. However, not much is known about the long-term durability of these geomembranes, especially in relation to the long expected lifespan of new tunnels (i.e. 100-150 years). Therefore, in this paper, the durability of two commercially available PVC-P geomembranes is studied with the help of a specifically designed accelerated ageing device in addition to mechanical and absorption tests. The degradation resulting from plasticizer loss is extrapolated to the long term, and a threshold value for the end-of-life of the PVC-P geomembrane is estimated from the mechanical tests.

Keywords: PVC geomembrane; waterproofing; durability; plasticizer loss

1 INTRODUCTION

Waterproofing geomembranes are one of the most widely used technologies for long-term water management in underground structures excavated with conventional technology (Luciani and Peila, 2019). Modern underground structures are designed for a lifespan of about 100-150 years, and they require very high internal surface quality (i.e. dry or almost dry surface). The waterproofing system, specifically the waterproofing geomembrane, plays a crucial in shielding these structures against water. Installed in between the primary and final linings, these geomembranes are not only difficult to repair but also impossible to replace in case of damage. Therefore, they have to be effective for all the life-span of the structure. As a result, the durability of these elements is becoming a concern for designer and owners of underground structures.

In this paper, the durability of waterproofing geomembranes – specifically, plasticized polyvinyl chloride (PVC-P) geomembranes – is evaluated as it is one of the most commonly used material in underground applications. PVC-P geomembranes have high workability and weldability and consequently they can be to different geometric details of the structure. Many studies have analysed the durability of PVC-P in different applications, such as power cables (Jakubowicz, Yarahmadi and Gevert, 1999; Ekelund, Edin and Gedde, 2007) and waterproofing of roofs, buildings and civil structures (i.e. dams, channels, artificial ponds) (Cazzuffi, 1995, 2016; Lambert, Duquennoi and Tcharkhchi, 1999; Newman *et al.*, 2004; Stark, Choi and Diebel, 2005; Blanco *et al.*, 2012). Various testing procedures have been developed for different applications, and several standardized tests have been used to assess the effect of different degradation mechanisms (e.g. UV rays, chemicals, heat, electricity, biological attack).

The evaluation of the effectiveness of a geomembrane is typically determined by comparing one or more of the mechanical properties of the aged material with the original one (Koerner, 2012). While such a procedure does not consider the actual chemical degradation of the material, it allows for an indirect estimation through easy-to-use tests and parameters that are familiar to designers and relevant to the application requirements. Unfortunately, the available studies and standards do not simulate the degradation conditions occurring in underground structures and therefore their results cannot be generalized directly to this field.

Apart from the lack of a reliable long-term degradation model for PVC-P geomembranes, currently, there is no defined threshold to determine the end-of-life of a PVC-P geomembrane. Benneton (1994) proposed a plasticizer loss ratio of 0.5; however, the basis of this value is not provided. Ideally, the threshold value should be based on a comparison of the required and available properties of the geomembrane. Although waterproofing geomembranes have been used in underground structures since the last fifty years, very few cases in literature report the properties of aged geomembranes in underground conditions (Usman and Galler, 2014; Maehner, Peter and Sauerlaender, 2018). Hence, to estimate the required lifespan (i.e. 150 years) of the geomembranes, the use of accelerated ageing tests is unavoidable.

In the following sections, the degradation phenomena affecting PVC-P geomembranes in underground applications are analysed, and a new device specifically developed for accelerated ageing tests is described. The device accelerates the ageing of the geomembrane in conditions similar to those in underground applications. Two commercial PVC-P geomembranes are tested, and mechanical tests are performed on the aged geomembranes to evaluate the effect of ageing on the properties of the material.

Further, to better analyse the influence of plasticizer loss on the behaviour of geomembranes, eight different formulations of PVC-P geomembranes are studied and tested for their mechanical properties. Long-term extrapolations of the ageing of PVC-P geomembranes are estimated on the basis of the plasticizer absorption tests. Finally, by combining the results of all the tests, the long-term durability of the two commercial membranes is assessed, and a threshold value for their end-of-life is defined, taking into account the potential actions on the waterproofing system during its operational life in underground.

2 PVC-P GEOMEMBRANES

2.1 FORMUALTION

PVC-P waterproofing geomembranes are composed of 30–40% PVC resin and other additives (Koerner, 2012), mainly plasticizers. Plasticizers are a group of more than 1000 different polymers used to change the behaviour of PVC from a rigid material to a semi-rigid or flexible one. They reduce the glass transition temperature of the polymer from about 80–100°C to values lower than the environmental temperature (Wypych, 2015). This results in higher flexibility and elongation at break, which are important properties for application in waterproofing systems. Typically, the plasticizer content in geomembranes ranges from 25–35% in weight.

Fillers (e.g. $CaCO_3$) added to the PVC resin may also account for 20–30% of the weight of the geomembrane. Fillers are used to reduce the price, but also to enhance the abrasion resistance and flame-retarding properties. However, they reduce the mechanical performance and the transparency of the geomembrane. This is why some Countries opt for translucid geomembranes as the transparency guarantees the purity of the material.

Other additives are also used in small percentages in the formulation of PVC-P to enhance specific properties of the geomembrane (e.g. biocides, pigments, flame-retardants) or to permit the production and extrusion of the material (e.g. stabilizers) (Wypych, 2009).

2.2 PVC-P DEGRADATION

PVC degradation occurs mainly because of dehydrochlorination: the loss of gaseous hydrochloride from the PVC chain and the formation of a double bond between the carbon atoms. The energy needed to initiate the degradation process comes from heat or ultraviolet (UV) rays. Van Krevelen and Te Nijenhuis (2009) identified 160°C as the initial degradation temperature, but the process can start at lower temperatures (about 110°C) in case of irregularities in the polymer chain structure (Wypych, 2015). Furthermore, the energy provided by UV rays or high temperature can cause also oxidation phenomena that alter the structure of the PVC chains. On the basis of the source of the energy that has started the reaction, this phenomenon is called photo-oxidation (UV rays) or thermal-oxidation (high temperature) (Wypych, 2015). However, in underground conditions, because high temperatures or UV rays are absent, neither dehydrochlorination nor oxidation poses a problem.

Even if PVC is slightly susceptible to microbial attack (Kirbas, Keskin and Güner, 1999; Andrady, 2011), bacteria and fungi are recognized as possible sources of damage to PVC-P (Booth, Cooper and Robb, 1968; Sabev, Handley and Robson, 2006). Some species of fungi feed on plasticizers and can change the composition and properties of the geomembrane. However, microbiological attacks occur only under specific environmental conditions (i.e. temperature, oxygen, pH), and these are not usually present in underground applications, where the geomembranes are installed in between two concrete layers (no air, high pH, low temperature). Microbial attacks are a concern only in some specific applications, such as cut-and-cover tunnels.

Therefore, the only relevant degradation phenomenon in underground applications is the loss of plasticizer. Because the plasticizer is not chemically bonded to the polymer chain, it can diffuse from the geomembrane into the surface and then in the environment (air, water, other polymers) (Storey, Mauritz and Cox, 1989; Papakonstantinou and Papaspyrides, 1994; Marcilla, Garcia and Garcia-Quesada, 2004). This loss can change the plasticizer content and the mechanical properties of the geomembrane. Thus, a study on the durability of PVC-P geomembranes calls for an analysis of the long-term behaviour of plasticizer loss.

3 TESTED MATERIALS

In this study, two commercial geomembranes were tested. The first one, hereinafter called material A, was a coloured geomembrane, with a thickness of 2.0 mm with a signal layer. The geomembrane contained a filler and had an initial plasticizer content of 24.0% in weight. The other one, referred to as material B, was a translucent 2.0 mm membrane without filler and with an initial plasticizer content of 26.7% in weight.

To analyse the effect of the plasticizer content on geomembrane properties, eight PVC-P formulations were studied and the geomembranes extruded with different content of plasticizer. The compositions of these materials are reported in Table 1.

Table 1 - Composition of the produced geomembranes

Sample	PVC (%)	Plasticizer (%)	Stabilizer 1 (%)	Stabilizer 2 (%)	Stabilizer 3 (%)	Filler (%)
1	67.4	30	0.5	2	0.1	0
2	72.4	25	0.5	2	0.1	0
3	77.4	20	0.5	2	0.1	0
4	82.4	15	0.5	2	0.1	0
5	47.4	30	0.5	2	0.1	20
6	52.4	25	0.5	2	0.1	20
7	57.4	20	0.5	2	0.1	20
8	62.4	15	0.5	2	0.1	20

4 ACCELERATED AGEING TESTS

4.1 EXISTING ACCELERATED AGEING TESTS

Several standardized accelerated ageing tests have been developed for PVC-P geomembranes: oxidation tests (EN 14575, 2005), UV weathering tests (EN 1297, 2005; ASTM G154, 2016), water immersion tests (EN 14415, 2004), chemical tests (EN 1847, 2009; ASTM D5747, 2008; ASTM D5496, 2015; ASTM D5322, 2017), and microbiological tests (EN 12225, 2000; ASTM G160, 2012; ASTM G21, 2015). These tests simulate and accelerate different degradation phenomena by amplifying the cause of degradation. For instance, oxidation and water immersion tests use temperatures up to 100°C to increase the pace of degradation, while UV, chemical and microbiological tests intensify other variables (e.g. high concentrations of chemicals, UV or bacteria).

Unfortunately, none of these tests are specifically designed for underground applications. They do not replicate the degradation process endured by waterproofing geomembranes underground such as constant flow of water only on one side of the geomembrane, presence of concrete or the absence of fungi or UV rays. Therefore, to better analyse the degradation of geomembranes in these peculiar conditions, a specifically designed test was developed.

4.2 NEW SPECIFICALLY DESIGNED ACCELERATED AGEING TEST DEVICE

In this study, a new accelerated ageing device was used to reproduce the tunnel lining (Luciani, 2019; Luciani *et al.*, 2019). The PVC-P geomembrane was positioned between two concrete slabs, which simulated the primary and final lining. A 500 g/m^2 polypropylene non-woven geotextile was installed between the geomembrane and the primary lining concrete to act as regularization and drainage layer. A constant water flow was maintained through the geotextile to mimic the drained water. The flow occurred only on one side of the geomembrane. It contributed to the removal of plasticizer from the geomembrane surface, maximizing its diffusion. The degradation was accelerated through the use of hot water, which was recirculated in a closed circuit and heated by a heating tank (Figure 1).

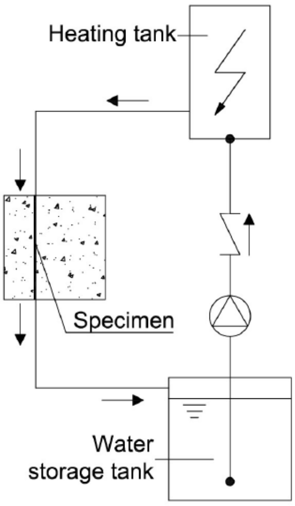

Figure 1 - Scheme of the developed device

The tests were performed at 45°C, 60°C and 75°C. These temperature points were chosen in order to prevent the initiation of dehydrochlorination (at 100°C) and other degradation phenomena that could overlap with plasticizer loss. The tests lasted for 270 days at 60°C and 75°C and for 180 days at 45°C. Material A was tested at all temperatures while material B was tested only at 45°C and 75°C. The specimens of materials A and B had a dimension of 15×15 cm and were obtained from the central part of a roll in order to avoid any problems owing to the boundary conditions during extrusion of the material.

4.3 RESULTS

In the hypothesis that plasticizer loss is the only degradation process relevant to geomembranes in underground applications, the loss of plasticizer can be evaluated through the loss of weight of the specimens. Accordingly, all the specimens were cleaned, dried in the desiccator for 72 hours and weighed before testing. After ageing, the specimens were cleaned with alcohol to remove surface precipitations, oven dried at 60°C for 48 hours and weighed again. Plasticizer loss was determined as the difference between the two measurements. The loss is expressed by the residual plasticizer content (C_P) or by the plasticizer loss ratio (P_L) (Benneton, 1994) as follows:

$$P_L(t) = \frac{M_{P_0} - M_P(t)}{M_{P_0}},$$

where M_{P_0} is the initial mass of plasticizer and M_P the mass at time t.

Figure 2 reports the results of the tests on the aged geomembranes. Obviously, the rate of degradation was higher at higher test temperatures. Material B behaved better, with a lower rate of plasticizer loss.

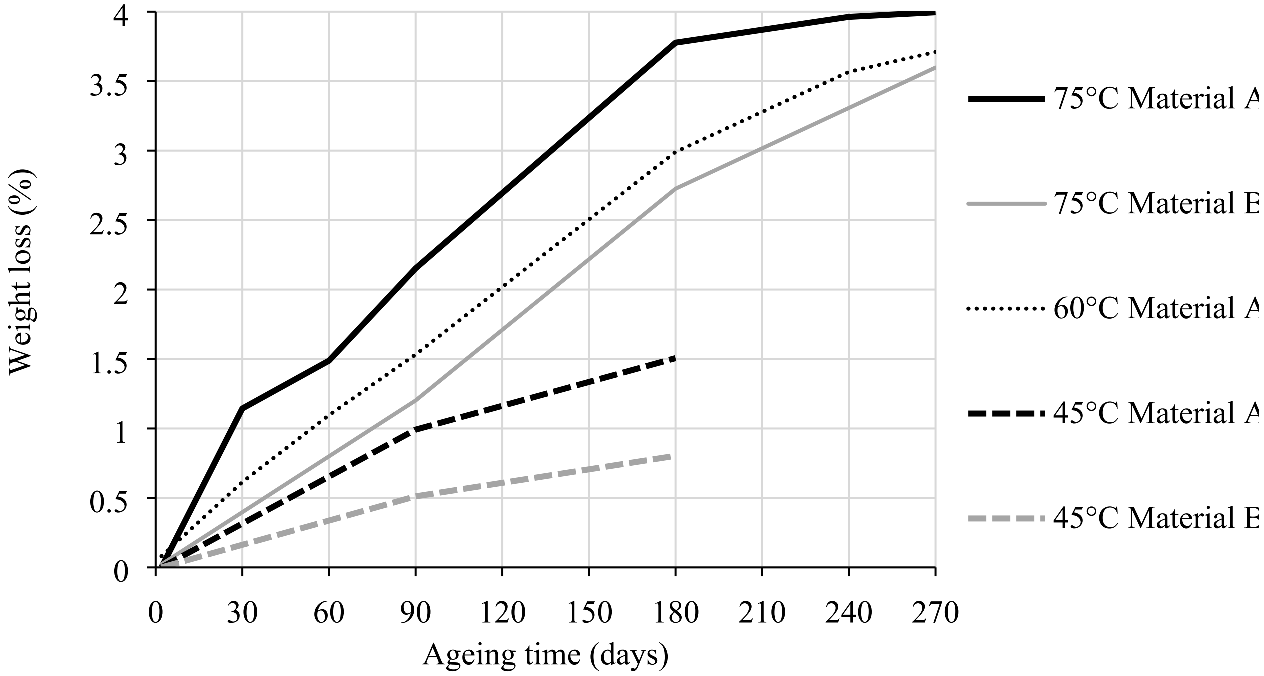

Figure 2 - Result of the accelerated ageing tests in terms of weight loss

The results of the accelerated ageing tests performed in the developed device were compared with those of the standardized tests in air (EN 14575, 2005) and water (EN 14415, 2004). The standardized tests were performed at 75°C and lasted for 90 days. Figure 3 shows results for both materials A and B. The new device enhanced plasticizer loss, due to the constant water flux that removes the plasticizer from the surface and thus facilitates its migration from inside the geomembrane to the surface.

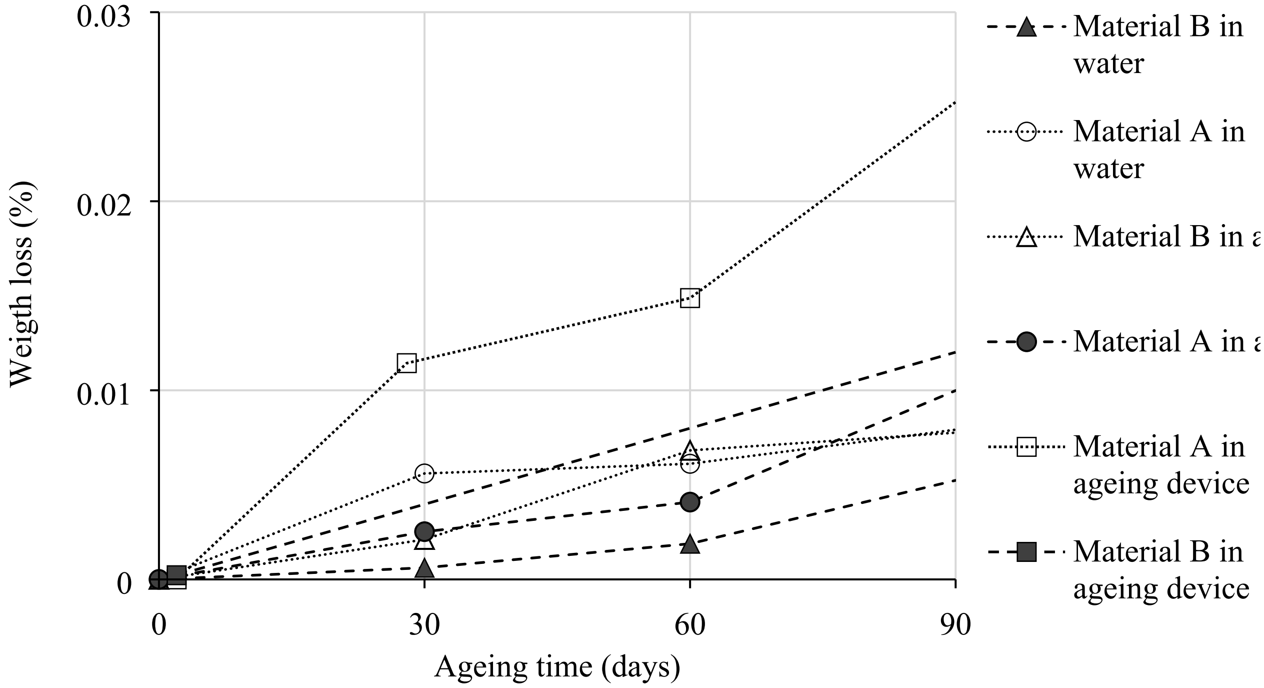

Figure 3 - Comparison of the developed and standardized accelerated ageing tests

5 TESTS ON THE GEOMEMBRANES

To analyse the effect of plasticizer loss on the material properties of the commercial geomembranes and the eight tailor-made geomembranes, all the materials were subjected to physical and mechanical tests. Moreover, plasticizer absorption tests were also carried out have been done to examine plasticizer absorption and desorption by these geomembranes.

5.1 PHYSICAL AND MECHANICAL TESTS

5.1.1 Density

Clean and dry specimens were used to determine the density of the geomembranes. Materials A and B had a density of 1.35 and 1.23 g/cm^3 respectively. The difference in values was due to the presence of a filler in material A. Aged specimens showed higher density because the plasticizer had a lower density (0.96 g/cm^3) than the membrane (Giroud and Tisinger, 1995). This trend was more evident in the case of the eight extruded geomembranes (Figure 4). The commercial membranes had a slightly lower density than the tailor-made ones, probably because of the different extrusion device used.

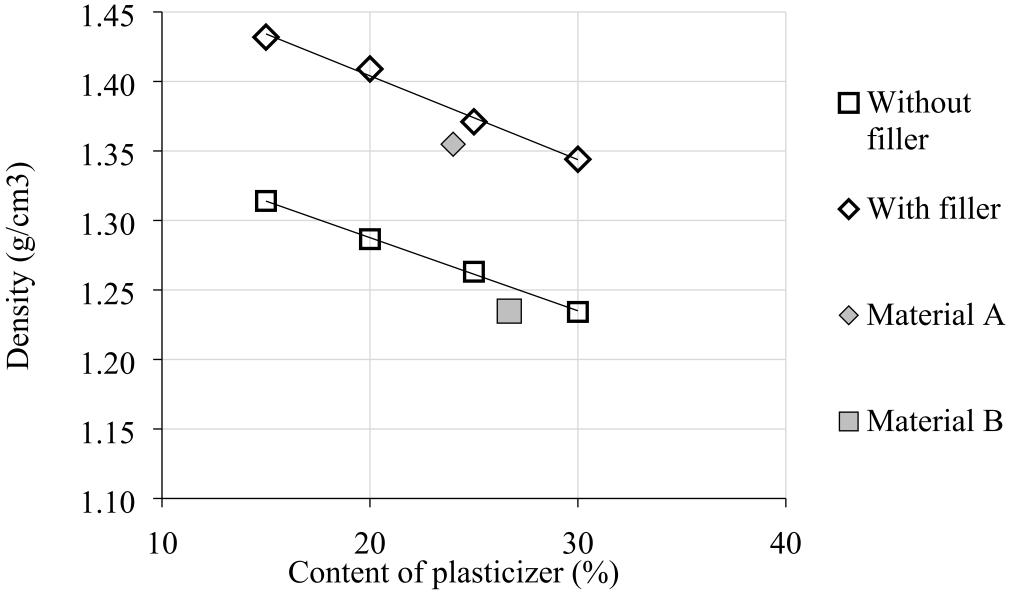

Figure 4 - Density of the ten tested geomembranes

5.1.2 Dimensional variation

One of the consequences of plasticizer loss is the shrinkage of the geomembrane. Assuming that porosity in PVC-P is always 0 and consequently the loss of plasticizer does not cause voids, Giroud (1995) proposed the following theoretical equation for shrinkage:

$$\frac{L}{L_0} = \left(1 - \frac{p_L C_{P_0} \rho_{GM_0}}{\rho_p}\right)^{1/3},$$

where L is the final dimension, L_0 the initial dimension, p_L is the plasticizer loss ratio, $C_{P_0}$the initial plasticizer content, ρ_{GM_0} the initial density of the geomembrane and ρ_p the density of the plasticizer. Although shrinkage occurs in all directions, it was measured in only two directions – longitudinal and transversal – because the shrinkage in the direction of the thickness of the specimens was too small for precise assessments. The side dimensions of the specimens were measured with a calliper with a precision of 0.01 mm before and after ageing, and the percentage variation was computed. Data were corrected to account for the influence of dimensional instability caused by the relatively high temperatures of the tests. Residual stresses are usually present in the material of the extruded geomembranes. These stresses are relaxed when the membrane is heated, and they cause shrinkage in the direction of extrusion and enlargement in the transversal direction. Therefore, three 15×15 cm specimens of both materials A and B were maintained at 45°C, 60°C and 75°C and their dimensions were measured until dimensional stability was reached. The final value obtained was used to calibrate the results of dimensional variation of the aged membranes (Figure 5).

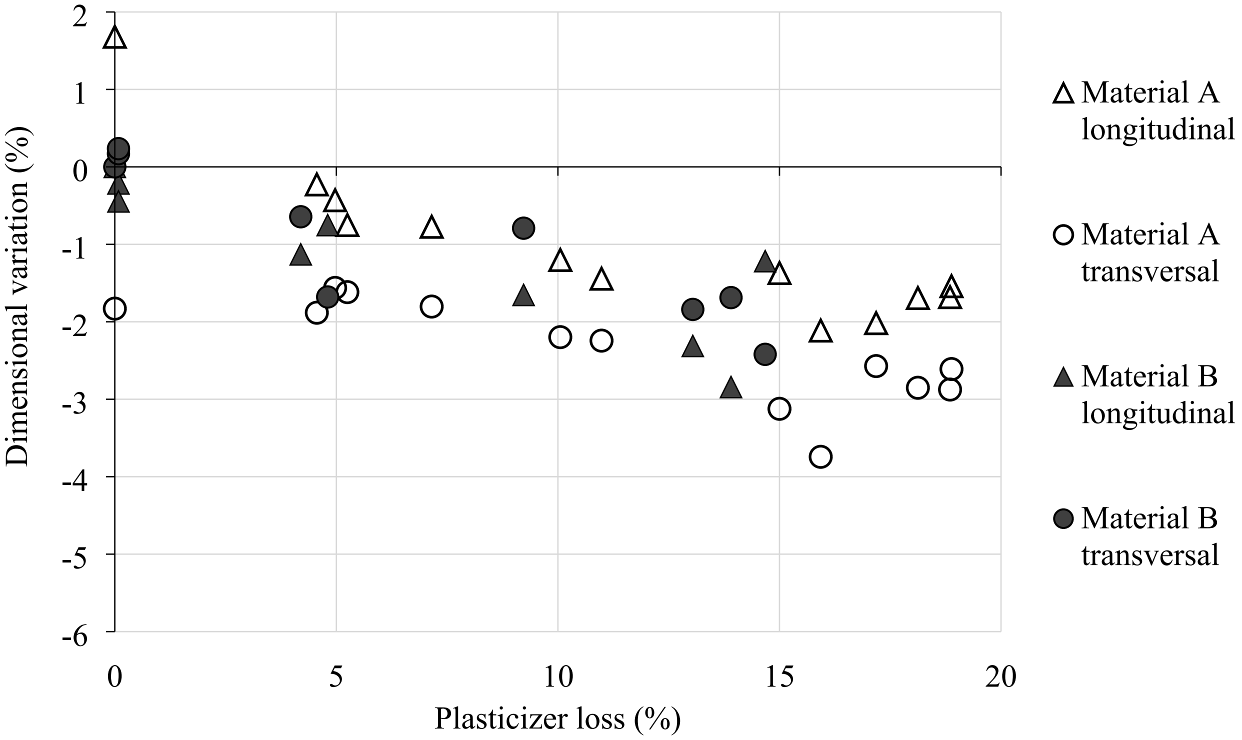

Figure 5 - Dimensional variation of the aged specimens at 75°C

Experimental data confirmed the reduction in the dimensions of the geomembrane, even though the theoretical equation proposed by Giroud (1995) overestimated the shrinkage. The overestimation may be attributed to very strict hypothesis conditions that cannot be not completely satisfied in reality.

5.1.3 Tensile tests

Tensile strength of the unaged commercial membranes was measured according to EN ISO 527 (2012). Five specimens each of materials A and B were tested in each direction. Only two specimens of the aged geomembranes were tested in each direction because of the lack of material. Tailor-made geomembranes were tested only in the longitudinal direction because the extrusion geometry did not permit testing in the other direction. The tests were performed at 100 mm/min. The tensile strength, the elongation at break and the elastic modulus in the range 0–1% of deformation were measured for each specimen. Figure 6 reports the tensile behaviour of materials A and B in the two directions.

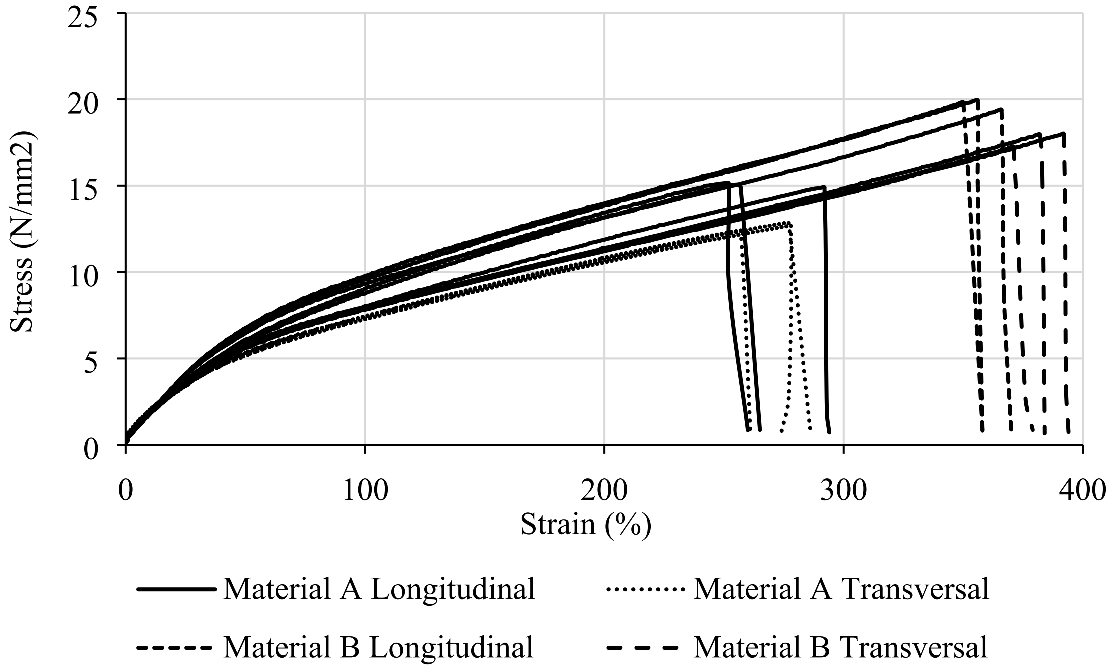

Figure 6 - Tensile behaviour of materials A and B

Material A had both lower elongation at break and tensile strength, confirming that mechanical properties are diminished by the presence of filler. Furthermore, the behaviour in the two directions was different for both materials because of the residual extrusion stresses in the geomembranes. A comparison of the aged geomembranes with the original commercial ones did not reveal a clear pattern of variation in the properties caused by plasticizer loss. This is because the ageing tests resulted in a loss of maximum 4% of plasticizer, which is not enough to clearly introduce changes in mechanical behaviour. Nonetheless, variations in the behaviour were evident: Figure 7 compares the tensile behaviour of the original material A and that of the same material aged for 270 days at 75°C. The aged material had higher tensile strength and elastic modulus and lower elongation at break.

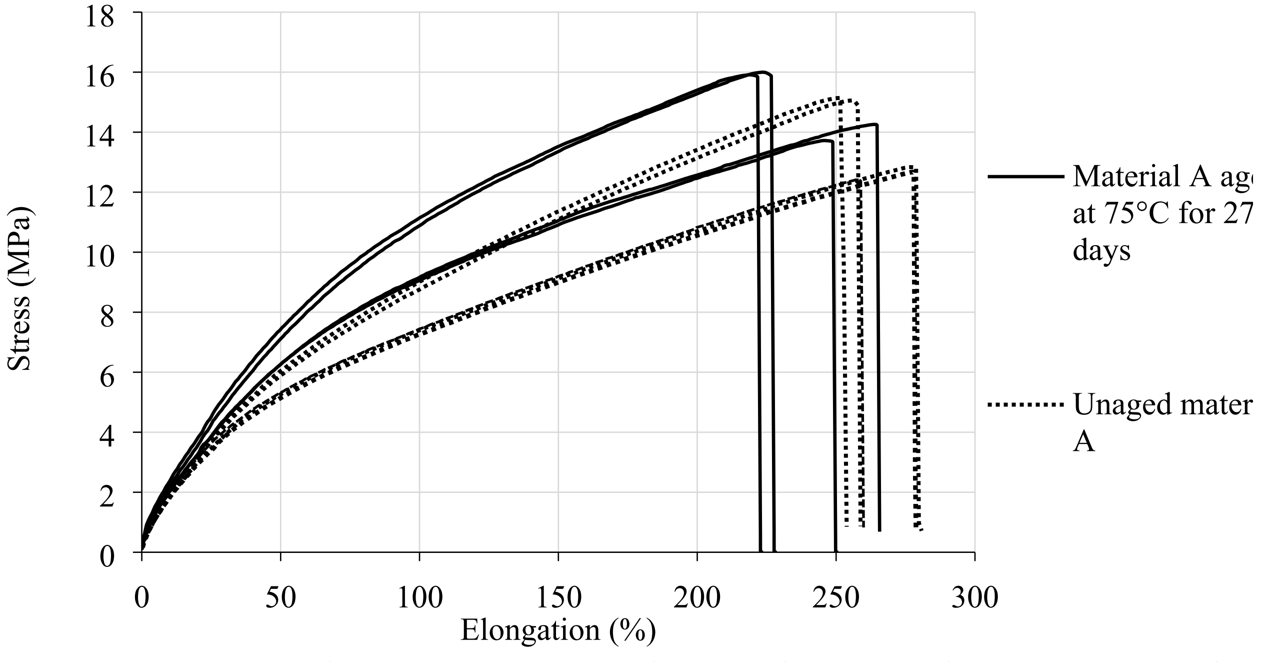

Figure 7 - Comparison of the tensile behaviour before and after ageing of material A at 75°C for 270 days

These data were corroborated by tests on the tailor-made geomembranes that clearly showed different behaviour because of different plasticizer contents. Figure 8, Figure 9 and Figure 10 summarize the results of the tests on tailor-made geomembranes in terms of tensile strength, elongation at break and elastic modulus, respectively. The variation in the properties showed a clear pattern.

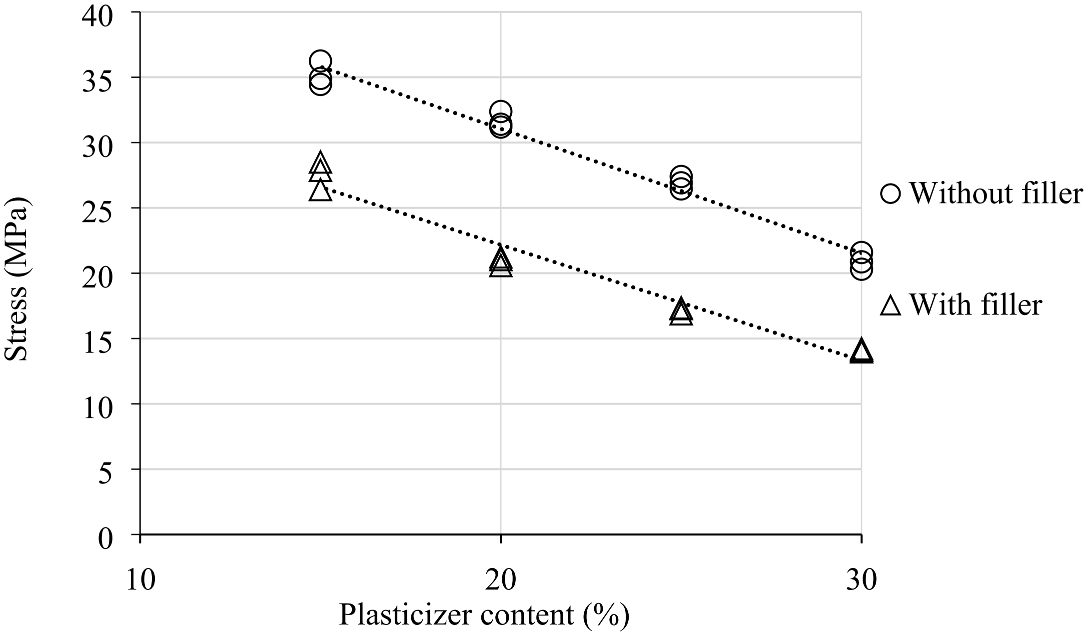

Figure 8 - Tensile strength of the tailor-made geomembranes

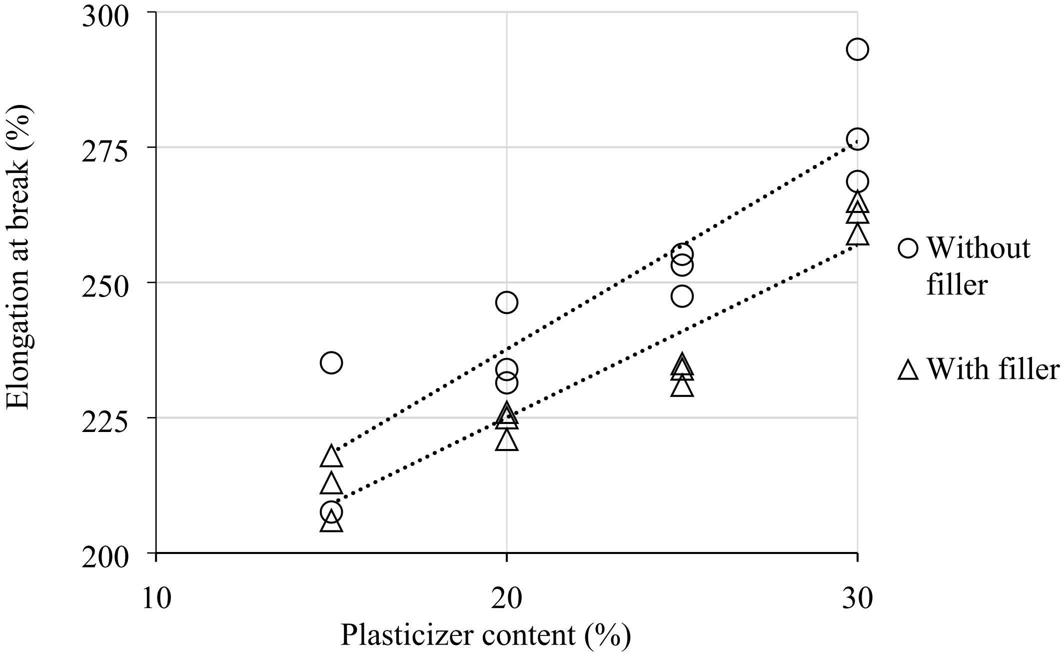

Figure 9 - Elongation at break of the tailor-made geomembranes

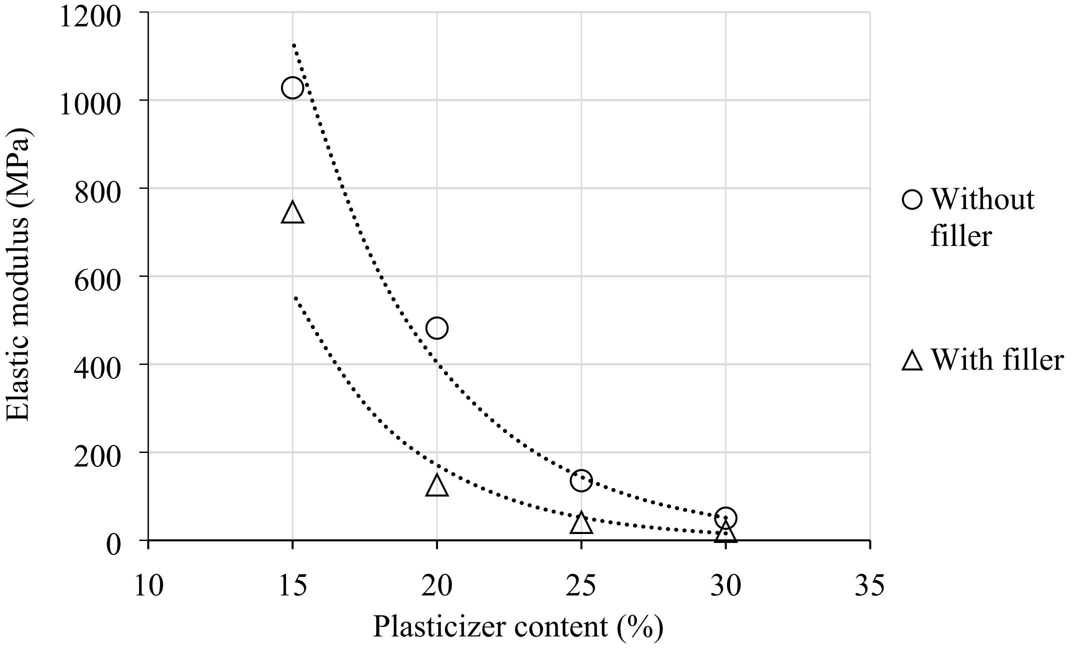

Figure 10 - Elastic modulus of the tailor-made geomembranes

Further, with regard to tensile behaviour (Figure 11 and Figure 12), the results showed that not only the final values but the entire path to failure changes: as plasticizer content reduced, the material changed from a rubber-like substance to an elasto-plastic one with a well-defined yielding point.

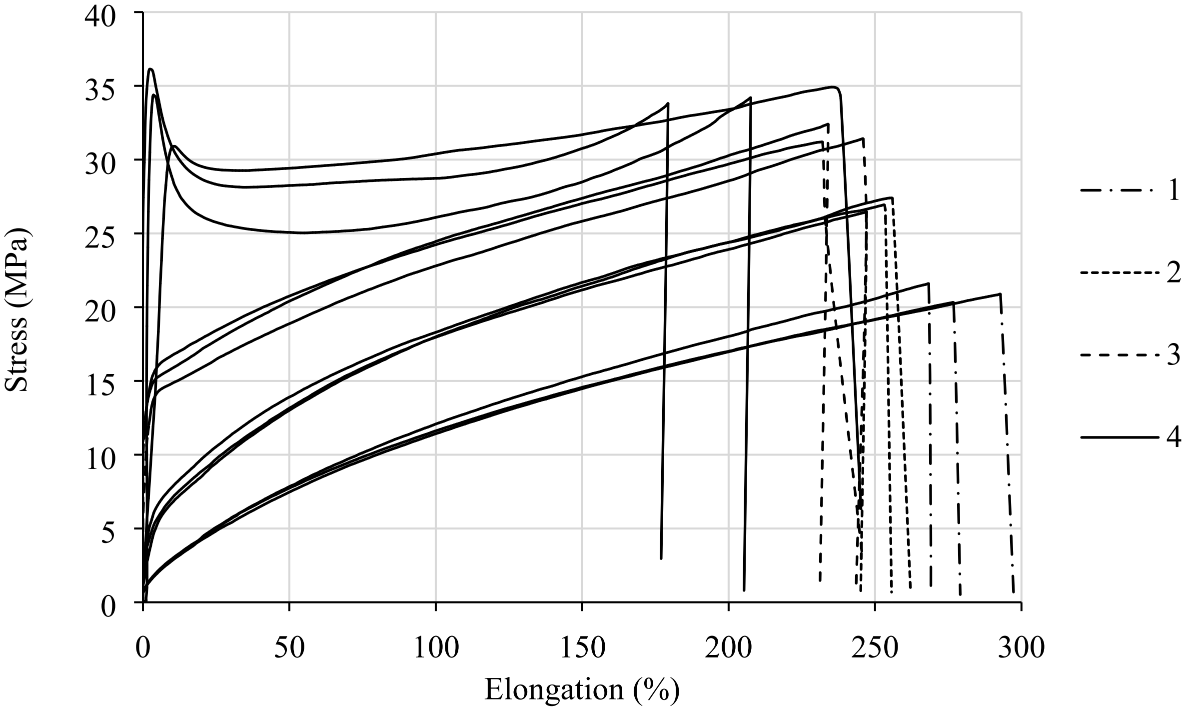

Figure 11 - Tensile behaviour of the geomembranes without filler

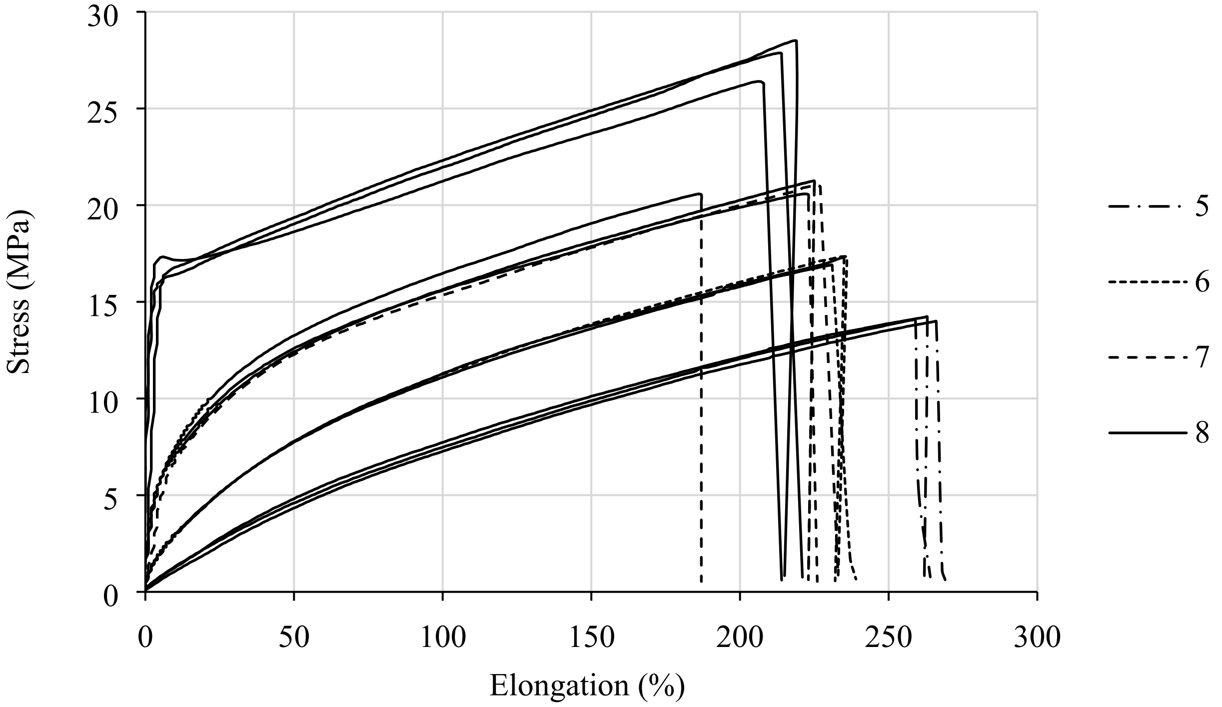

Figure 12 - Tensile behaviour of the geomembranes with filler

5.1.4 Flexibility at low temperature

The flexibility of all the materials at low temperature was tested in accordance with EN 495 (2013). The tested specimens measured 50×100 mm, were folded at 180° and conditioned for 12 hours. None of the specimens showed any cracks at -25°C.

5.1.5 Surface hardness

Surface hardness was assessed in accordance with ISO 48-4 (2018) with a Shore A durometer. Hardness increased with plasticizer loss (Figure 13). Extruded geomembranes had higher surface hardness than commercial ones, but they also confirmed the variation pattern with plasticizer loss.

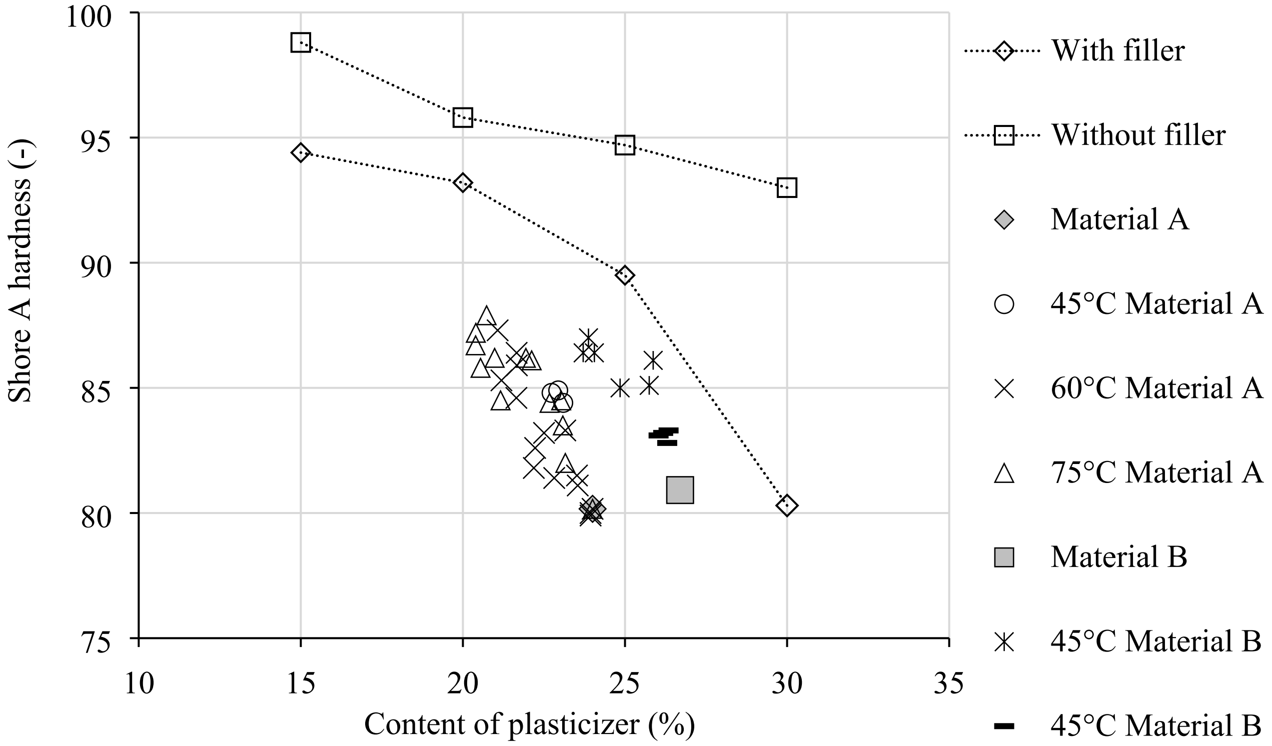

Figure 13 - Shore A hardness for the studied geomembranes

5.2 PLASTICIZER ABSORPTION TESTS

Since plasticizer loss is recognized as the most relevant degradation phenomenon occurring to PVC-P geomembranes in underground applications, in the following further effort is devoted to analysing the mechanisms and parameters influencing plasticizer loss.
The suitability of the plasticizer to move in the PVC resin is a function of the type of plasticizer, the temperature and the plasticizer concentration. Accordingly, specific tests were performed to evaluate this phenomenon under different conditions. Plasticizer movement in the geomembrane can be considered a diffusion problem, which makes diffusion coefficient the most important variable. In the following section, plasticizer absorption tests are described. While plasticizer loss is a desorption phenomenon, the use of absorption tests to evaluate plasticizer loss has been suggested by some authors (Griffiths, Krikor and Park, 1984). This is based on the assumption that any hyteretical phenomenon between sorption and desorption in plasticizer-PVC systems can be considered negligible.

The diffusion coefficient can be determined from absorption tests by integrating Fick’s second law. The procedure, as reported by several authors (Griffiths, Krikor and Park, 1984; Storey, Mauritz and Cox, 1989; Papakonstantinou and Papaspyrides, 1994), involves immersing specimens of geomembrane in the plasticizer. The specimens’ weight is measured before the test and at different times during the test. This yields the rate of absorption of the plasticizer. Considering the specific boundary conditions, Fick’s law can be solved (Crank, 1979), and the diffusion coefficient D can be obtained from the experimental data as follows:

$$D = \frac{m^2 \pi}{4A^2 (c_0 - c_b)^2},$$

where m is the slope of the experimental curve obtained by plotting the increase in weight versus the time, A is the area of the specimen, c_0 is the concentration of plasticizer outside the geomembrane and c_b is the concentration in the geomembrane. Since plasticizer absorption occurs on two sides of the geomembrane, the resulting increase in weight has to be halved while the absorption through the lateral surface is considered negligible. This method is valid only until the absorption curve from one side reaches the one from the other side because at that point, the used solution of Fick's law is no longer valid. Test durations have always ensured that this limit is not reached.

For the absorption tests in this study, circular specimens of commercial and tailor-made geomembranes with a diameter of 30 mm were obtained with the help of a hollow metallic cutter. All the specimens were cleaned, dried for 72 hours in the desiccator and then weighed. The tests were performed at four temperatures: 20°C, 45°C, 60°C and 75°C. The variation in weight was measured every 10 minutes for 1 hour. For tests conducted at 20°C, the measurement was taken every 4 hours for 24 hours because low temperatures imply lower diffusion coefficient and consequently slower absorption. The tests used the same plasticizer as that used for the production of commercial and tailor-made geomembranes. A different plasticizer may yield different results (Griffiths, Krikor and Park, 1984; Storey, Mauritz and Cox, 1989).

As an example, Figure 14 shows the absorption curve obtained for the two commercial geomembranes at 20°C.

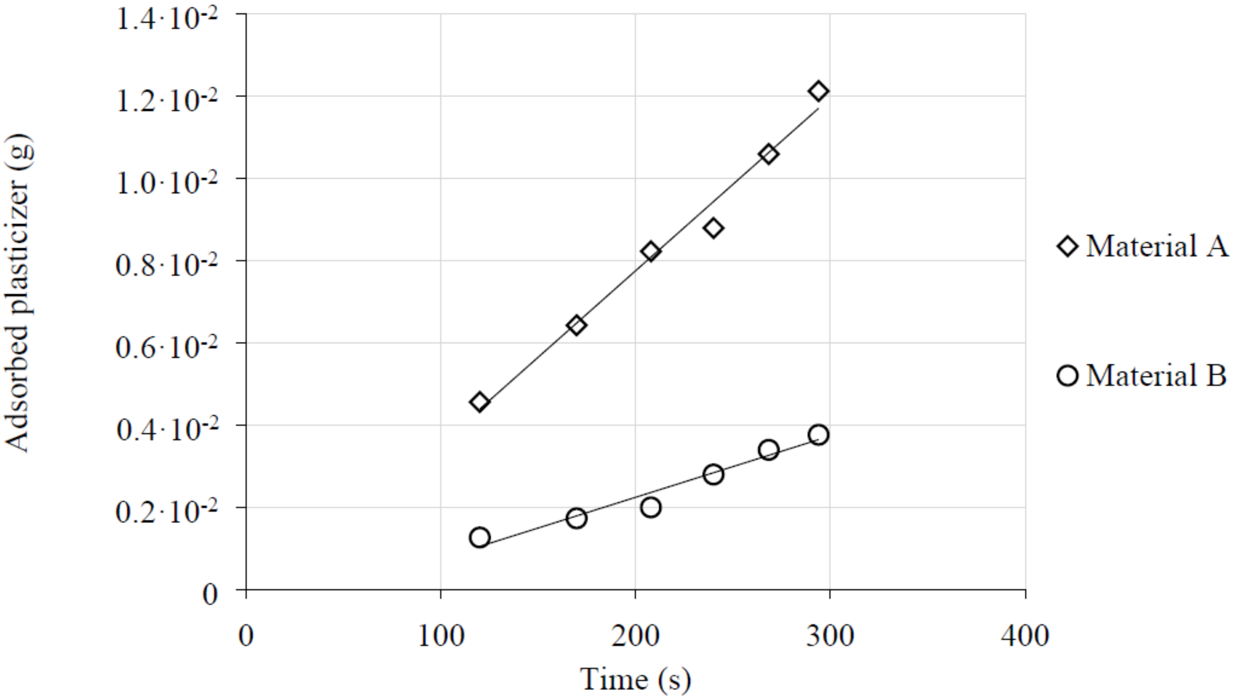

Figure 14 - Results of the plasticizer absorption tests on the two commercial geomembranes

The diffusion coefficient was higher for material A than for material B, confirming that the material without filler has a lower loss of plasticizer. The dependence of the diffusion coefficient on temperature can be described by Arrhenius' equation (Figure 15) as follows:

$$D = D_0 e^{-\frac{E_A}{RT}},$$

where D_0 is a constant, E_A is the activation energy, R the gas constant and T is the temperature. The values of D_0 and E_A were obtained from the experimental data (Table 2). The commercial membranes were in line with the values obtained for the tailor-made geomembranes.

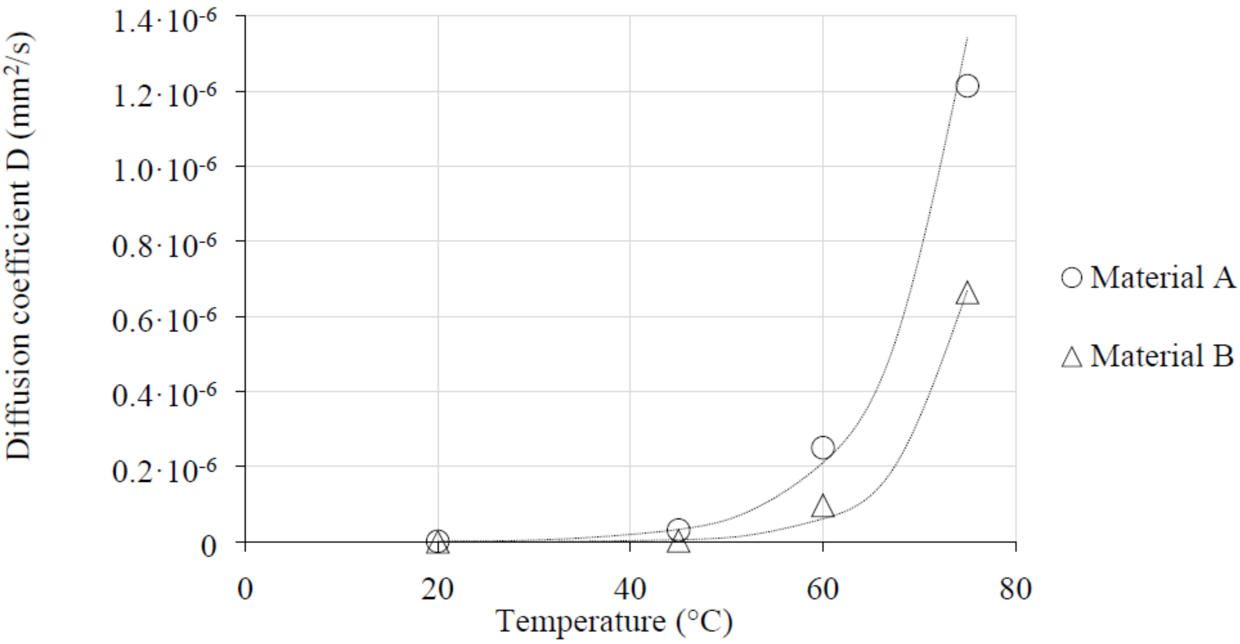

Figure 15 – Temperature dependence of the diffusion coefficient

Table 2 - Parameters of temperature dependence for materials A and B

	D_0	E_A
	(mm²/s)	(kJ/mol)
Material A	$2.66\ 10^9$	102.5
Material B	$5.60\ 10^{13}$	133.1

The dependence of the diffusion coefficient on the plasticizer content was ascertained from the tests on the tailor-made geomembranes at the different temperatures. As an example, Figure 16 shows the relationship between plasticizer content and diffusion coefficient at 75°C.

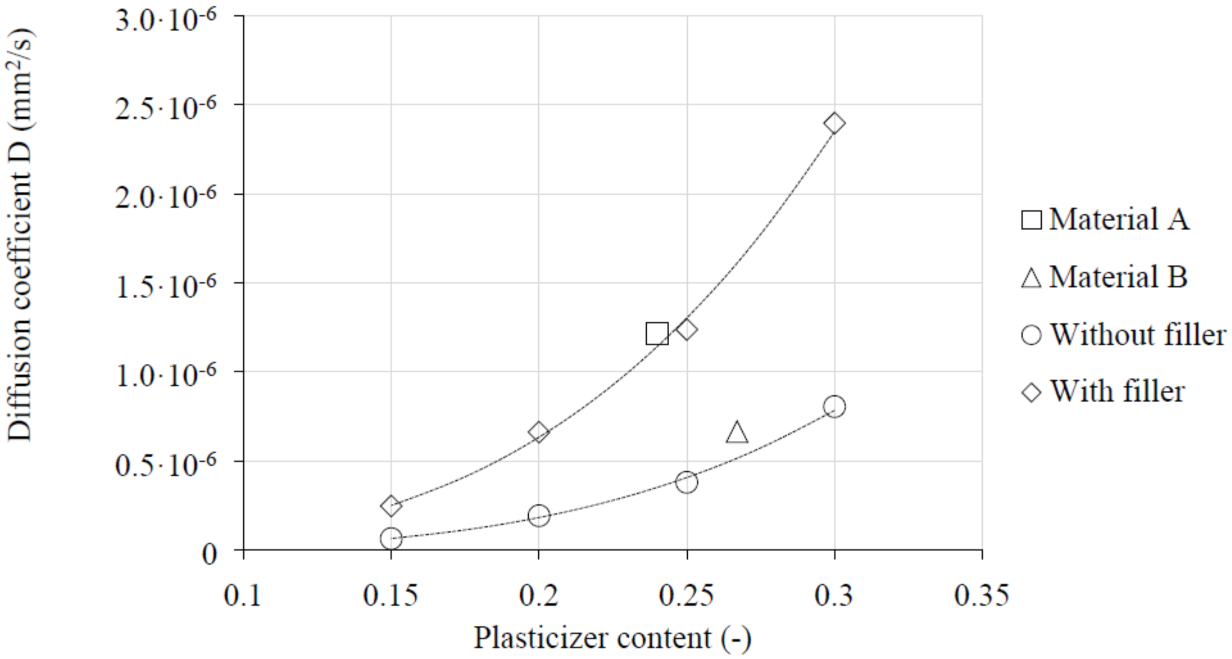

Figure 16 - Diffusion coefficient as a function of plasticizer content

The diffusion coefficient follows a potential law with concentration as follows:

$$D = D_1 {C_P}^b,$$

where D_1 and b are constant parameters, and C_P is the plasticizer content expressed as mass of plasticizer over mass of the geomembrane. Table 3 reports the obtained values of the constants.

Table 3 - Parameters of concentration dependence from the absorption tests on the tailor-made geomembranes

	Temperature	D_1	b
	(°C)	(mm²/s)	(-)
Material without filler	20	$1.62\ 10^{-7}$	4.94
	45	$5.77\ 10^{-7}$	2.77
	60	$1.79\ 10^{-5}$	3.85
	75	$5.92\ 10^{-5}$	3.59
Material with filler	20	$5.13\ 10^{-6}$	4.94
	45	$1.34\ 10^{-6}$	2.63
	60	$1.46\ 10^{-5}$	3.16
	75	$1.15\ 10^{-4}$	3.23

6 LONG-TERM EXTRAPOLATION

The results of the accelerated ageing tests are extrapolated to longer durations (up to 150 years or the required lifespan of the underground structures) and temperatures that mimic real application cases (for example 15°C can be considered the standard temperature for shallow or urban tunnels). Arrhenius equation is the most commonly used method to correlate the rate of a phenomenon (in this case of the loss of plasticizer) with temperature. However, this method typically results in overestimation of the degradation phenomenon. Using the data coming from the accelerated ageing tests, given a job-site temperature of 15°C the plasticizer should be totally exhausted in less than 30 years, according to estimates derived from Arrhenius equation. However, natural degradation data (Usman and Galler, 2014; Maehner, Peter and Sauerlaender, 2018) suggest that after 30–40 years, the loss of plasticizer is negligible.

This discrepancy can be attributed to the incorrect hypothesis implicit in the use of Arrhenius correlation. The method assumes that the reaction rate is constant, while plasticizer loss is actually dependent on the content of the plasticizer and on the difference of plasticizer concentration inside and outside the material, which changes with time. The former dependence, evident in the results of the absorption tests, is due to the fact that, as plasticizer is lost, the PVC-P structure becomes stiffer, and the free volume reduces, leading to higher difficulties in the movement of plasticizer molecules.

To account for these issues and to better simulate the physical phenomenon (i.e. diffusion) Fick's law was used to extrapolate the results of the experimental tests to the durations and temperatures of interest. The differential equation is solved in the thickness direction in the domain $0 < x < x_{max}$ with the boundary and initial conditions specific to underground applications:

- $c(x,0) = C_0$
  the initial concentration in the geomembrane is uniform (C_0);
- $c(0,t) = 0$
  the concentration at the boundary in contact with the geotextile is always zeroed by the water flux;
- $\left.\frac{\partial c(x,t)}{\partial x}\right|_{x = x_{max}} = 0$
  at the boundary in contact with the concrete, there is no flux of plasticizer because of the absence of water or air flux that removes the plasticizer from the surface.

In these specific conditions the solution of Fick's second law is

$$c(x,t) = -\sum_{n=1}^{\infty} C_0 \frac{4}{(2n-1)\pi} e^{-D\left(\frac{2n-1}{2x_{max}}\pi\right)^2 t} \sin\left(\frac{2n-1}{2x_{max}}\pi x\right).$$

With this equation, it is possible to compute the concentration of the plasticizer in the geomembrane over time, determine the average plasticizer content in the section and compare the values with the plasticizer loss data from the accelerated ageing test. The parameter crucial to the process is the diffusion coefficient. The curve resulting from the plasticizer absorption data of the commercial materials at the test temperature does not fit the experimental data (Figure 17). If the dependence of the diffusion coefficient on plasticizer content is implemented in the computation of the theoretical equation, the gap reduces. This implementation was performed using the relation obtained from the absorption tests on the tailor-made geomembranes and the parameters reported in Table 3. The results of materials1–4 were used for material B and those of materials 5–8 for material A.

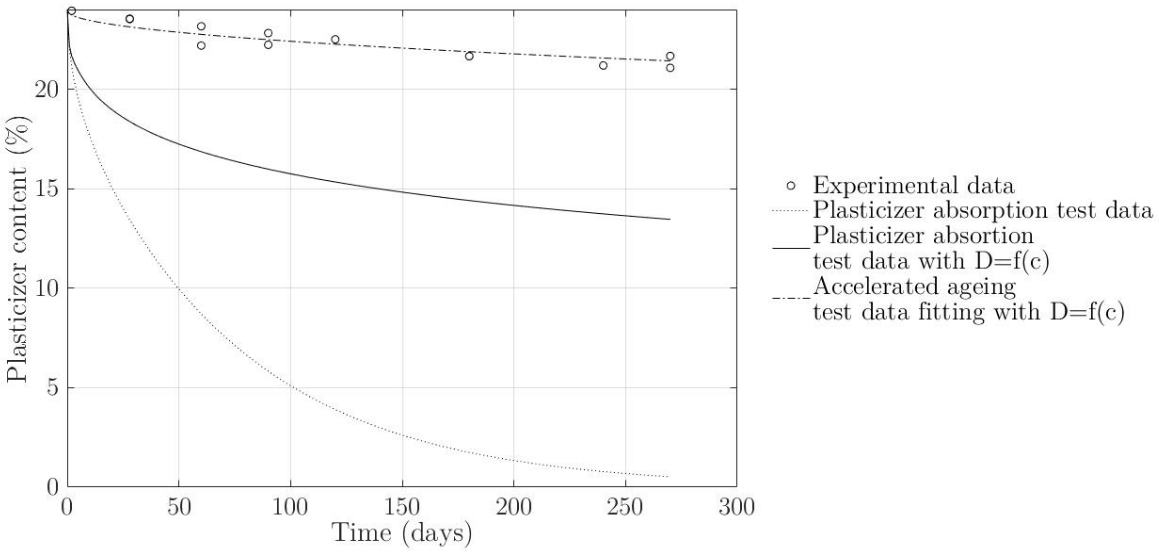

Figure 17 - Comparison between the experimental data and the developed model

Nevertheless, a gap remained between the data predicted by the equation and the experimental one. This gap can be due to the different test conditions: in the absorption test, the specimens were perfectly clean and dry whereas in the accelerated ageing test, the PVC-P geomembrane was installed, as on the job-site, without any cleaning of the surface and not perfectly dry. The plasticizer loss can, therefore, be partially influenced by the surface phenomenon. Moreover, on the aged specimens, calcium carbonates coming from the concrete appeared to have partially formed thin local layers, possibly further reducing the diffusion. Finally, the hysteresis of the sorption-desorption curve may have resulted in a reduction of the desorption quantity compared to the same adsorption conditions.

Conversely, the diffusion coefficient can be evaluated by fitting the curve to the experimental data (Figure 17), and the long-term plasticizer loss can be extrapolated using both the value of the diffusion coefficient obtained from the plasticizer absorption tests and fitting the experimental data. In both the cases, the dependence on the plasticizer content in the geomembrane was considered.

Because the plasticizer loss had to be evaluated at the job-site temperature, the diffusion coefficients needed to be computed at that temperature. This was possible using the parameters of the Arrhenius correlation obtained from the plasticizer absorption tests on the commercial geomembranes. As mentioned, the temperature in an urban or shallow tunnel is about 15°C. For this temperature, the computed diffusion coefficients are reported in Table 4.

Table 4 - Diffusion coefficients obtained for materials A and B at 15°C with the two procedures

	D (mm^2/s)	
	Plasticizer absorption tests	Accelerated ageing tests
Material A	$6.48\ 10^{-10}$	$4.23\ 10^{-11}$
Material B	$3.58\ 10^{-11}$	$2.26\ 10^{-12}$

Figure 18 and Figure 19 show the extrapolations for up to 150 years of plasticizer loss for materials A and B at 15°C.

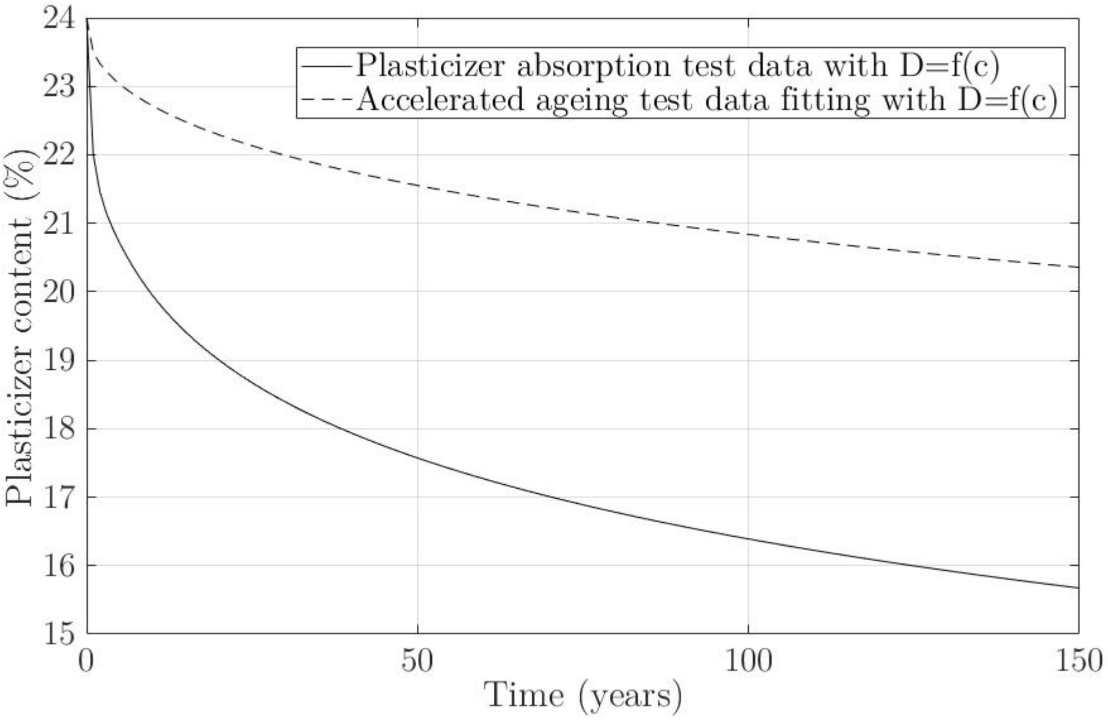

Figure 18 - Long-term extrapolation at 15°C for material A

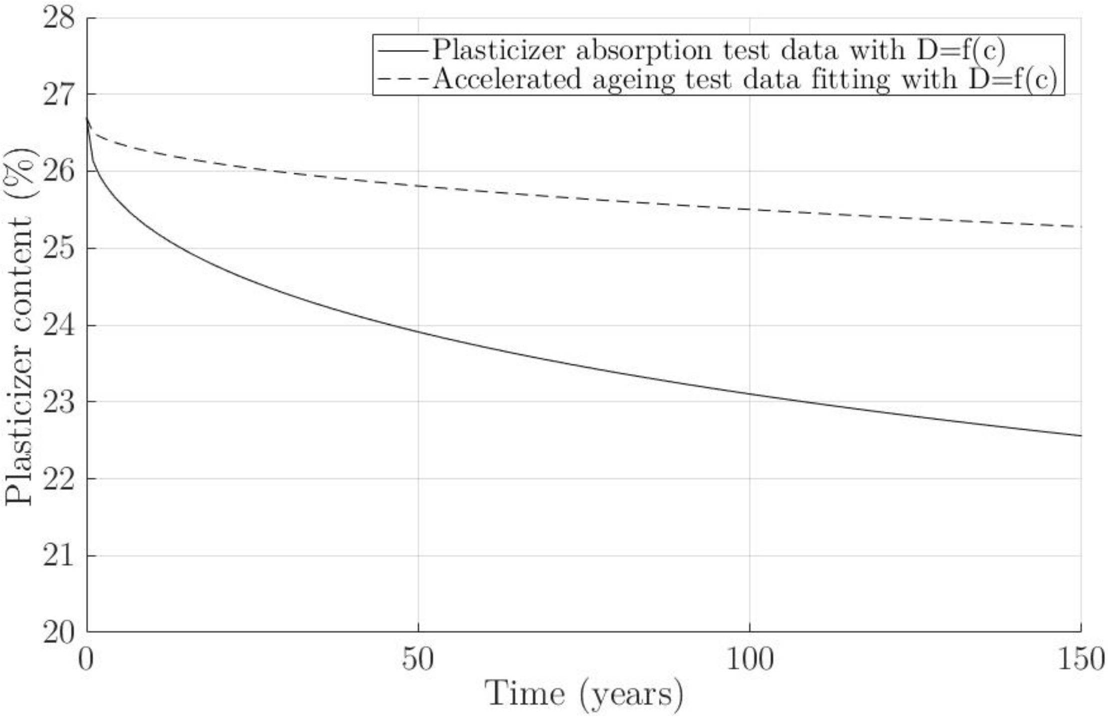

Figure 19 - Long-term extrapolation at 15°C for material B.

Similar projections can be made for other environments. For example, the highest temperature measured in deep tunnels (e.g. Brenner Base tunnel, Turin-Lyon Base tunnel) is about 45°C (Parisi *et al.*, 2017). This is a very demanding condition for PVC-P geomembranes, as confirmed by the extrapolation of plasticizer loss (Figure 20 and Figure 21).

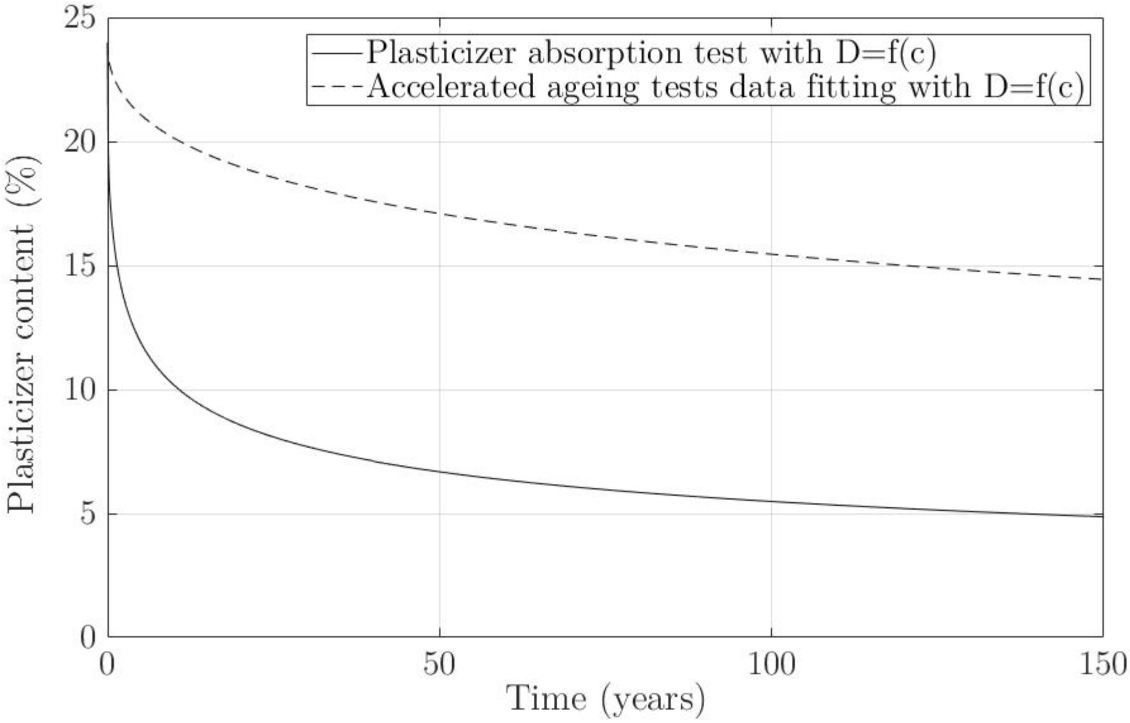

Figure 20 - Long-term extrapolation at 45°C for material A

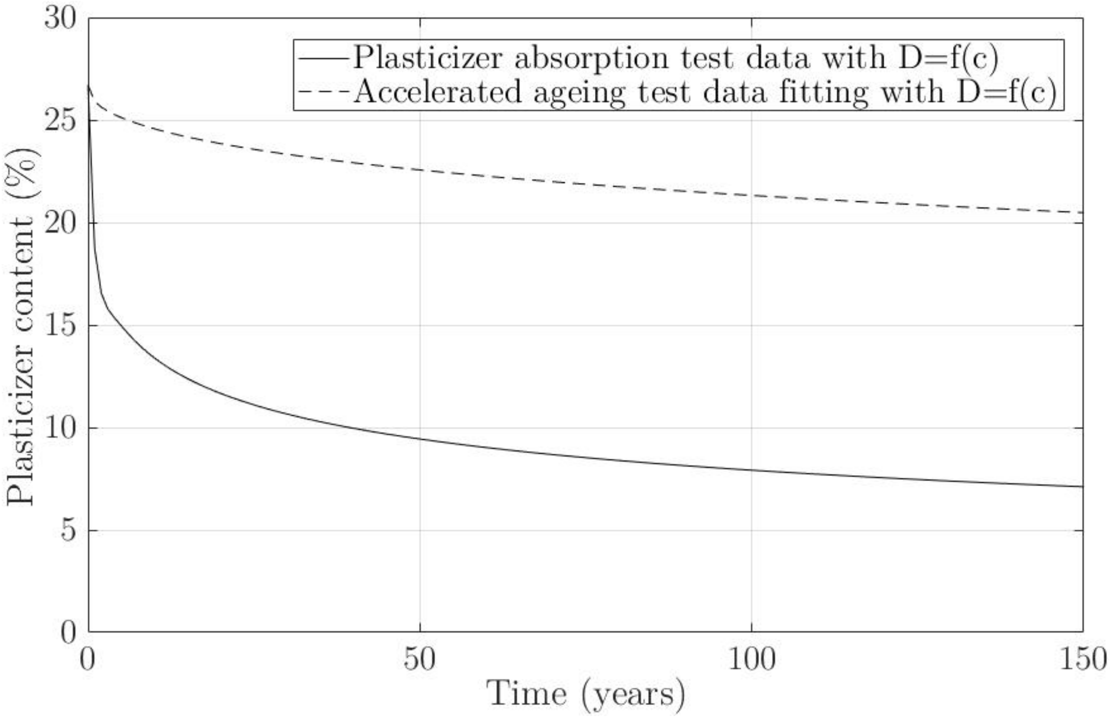

Figure 21 - Long-term extrapolation at 45°C for material B

7 DURABILITY ASSESSMENT

To determine the end-of-life of the waterproofing geomembrane, the time-dependent degradation resulting from plasticizer loss was linked with the corresponding variations in the available properties and compared with the desired properties during the life of the structure (ISO/TS 13434, 2008). Therefore, an analysis of the impact on the waterproofing system during all the phases of its life was necessary.

The installation and casting phase is the most crucial for the continuity and integrity of the geomembranes. Wrong welding or damages caused by job-site traffic, accidental dropping of tools, or rebars installation can cause holes in the geomembrane (Peggs, 2003; Mahuet, 2005; Benneton, 2008) and render the system ineffective. However, these actions are not influenced by the degradation. The actions on the geomembrane during operation are mainly compression resulting from load transmission from the primary lining to the final lining and the shrinkage caused by the loss of plasticizer.

Issues related to compression are mainly caused by the irregularities of the concrete surface. On one side, the shotcrete is usually uneven; therefore, a correct design of the regularization layer is important. On the other side, the cast-in-place concrete of the final lining should be smooth as it is casted in contact with the geomembrane. However, honeycombs, irregularities or incorrect design of the regularization layer can lead to partial or complete penetration of external elements (e.g. concrete aggregates, metallic fibres) into the geomembrane. Mechanical tests performed on the geomembranes showed that with the loss of plasticizer, the surface hardness of the material increases and, consequently, as the degradation progresses, the material becomes less susceptible to the penetration of external elements.

Reduction of elongation at break of the geomembrane is not a concern because the elongation is always higher than 100%, which is a very high value considering that the geomembrane is installed in between two concrete layers that will never withstand such a deformation.
Shrinkage resulting from the loss of plasticizer can be estimated from the theoretical equation proposed by Giroud (1995). Because the geomembrane is not free to shrink, this phenomenon leads to the formation of stresses in the material. These stresses can be evaluated from the tensile behaviour of the material, known the deformation due to the shrinkage. It is important to take into account that, as seen with the tensile tests on the tailor-made geomembranes, tensile behaviour changes with reduction in the plasticizer content: geomembranes change from a rubber-like material to an elasto-plastic one with a clear yielding point. Even if plastic deformation does not directly indicate failure of the waterproofing geomembrane, it causes an irreversible thinning of the geomembrane. Furthermore, in the event of an external element penetrating the geomembrane, locally concentrated stresses can occur, which may be further intensified by plastic deformation and lead to a local failure.

Therefore, a threshold value of the end-of-life of a geomembrane can be identified, on the safe side, at the value of plasticizer loss ratio that causes plastic deformation on the geomembranes. The mechanical tests results showed that the studied commercial geomembrane started to deform plastically at a plasticizer content of 15% and for a deformation of about 6%. Consequently, to avoid plastic deformation of the geomembrane, the limit is fixed to the minimum between 6% of elongation and the plasticizer loss ratio corresponding to a value of 15% of plasticizer content. Material A reached the plasticizer loss ratio limit while material B reached the elongation limit (Figure 22). For both materials, the limit of plasticizer loss ratio was 0.45.

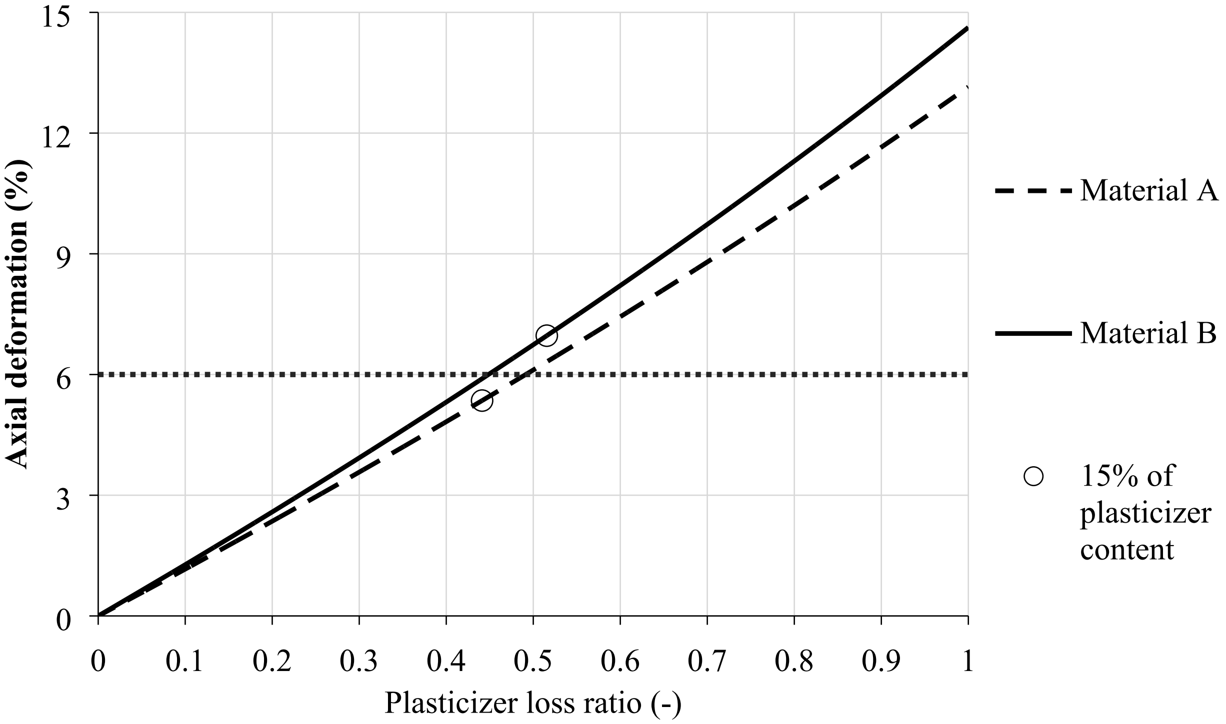

Figure 22 - Evaluation of the limiting value based on shrinkage

Given this threshold value, the end-of-life time of the two commercial membranes can be evaluated on the basis of the developed long-term extrapolations.
Table 5 reports the plasticizer loss ratios obtained in the simulation for the two materials.

Table 5 - Long-term extrapolation for materials A and B at 15°C and 45°C in terms of plasticizer loss ratio

			Plasticizer loss ratio (-)		
			50 years	100 years	150 years
15°C	Material A	Plasticizer absorption tests data with $D = f(C)$	0.32	0.38	0.41
		Accelerated ageing tests data with $D = f(C)$	0.13	0.17	0.19
	Material B	Plasticizer absorption tests data with $D = f(C)$	0.14	0.18	0.20
		Accelerated ageing tests data with $D = f(C)$	0.05	0.06	0.07
45°C	Material A	Plasticizer absorption tests data with $D = f(C)$	*0.77*	*0.82*	*0.84*
		Accelerated ageing tests data with $D = f(C)$	0.35	0.42	*0.47*
	Material B	Plasticizer absorption tests data with $D = f(C)$	*0.54*	*0.60*	*0.64*
		Accelerated ageing tests data with $D = f(C)$	0.20	0.26	0.29

At 15°C both materials were found to be effective for more than 150 years. Conversely, at 45°C, the extrapolation based on the experimental data showed a lifespan of 100 years for material A and beyond 150 years for material B, although neither was effective for 50 years considering the extrapolation based on the plasticizer absorption tests.

8 DISCUSSION

Long-term extrapolations should be handled with care because they are based on several simplifying hypotheses. The longer the extrapolation period, the higher the possible error in the estimation. Nevertheless, the model used in this paper is based on a theoretical equation describing the diffusion phenomenon, and it fits well with the experimental data.

The results of the plasticizer absorption tests can be considered the upper limit of possible plasticizer loss because of the assumption that the constant flux on the geotextile removes all the plasticizer from the surface. Further, the test conditions emphasize absorption. Indeed, in test conditions, the geomembrane specimens were perfectly clean on the surface and dry and the only material in contact with the PVC-P was the plasticizer. However, in real-world applications and in the accelerated ageing tests, the geomembrane has a certain moisture and is not perfectly clean; consequently, the diffusion of plasticizer is lower. The difference in the results of the accelerated ageing tests and those from the plasticizer absorption tests can be therefore attributed to this difference in the initial conditions. Moreover, the precipitation of calcium carbonate present in the water coming from the concrete can reduce the ability of the plasticizer to migrate from the surface to the water. In fact, if the calcium carbonate permeates the PVC matrix, it can further reduce the diffusion coefficient value. Usman and Galler (2014) provided evidence for the presence of calcium carbonate in geomembranes used in underground applications.

The extrapolations can be considered consistent with the two case studies reported in literature (Usman and Galler, 2014; Maehner, Peter and Sauerlaender, 2018). The two studies reported on naturally aged (after 30 and 43 years) PVC-P geomembranes with fillers. The temperature conditions were not reported, but since they refer to urban and shallow tunnels in Europe, it can be assumed to be close to 15°C. In both studies, the researchers did not report any variation in the mechanical properties. Unfortunately, data on the plasticizer content of the membranes were not reported. Nevertheless, it is possible to compare qualitatively the extrapolation at 15°C for 50 years for material A with the data reported in this study. The evaluated plasticizer loss ratio is 0.13 according to the accelerated ageing tests and 0.32 according to the plasticizer absorption tests. The latter is too high and should have resulted in more relevant changes in the mechanical properties. Although the reported cases studies are few in number and lack relevant information (e.g. temperature, water composition and flux, membrane composition and plasticizer content and type), they seem to confirm the extrapolations based on the experimental data obtained from the accelerated ageing tests, suggesting that the values possibly represent the loss of plasticizer in the real underground conditions.

9 CONCLUSIONS

The durability of waterproofing geomembranes is of great importance given the increasing quality requirements and lifespan of underground structures. Plasticizer loss has been identified as the only relevant degradation phenomenon to PVC-P geomembranes in underground applications. To analyse the long-term degradation of PVC-P geomembranes in underground application conditions, in this study, a specifically designed accelerated ageing device has been used for the tests. Furthermore, plasticizer absorption tests have been used to estimate the dependence of plasticizer loss on temperature and plasticizer content.

On the basis of these tests, an equation for extrapolating plasticizer loss in the long-term has been developed. This procedure takes into account the temperature of application at the job site. Two estimates have been derived: one for the possible upper limit of plasticizer loss, derived from the absorption tests, and the other more similar to what occurs in the reported real cases but less conservative, obtained from the accelerated ageing tests. By analysing the changes in physical and mechanical properties of aged and tailor-made geomembranes, with different content levels of plasticizer, a value of plasticizer loss ratio that can be considered as a threshold for the end of the effectiveness of the geomembrane has been evaluated at 0.45. While this value is close to that reported earlier by Benneton (1994) (0.5), the earlier value was not backed by justification.

While the procedure for long-term extrapolation and the proposed test device can be applied to other geomembranes, the final results and the threshold value reported here may be applicable only to the two analysed commercial geomembranes. Further tests are needed to extend these results to other materials, given the numerous possibilities in terms of plasticizer type and PVC-P formulation. Further, the proposed limit is conservative because it does not take into account the effect of relaxation of the geomembrane that may be relevant to plastic materials and to stresses applied very slowly.

Nevertheless, this study permits to assess that in many underground applications (urban tunnels, shallow tunnels) both the geomembranes analysed, with and without filer, may be effective for up to 150 years. In more demanding environments, the material without filler yields better performance in terms both of mechanical properties and long-term durability, as it shows a lower rate of plasticizer loss.

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