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# Durability of Poly (Vinyl Chloride)-Based Geomembranes in Aggressive Liquid Media

NORDTEST Technical Report 393

## Abstract

Mechanically unstressed PVC- based geomembranes, including welds, were immersed in three different test liquids which simulated common chemicals in transportation and waste deposit environments. The exposures were performed at three controlled temperatures in order to achieve an acceleration of degradation processes. The samples were characterised using tensile test, residual stability, infrared spectroscopy (FTIR), and determination of change in weight and dimensions.

The dimensions in both length and cross direction increase during exposure at different temperatures in the metal ions solution. The material also significantly loses its weight upon exposure. The weight loss increases with exposure time and with temperature. The metal ions solution significantly affects mechanical properties of the material as well. The elongation at break and the modulus decreases tremendously due to exposure in metal ions solution. The most pronounced change in the IR-spectra from the material exposed to the metal ions solution was associated with appearance of a strong absorption band at  $1630\text{ cm}^{-1}$ . As nitrate salts of the respective metal were used in preparation of the metal ions solution we believe that the absorption band at  $1630\text{ cm}^{-1}$  is attributed to a covalent nitrate  $-O-NO_2$ . After 12 months ageing at  $90\text{ }^\circ\text{C}$ , a significant reduction of the plasticiser content was observed in the middle of the membrane.

The material loses only slightly its weight upon exposure to the chloride ions solution and to the synthetic diesel oil. The weight loss is not significantly affected by exposure time. There is no significant change in dimensions upon exposures and there is no significant difference in dimension change between length and cross direction. The only change which is observed by FTIR-measurements, as a result of exposure in the chloride ions solution is appearance of new bands at  $1530$  and  $1560\text{ cm}^{-1}$  in the spectra. After 12 months ageing at  $90\text{ }^\circ\text{C}$ , a reduction of the plasticiser content is observed.

The synthetic diesel oil significantly affects mechanical properties of the materials. Already after seven weeks of exposure the elongation at break decreased by at least 70 % of the original value at all temperatures while Young's modulus increased by factor 2,5 indicating a great change in stiffness. The only change which is observed in the IR-spectra as a result of exposure is appearance of a new broad band between  $1600$  and  $1670\text{ cm}^{-1}$ . At the same time bands characteristic for the plasticiser almost disappear. The IR-spectra indicates that the plasticiser is extracted from the material and replaced by the diesel oil. It also appears that this effect is stronger in the material containing linear plasticiser compared with the material containing polymeric plasticiser.

**Key Words:** Durability, lifetime, geomembrane, leachate, accelerated ageing, poly (vinyl chloride), PVC

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# 1 Background and introduction

Ground water is a very valuable resource that must be protected from all sorts of contamination. The risk of contamination is greatest in connection with transportation (roads, railways, and airports), industry handling chemicals and waste deposits. A way to protect ground water is by using membranes as impermeable barriers in the ground.

Within the wide range of materials introduced for geomembranes, polyethylene (PE) and poly (vinyl chloride) (PVC) are among the most frequently used. The cost-effective use together with the set of favourable technical properties has caused the rapid growth of these materials.

One problem that remains is that materials with attractive installation properties can be adopted by the industry on the basis of a quality specification that has little correlation to long-term performance in the field. To avoid this problem, it is important to have appropriate test methods for a reliable prediction of service life. The design lifetime of constructions is often ranging between 50 and 120 years while some waste deposits are supposed to be intact for hundreds of years.

Long-term performance or durability is defined as "Ability of a construction and its parts to perform its required function over a period of time and under the influence of agents". The durability of geomembranes can be limited owing to such factors as mechanical damage, UV-light, oxidation, biodegradation, and the action of liquid chemicals. In deposits, different constituents from solid wastes can be leached by water which seeps through the deposit and accumulates on a geomembrane. Thus, the geomembrane will remain in contact with such liquid chemicals for a very long period of time.

The contact of polymeric materials with aggressive liquid media is accompanied by a complex range of physical and chemical processes. The following fundamental processes may occur:

- chemical degradation of the polymer
- sorption of the components of the aggressive medium
- solution of the polymer
- desorption of various additives
- change in the physical structure of the polymer.

In service, the various agents and other degradation factors may interact to increase the rate of degradation (synergistic effects).

For the present, there are only standards available which describe methods for testing of short-term compatibility of materials with some chemicals [1]. The results from such tests give no information suitable for prediction of long-term durability. Appropriate test methods for a reliable prediction of service life of geomembranes should include accelerated methods in various chemicals comprising not only materials but also joints because of the crucial importance of good jointing properties.

The aim of this research project was to investigate the influence of some frequently occurring liquid agents on the durability of PVC-based geomembranes. An accelerated test method which can be used for prediction of lifetime of geomembranes is also suggested. Furthermore, various methods for evaluation of degradation and failure were used, as the role of such methods is critical in the effectiveness of a durability testing programme.

## 2 Experimental

### 2.1 Materials

Two types of geomembranes were used in this project. The first PVC-membrane, called Protan GG, was exposed to all environments and temperatures used. The second membrane, called Protan GO, was exposed in parallel with the first one but in the synthetic diesel oil only. The membranes are produced by Protan A/S in Drammen, Norway.

Protan GG consists of two black layers of PVC with glass fibre reinforcement in between, see figure 1. The total thickness of the membrane is 2 mm. The layers consist of PVC with a linear phtalate plasticiser. The two layers have various thermal stability: the top layer has residual stability time according to ISO 182-2 pHTS = 140 min while the bottom layer has pHTS = 86 min.

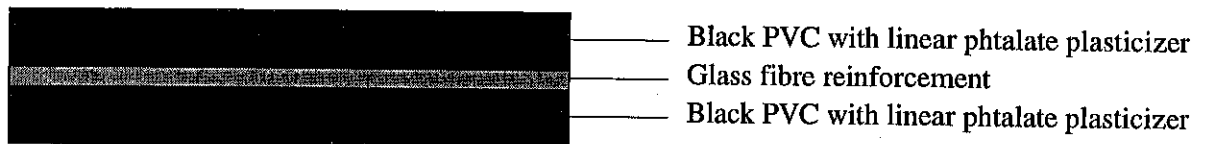


Figure 1: Composition of "Protan GG"

Protan GO consists of a grey top layer and an orange bottom layer of PVC with glass fibre reinforcement in between, see figure 2. The total thickness of the membrane is 2 mm. The layers consist of PVC with a polymeric plasticiser, polyphthalate.



Figure 2: Composition of "Protan GO"

Welds of the two membranes were produced, using hot air welding and 50 mm overlap.

IR spectra have been obtained from the bottom layer surface and from the middle of the membranes near the reinforcement of the exposed materials. The material was sliced with a microtome as shown in figure 3.

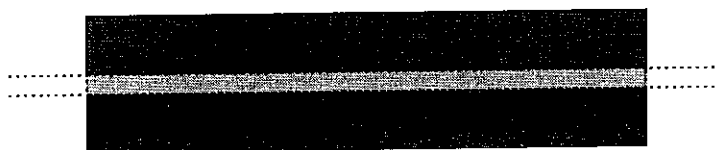


Figure 3: Slicing of the membranes for FTIR-analyses

## 2.2 Accelerated ageing

The quality of a durability prediction is closely related to the accuracy of the environmental simulation performed in the test. In this investigation, a survey of content and concentration of waste leachates in Nordic and European countries [2] provided the basis for the selection of the chemical environments in our tests.

Mechanically unstressed material was immersed in the test liquids for a twelve month test duration. The acceleration was achieved by an increase in temperature using the assumption that the degradation mechanisms can be described by a simple model given by the Arrhenius equation.

### 2.2.1 Chemical environment

Three different liquid media were chosen for the accelerated ageing:

#### A. Solution of metal ions:

Iron, Fe	1470 mg/l
Manganese, Mn	230 mg/l
Zinc, Zn	200 mg/l
Chromium, Cr	1,5 mg/l
Lead, Pb	0,44 mg/l
Copper, Cu	0,08 mg/l

For preparation of the solution nitrate salts of the respective metals were used. The nitrate salts are easily dissolvable and they don't form complex or precipitates with one another. Nitrate salts will also make the solution slightly oxidising.



The concentrations are taken from analyses of the leachate compositions from depositions in Great Britain and (West)Germany [3]. All depositions are in the acid phase. The leachate compositions of Swedish depositions show much lower concentrations of metal ions but this could be explained by the fact that there are very few analyses of depositions in the acid phase (new depositions) to be found in the literature. Furthermore, in Sweden samples of leachates are often collected in reception ditches and levelling depositories where the concentration is diluted and thus not representative for the leachate to which the geomembrane is exposed.

#### **B. Solution of salts for de-icing of roads, mainly NaCl:**

Chlorine, Cl	2600 mg/l
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#### **C. Synthetic diesel oil:**

Liquid paraffin	70 %
o-Dichlorobenzene	15 %
Dekahydronaphthalene (Decalin)	10 %
1,2,3,4-Tetrahydronaphthalene (Tetralin)	5 %

No commercial grade of diesel oil would withstand the long duration at the ageing temperatures without turning into coke. This synthetic diesel oil corresponds to a commercial diesel oil with 20 % aromatic content. Use of a synthetic diesel oil also makes it easier to reproduce the test conditions.

## **2.3 Evaluation methods**

### **2.3.1 Dimensional and weight changes**

The weight of each test sample was determined to the nearest 10 mg.

After exposure the samples from the metal and chloride ions solutions were rinsed in tap water, wiped off with paper and conditioned at standard laboratory atmosphere, 23 °C/50 % RH. The samples were then weighed and kept in the conditioning room until constant weight was achieved.

The samples that had been exposed to synthetic diesel oil were wiped off and carefully cleaned with paper soaked in methanol before weighing at standard laboratory atmosphere until constant weight.

The dimensions of the rectangular test samples were determined with a vernier calliper before exposure to the respective ageing temperature/chemical environment.

The distance between small holes at the edge of the sample was measured, giving the dimensions in length and cross direction of each test sample, see the broken lines in figure 4.

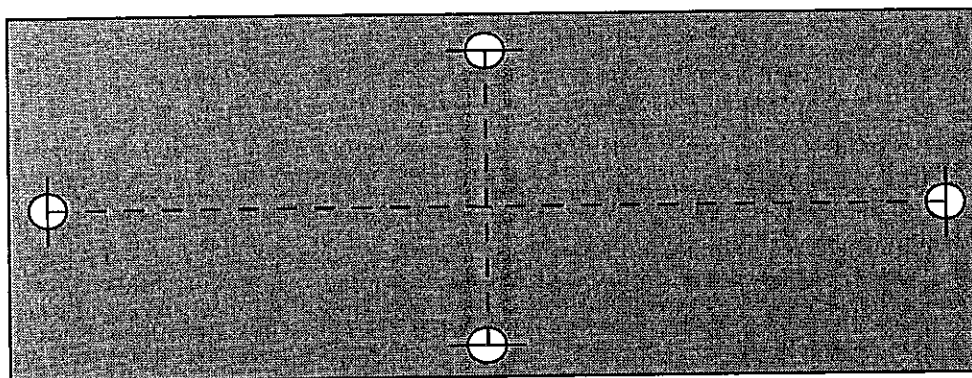


Figure 4: Test sample

The dimensions of the test samples after the respective exposure were determined after the cleaning and conditioning procedure described above under weight change.

### 2.3.2 Tensile properties

The membranes and welds were subjected to tensile tests before and after the respective accelerated ageing.

The membrane was tested as follows:

Tensile test according to ISO 1184.

- Strips, 50 mm wide, gauge length 100 mm.
- Test speed G, 100 mm/min.

The following parameters were determined (average of five specimens in each direction):

1. Stress at break [MPa]
2. Strain at break [%]
3. Energy at break [J]
4. Modulus [MPa]

The welds were tested as follows:

90 ° peel test, using the same size of test specimens and test speed as above. Load at break/width of weld [kN/m] was determined.

The tensile tests were performed with an Instron 5566 universal test machine. Elongation of the test specimens was determined optically using a video camera connected to the Instron test machine.

### **2.3.3 Residual stability**

Consumption of the stabilisers was monitored using dehydrochlorination measurements at 190 °C according to ISO 182-2. The weight of the samples was  $2,0 \pm 0,1$  g. The results are presented as stability time, pHTS, expressed in minutes.

The material was sliced with a microtome and the two layers were cut into pieces and tested separately. The stability time for each layer of the unaged material, 6 months aged and 12 months aged material at three different ageing temperatures, was measured.

### **2.3.4 Fourier Transform Infrared Spectroscopy, FTIR**

The FTIR investigation was carried out with a Cygnus 100 Mattson spectrophotometer equipped with attenuated total reflectance (ATR) attachment with KRS-5 crystal. IR spectra have been obtained from the bottom layer surface and from the middle of the membranes near the reinforcement of the materials exposed at the highest temperature in each liquid.



### 3 Results and discussion

Poly (vinyl chloride) - PVC generally contains plasticisers and stabilisers in order to provide plasticity and long term stability to the material. Long term performance of PVC - based geomembranes in deposits can be significantly limited by such factors like mechanical damage, chemical degradation and physical degradation.

Chemical degradation occurs mainly due to oxidation, dehydrochlorination processes in PVC and due to aggressive action of liquid chemicals. Oxidative degradation occurs due to action of oxygen and leads to the formation of carbonyl groups. Dehydrochlorination starts normally from the labile sites of the polymer leading to the formation of separate double bonds or polyene sequences. Aggressive action of liquid chemicals can affect PVC and additives, specially plasticisers, in many different ways. Physical degradation occurs mainly due to diffusional desorption of plasticisers and stabilisers leading to loss of elasticity and other mechanical properties.

Mechanically unstressed material, including welds, was immersed in three different test liquids which simulated common chemicals in transportation and waste deposit environments. The exposures were performed at three controlled temperatures in order to achieve an acceleration of degradation processes. The samples were characterised using tensile test, residual stability, infrared spectroscopy (FTIR) and determination of change in weight and dimensions.

#### 3.1 Durability in metal ions solution

The samples were exposed to the solution of metal ions as described in 2.2.1 at 70, 80 and 90 °C for the time periods of 3, 6, 9 and 12 months. The effect of the exposure was monitored using measurements of weight, dimensions, residual stability, IR-spectroscopy, and tensile properties (elongation at break, Young's modulus, etc.).

Measurements of weight and dimensions are summarised in the appendix - table 1. The material significantly loses its weight upon exposure to the metal ions solution. The weight loss increases with exposure time and with temperature. After twelve months of exposure the weight loss is about 2,5 % at 70 °C, 5 % at 80 °C, and 9 % at 90 °C.

Determination of the dimensions after exposures was difficult to perform because the test samples become wavy and distorted. The test results are therefore somewhat uncertain. There is no significant difference in dimension change between length and cross direction. The dimensions in both length and cross direction increase during exposure at different temperatures. After three months exposure the dimensions increased by about 7 % at 70 °C, 11 % at 80 °C, and 16 % at 90 °C. After six months the corresponding values were 14 %, 17 %, and 21 %. Additional exposure (9 and 12 months) appears to produce less dimension change than six months exposure.

The method used for the relative determination of the remaining amount of active stabiliser is described in ISO 182-2. The results are summarised in table 1 as induction time pHTS expressed in minutes.

The unaged material from the top and bottom layer gives different values. Even the rate of stabiliser depletion is different indicating that the two layers contain probably different stabiliser systems. Substantial effect of the exposure is clearly shown in table 1. The unaged material in the top layer gives the highest value but upon prolonged exposure this value decreases rapidly, significantly depending on exposure temperatures.

**Table 1**

Ageing temperature [°C]	Induction time pHTS for the black material aged in metal ions solution [min]					
	Top layer			Bottom layer		
	Unaged	Aged 6 months	Aged 12 months	Unaged	Aged 6 months	Aged 12 months
70	140	120	68	86	87	71
80	140	66	33	86	70	40
90	140	41	28	86	45	27

The results of the tensile test: stress and elongation at break, energy at break, and Young's modulus are summarised in the appendix - table 2. It is clear that the metal ions solution significantly affects mechanical properties of the material. No significant difference is observed between length and cross direction. The biggest change is monitored after three months exposure. Change in elongation at break of length direction is presented in figure 5 below.

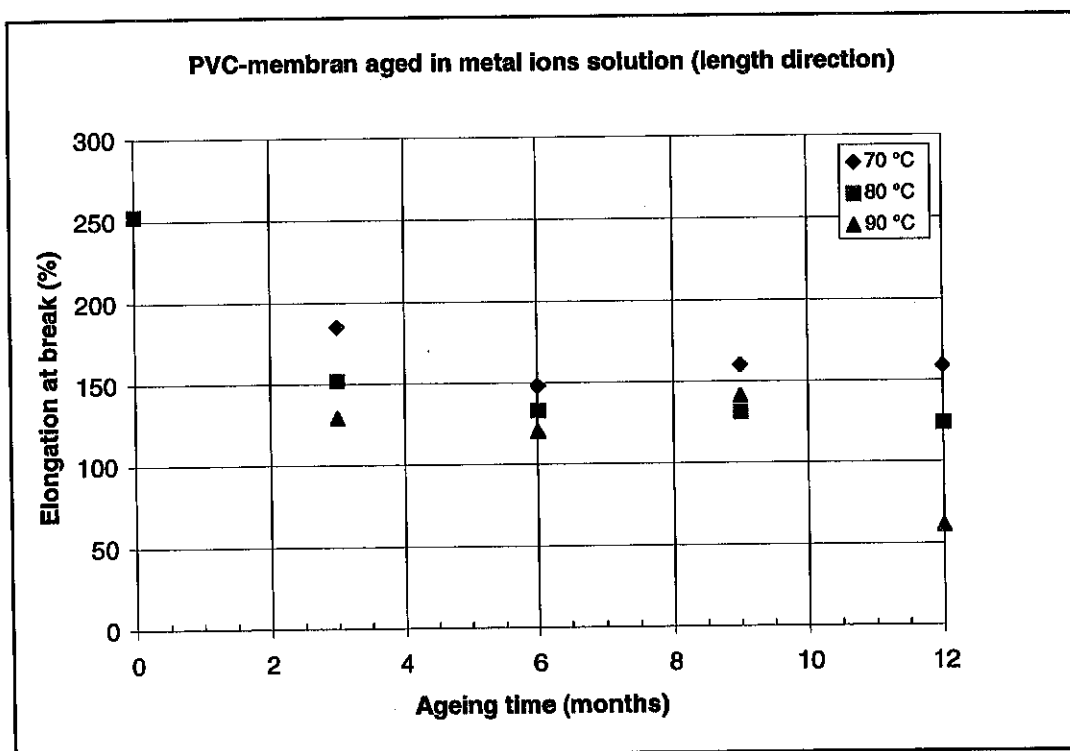


Figure 5: Change in elongation at break of length direction of the material aged in metal ions solution at 70, 80 and 90 °C as a function ageing time.

Tensile modulus measurements are among the most important indications of the strength in a material. The modulus indicates the relative stiffness of a material and is determined from a stress-strain diagram. Only a slight difference is observed between length and cross direction (645 MPa and 566 MPa respectively). Change in modulus of the length direction is presented in figure 6 below. It is evident that the modulus decreases tremendously due to exposure in metal ions solution.

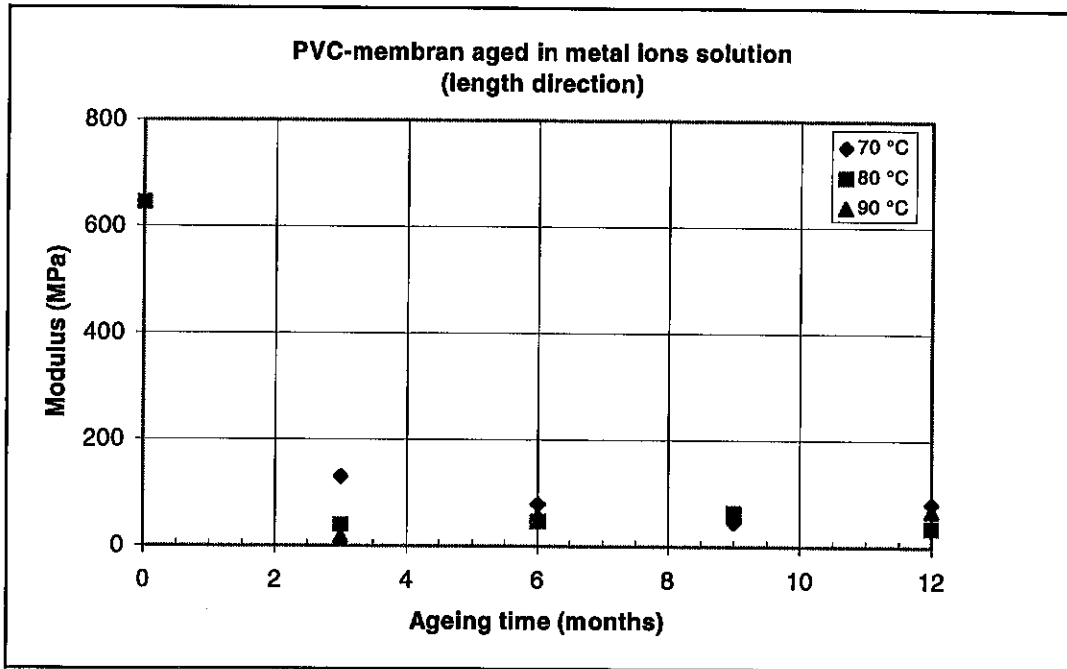


Figure 6: Change in Young's modulus of the length direction of the material aged in metal ions solution at 70, 80 and 90 °C as a function ageing time.

The degradation of the material was also followed by FTIR-measurements. IR spectra have been obtained from the bottom layer surface and from the middle of the membranes near the reinforcement of the materials exposed at the highest temperature in the solution of metal ions. No significant difference was observed between spectra from the surface and from the middle of the exposed membrane.

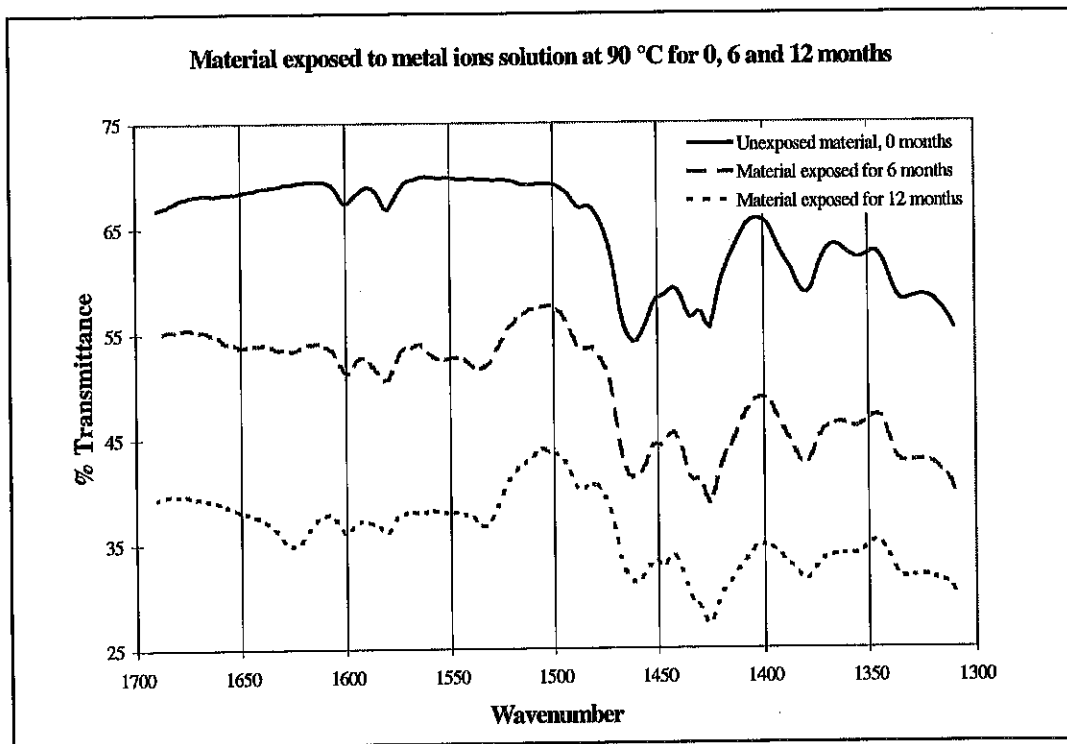


Figure 7: IR-spectra from the middle of the membrane after 0, 6 and 12 months exposure.

The most pronounced change in the IR-spectra was associated with appearance of a strong absorption band at  $1630\text{ cm}^{-1}$ . As nitrate salts of the respective metal were used in preparation of the metal ions solution we believe that the absorption band at  $1630\text{ cm}^{-1}$  is attributed to a covalent nitrate  $-\text{O}-\text{NO}_2$  as in the previous investigation [4]. Even new bands at  $1530$  and  $1560\text{ cm}^{-1}$  appear in the spectra as a result of exposure. After 12 months ageing at  $90\text{ }^\circ\text{C}$ , a significant reduction of the plasticiser content was also observed in the middle of the membrane.

### 3.2 Durability in chloride ions solution

The samples were exposed to the solution of chloride ions (see 2.2.1) at  $70$ ,  $80$  and  $90\text{ }^\circ\text{C}$  for the time periods of 3, 6, 9 and 12 months. The effect of the exposure was monitored using measurements of weight, dimensions, residual stability, IR-spectroscopy, and tensile properties (elongation at break, Young's modulus, etc.).

Measurements of weight and dimensions are summarised in the appendix - table 1. The material loses only slightly its weight upon exposure to the chloride ions solution. The weight loss is not significantly affected by exposure time. After twelve months of exposure the weight loss is about 1 % at  $70\text{ }^\circ\text{C}$ , 1,5 % at  $80\text{ }^\circ\text{C}$ , and 3 % at  $90\text{ }^\circ\text{C}$ .

Determination of the dimensions after exposures was difficult to perform because the test samples became distorted. The test results are therefore somewhat uncertain. There is no significant change in dimensions (less than 0,3 %) upon exposures and there is no significant difference in dimension change between length and cross direction.

The method used for the relative determination of the remaining amount of active stabiliser is described in ISO 182-2. The results are summarised in table 2 as induction time pHTS expressed in minutes.



The unaged material from the top and bottom layer gives different values. The effect of the exposure is shown in table 2. The unaged material in the top layer gives the highest value but upon prolonged exposure this value decreases, depending on exposure temperatures. The values of the bottom layer increase after six months exposure which is difficult to explain.

**Table 2**

Ageing temperature [°C]	Induction time pHTS for the black material aged in chloride ions solution [min]					
	Top layer			Bottom layer		
	Unaged	Aged 6 months	Aged 12 months	Unaged	Aged 6 months	Aged 12 months
70	140	144	127	86	131	91
80	140	118	79	86	106	75
90	140	70	27	86	95	19

The results of the tensile test: stress and elongation at break, energy at break, and Young's modulus are summarised in the appendix - table 2. The chloride ions solution does not significantly affect mechanical properties of the material. After twelve months exposure the elongation at break decreased by about 12 % of the original value at 70 °C, 16 % at 80 °C, and 24-28 % at 90 °C. No significant difference is observed between length and cross direction. Change in elongation at break of length direction is presented in figure 8 below.

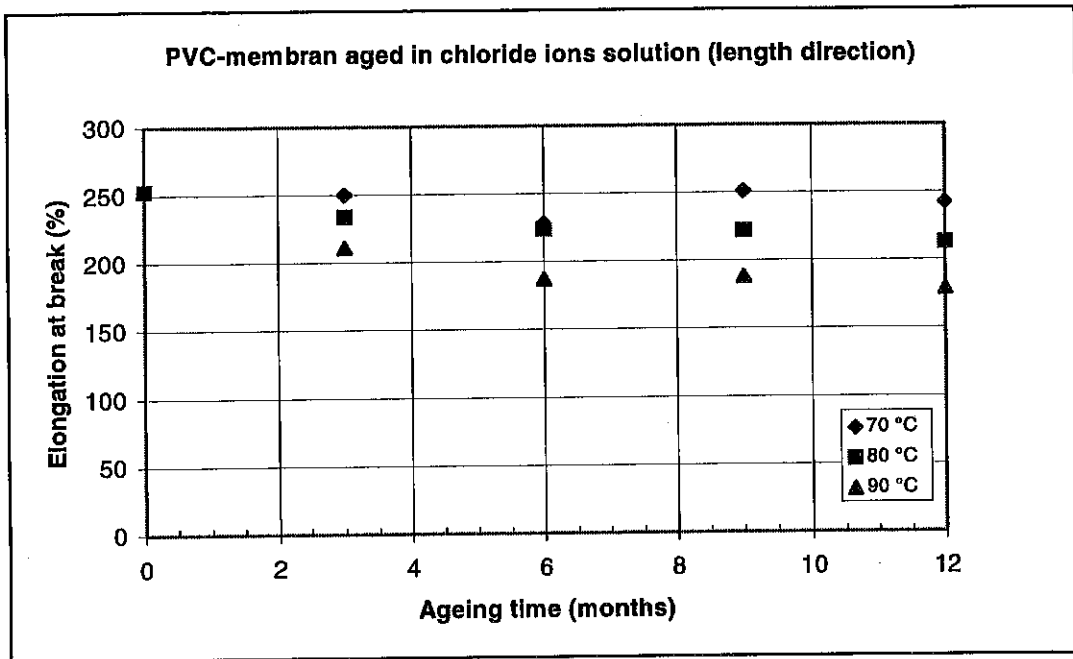


Figure 8: Change in elongation at break of length direction of the material aged in chloride ions solution at 70, 80 and 90 °C as a function ageing time.

Only a slight difference in tensile modulus is observed between length and cross direction (645 MPa and 566 MPa respectively). Change in modulus of the length direction is presented in figure 9 below. It is evident that the modulus is not significantly affected by the exposure in chloride ions solution.

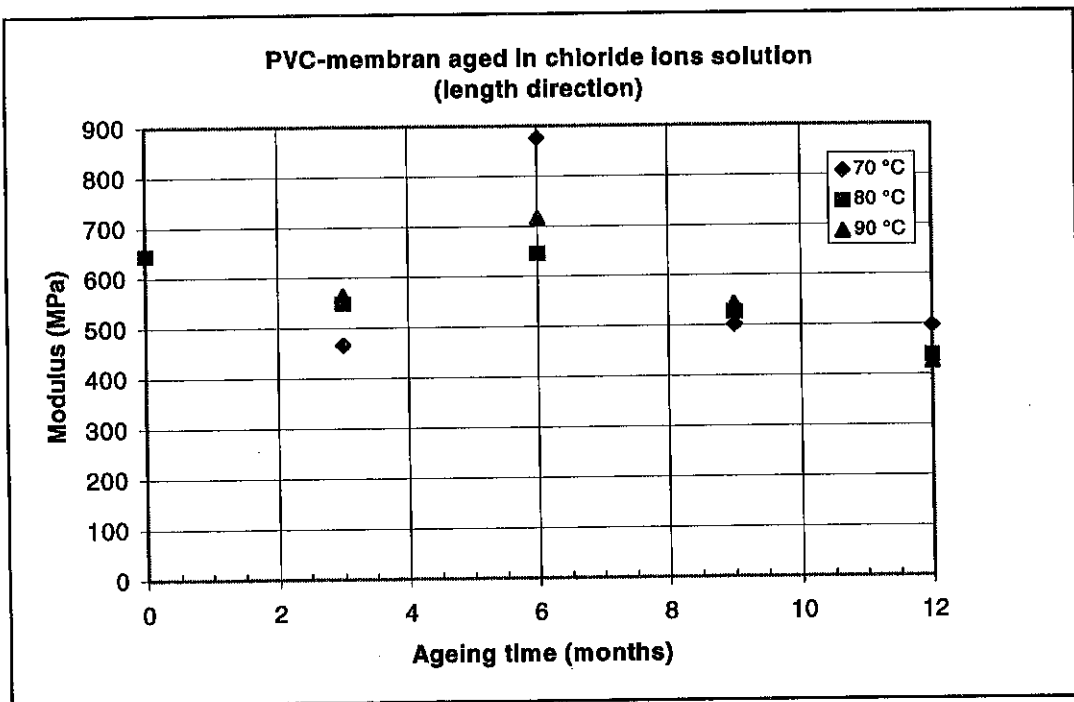


Figure 9: Change in Young's modulus of the length direction of the material aged in chloride ions solution at 70, 80 and 90 °C as a function ageing time.

The degradation of the material was also followed by FTIR-measurements. IR spectra have been obtained from the bottom layer surface and from the middle of the membranes near the reinforcement of the materials exposed at the highest temperature in the solution of chloride ions. No significant difference was observed between spectra from the surface and from the middle of the exposed membrane. The only change which was observed as a result of exposure was appearance of new bands at 1530 and 1560  $\text{cm}^{-1}$  in the spectra. After 12 months ageing at 90 °C, a reduction of the plasticiser content was also observed. As no significant difference was observed between spectra from the surface and from the middle of the exposed membrane it should indicate an internal diffusion kinetic of the reaction (the reaction takes place in the whole volume of the material).

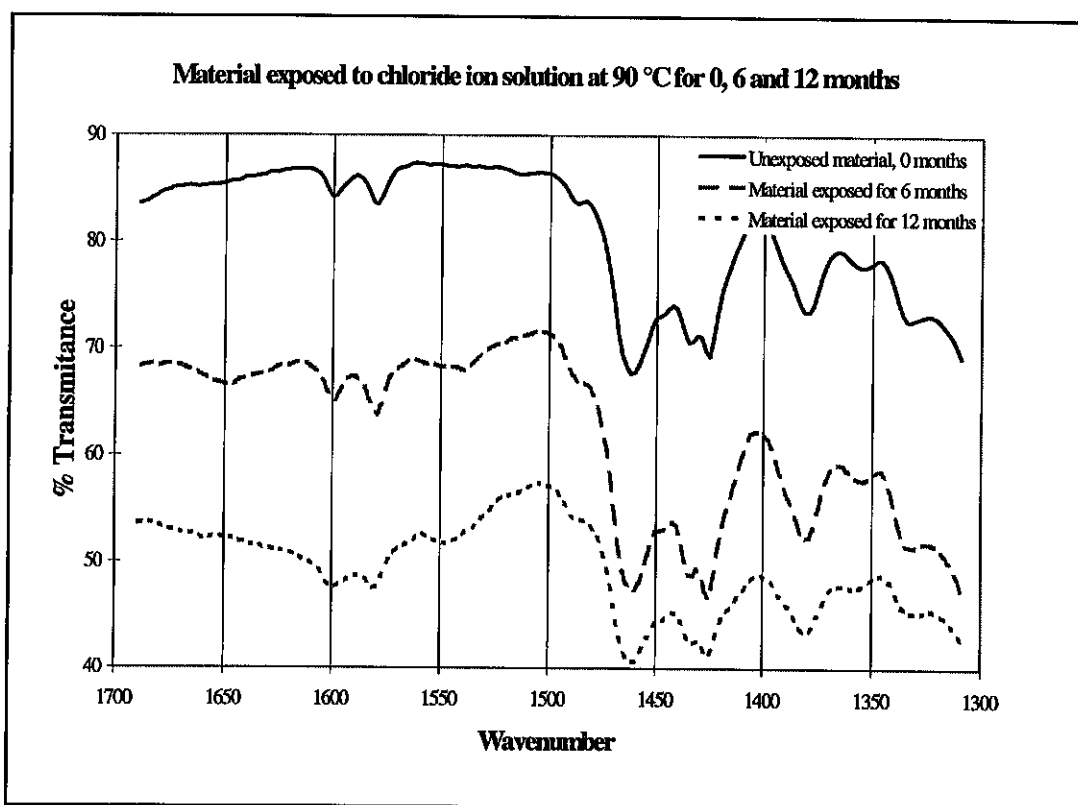


Figure 10: IR-spectra from the middle of the membrane after 0, 6 and 12 months exposure.

### 3.3 Durability in synthetic diesel oil

Two types of geomembranes were used in this project. The samples were immersed in the synthetic diesel oil described in 2.2.1 at 50, 60, and 70 °C for the time periods of 7, 14, 21, 28, and 35 weeks. The effect of the exposure was monitored using measurements of weight, dimensions, IR-spectroscopy, and tensile properties (elongation at break, Young's modulus, etc.).

Measurements of weight and dimensions are summarised in the appendix - table 1. The material loses only slightly its weight upon exposure to the synthetic diesel oil. The weight loss is not significantly affected by exposure time. Protan GG (containing linear phthalate plasticiser) loses only 0,1 - 0,3 % of its weight while Protan GO GG (containing polymeric plasticiser) loses 0,2 - 0,7 %.

Determination of the dimensions after exposures was difficult to perform because the test samples became distorted. The test results are therefore somewhat uncertain. There is no significant change in dimensions (less than 1 %) upon exposures and there is no significant difference in dimension change between length and cross direction and no significant difference between the two materials.

The results of the tensile test: stress and elongation at break, energy at break, and Young's modulus are summarised in the appendix - table 2. The synthetic diesel oil significantly affects mechanical properties of the material. Already after seven weeks of exposure of Protan GG the elongation at break decreased by about 70 % of the original value at 50 °C and 60 °C, and 90 % at 70 °C. For Protan GO the corresponding values are about 90 % of the original value at 50 °C and 60 °C and about 70 % at 70 °C.

The modulus indicates the relative stiffness of a material. In this case values of Young's modulus increased by factor 2,5 indicating a great change in stiffness. No significant difference was observed between length and cross direction. The results of weight and tensile measurements indicate that the materials exposed to the synthetic diesel oil lose their plasticiser and consequently lose their elasticity.

The degradation of the materials was also followed by FTIR-measurements. IR spectra have been obtained from the bottom layer surface and from the middle of the membranes near the reinforcement of the materials exposed at the highest temperature in synthetic diesel oil. No significant difference was observed between spectra from the surface and from the middle of the exposed membranes. The only change which was observed as a result of exposure was appearance of new broad band between 1600 and 1670  $\text{cm}^{-1}$  in the spectra. At the same time bands characteristic for the plasticiser (i.a. 1720  $\text{cm}^{-1}$ , 1600  $\text{cm}^{-1}$ , 1575  $\text{cm}^{-1}$ , 1286  $\text{cm}^{-1}$ , and 1124  $\text{cm}^{-1}$ ) almost disappeared. The IR-spectra indicate that the plasticiser was extracted from the material and replaced by the diesel oil. It also appears that this effect is stronger in the material containing linear plasticiser compared with the material containing polymeric plasticiser (see figures 11 and 12).

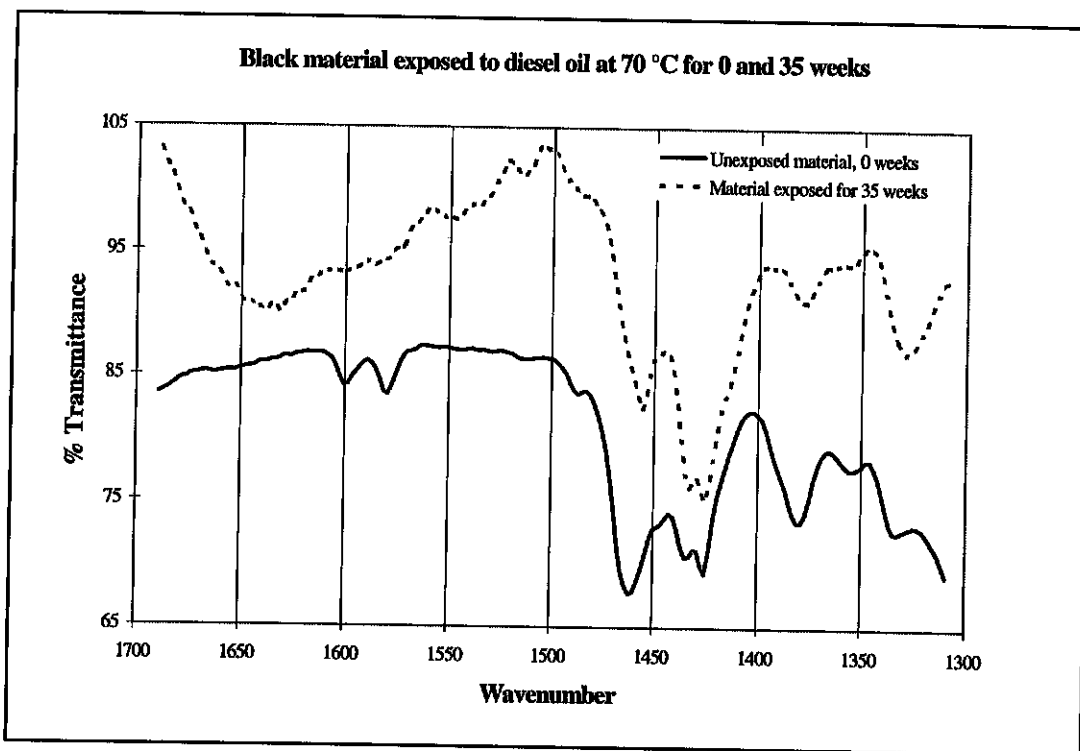


Figure 11: IR-spectra from the middle of the membrane Proran GG after 0 and 35 weeks of exposure in synthetic diesel oil.

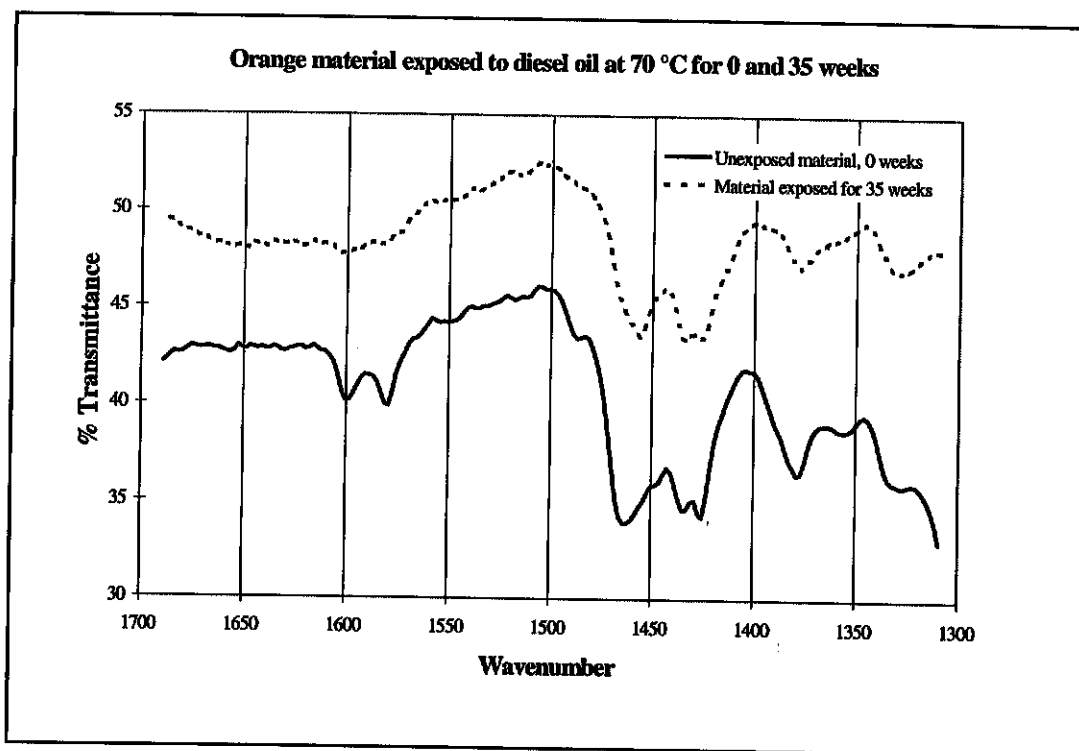


Figure 12: IR-spectra from the middle of the membrane Proran GO after 0 and 35 weeks of exposure in synthetic diesel oil.

### **3.4 Durability of welds**

The result from the tensile tests of the welded material show that the hot air welds are stronger than the material after exposure to all test liquids, temperatures, and exposure times. All the test samples have broken in the material leaving the hot air weld intact.

## 4 Conclusions

Mechanically unstressed material, including welds, was immersed in three different test liquids which simulated common chemicals in transportation and waste deposit environments. The exposures were performed at three controlled temperatures in order to achieve an acceleration of degradation processes. The samples were characterised using tensile test, residual stability, infrared spectroscopy (FTIR), and determination of change in weight and dimensions.

The dimensions in both length and cross direction increase during exposure at different temperatures. The material significantly loses its weight upon exposure to the metal ions solution. The weight loss increases with exposure time and with temperature. After twelve months of exposure the weight loss is about 2,5 % at 70 °C, 5 % at 80 °C, and 9 % at 90 °C. The metal ions solution significantly affects mechanical properties of the material as well. The elongation at break and the modulus decreases tremendously due to exposure in metal ions solution. No significant difference is observed between length and cross direction. The biggest change is monitored after three months exposure.

The most pronounced change in the IR-spectra from the material exposed to the metal ions solution was associated with appearance of a strong absorption band at 1630  $\text{cm}^{-1}$ . As nitrate salts of the respective metal were used in preparation of the metal ions solution we believe that the absorption band at 1630  $\text{cm}^{-1}$  is attributed to a covalent nitrate  $-\text{O}-\text{NO}_2$  as in the previous investigation [4]. Even new bands at 1530 and 1560  $\text{cm}^{-1}$  appear in the spectra as a result of exposure. After 12 months ageing at 90 °C, a significant reduction of the plasticiser content was observed in the middle of the membrane.

The material loses only slightly its weight upon exposure to the chloride ions solution. The weight loss is not significantly affected by exposure time. There is no significant change in dimensions (less than 0,3 %) upon exposures and there is no significant difference in dimension change between length and cross direction. The only change which is observed by FTIR-measurements as a result of exposure is appearance of new bands at 1530 and 1560  $\text{cm}^{-1}$  in the spectra. After 12 months ageing at 90 °C, a reduction of the plasticiser content was observed.

The material loses only slightly its weight upon exposure to the synthetic diesel oil. The weight loss is not significantly affected by exposure time. There is no significant change in dimensions (less than 1 %) upon exposures and there is no significant difference in dimension change between length and cross direction and no significant difference between the two materials. The synthetic diesel oil significantly affects mechanical properties of the material. Already after seven weeks of exposure the elongation at break decreased by at least 70 % of the original value at all temperatures while Young's modulus increased by factor 2,5 indicating a great change in stiffness. No significant difference was observed between length and cross direction.

No significant difference is observed between IR-spectra from the surface and from the middle of the membrane exposed to the synthetic diesel oil. The only change which is observed as a result of exposure is appearance of new broad band between 1600 and 1670  $\text{cm}^{-1}$  in the spectra. At the same time bands characteristic for the plasticiser (i.a. 1720  $\text{cm}^{-1}$ , 1600  $\text{cm}^{-1}$ , 1575  $\text{cm}^{-1}$ , 1286  $\text{cm}^{-1}$ , and 1124  $\text{cm}^{-1}$ ) almost disappear. The IR-spectra indicate that plasticisers are extracted from the materials and replaced by diesel oil. It also appears that this effect is stronger in the material containing linear plasticiser compared with the material containing polymeric plasticiser.





## 5 References

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Table 1: Dimensional and weight changes

<b>50 °C Synthetic diesel oil, Black material, Length direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,31	-0,46	-0,3
14	+1,10	+0,26	-0,3
21	-0,36	-0,47	-0,2
28	-0,41	-0,40	-0,2
35	-0,38	-0,48	-0,2

<b>50 °C Synthetic diesel oil, Black material, Cross direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,34	-0,50	-0,3
14	+0,90	+0,93	-0,3
21	-0,32	-0,55	-0,2
28	-0,30	-0,34	-0,2
35	-0,03	-0,60	-0,2

<b>60 °C Synthetic diesel oil, Black material, Length direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,32	-0,42	-0,2
14	+1,56	+0,77	-0,2
21	-0,39	-0,46	-0,1
28	-0,17	+0,25	-0,1
35	-0,13	+0,25	-0,2

<b>60 °C Synthetic diesel oil, Black material, Cross direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,27	-0,55	-0,1
14	-0,15	+0,42	-0,1
21	-0,33	-0,69	-0,1
28	+0,11	-0,64	-0,2
35	+0,22	-0,33	-0,2

<b>70 °C Synthetic diesel oil, Black material, Length direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,48	-0,34	-0,1
14	-1,50	+0,63	-2,0
21	-0,36	-0,43	-0,1
28	-0,33	-0,40	-0,1
35	-0,17	-0,37	-0,1

<b>70 °C Synthetic diesel oil, Black material, Cross direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,18	-0,35	-0,1
14	+0,67	-0,70	-0,1
21	-0,25	-0,32	-1,0
28	-0,35	-0,59	-0,2
35	-0,33	-0,51	-0,1

<b>50 °C Synthetic diesel oil, Grey material, Length direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,43	-0,52	-0,3
14	-0,40	-0,26	-0,7
21	-0,16	-0,53	-0,3
28	-0,06	-0,46	-0,4
35	-0,44	-0,43	-0,6

<b>50 °C Synthetic diesel oil, Grey material, Cross direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,25	-0,45	-0,3
14	-0,00	+0,01	-0,7
21	-0,25	-0,44	-0,3
28	-0,25	-0,46	-0,4
35	-0,28	-0,51	-0,6

<b>60 °C Synthetic diesel oil, Grey material, Length direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,17	-0,39	-0,2
14	+1,32	+0,84	-0,5
21	-0,09	-0,41	-0,3
28	-0,26	-0,17	-0,3
35	-0,24	-0,12	-0,3

<b>60 °C Synthetic diesel oil, Grey material, Cross direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,25	-0,50	-0,2
14	+0,89	+1,68	-0,4
21	-0,23	-0,52	-0,3
28	-0,09	-0,47	-0,3
35	+0,08	-0,46	-0,3

<b>70 °C Synthetic diesel oil, Grey material, Length direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,22	-0,40	-0,2
14	+1,30	+0,47	-0,3
21	-0,20	-0,34	-0,2
28	-0,26	-0,37	-0,3
35	-0,10	-0,43	-0,2

<b>70 °C Synthetic diesel oil, Grey material, Cross direction</b>			
<b>Time (weeks)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
7	-0,29	-0,77	-0,2
14	+0,20	-0,49	-0,2
21	-0,17	-0,47	-0,2
28	-0,32	-0,43	-0,2
35	-0,26	-0,44	-0,2

<b>70 °C Metal ions, Black material, Length direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	+7,63	+7,20	-0,5
6	+11,53	+16,49	-0,8
9	+8,56	+9,64	-1,3
12	+9,29	+9,55	-2,4

<b>70 °C Metal ions, Black material, Cross direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	+7,91	+6,27	-0,5
6	+16,01	+11,40	-0,8
9	+9,51	+10,17	-1,7
12	+10,42	+9,85	-2,5

<b>80 °C Metal ions, Black material, Length direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	+8,91	+12,65	-1,5
6	+11,40	+22,82	-2,8
9	+14,01	+16,07	-3,9
12	+14,22	+7,77	-5,7

<b>80 °C Metal ions, Black material, Cross direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	+12,28	+9,09	-1,5
6	+19,13	+14,85	-2,8
9	+16,93	+12,81	-3,7
12	+17,44	+12,95	-4,2

<b>90 °C Metal ions, Black material, Length direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	+11,38	+17,37	-3,1
6	+18,45	+25,10	-6,4
9	+10,10	+10,46	-8,5
12	+3,30	+9,83	-9,1
<b>90 °C Metal ions, Black material, Cross direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	+18,79	+16,75	-3,0
6	+20,66	+18,90	-6,3
9	+12,13	+11,60	-8,1
12	+10,12	+6,87	-8,9

<b>70 °C Chloride ions, Black material, Length direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	-0,15	-0,12	-0,8
6	-0,19	0,00	-1,0
9	-0,02	0,00	-0,9
12	+0,06	-0,10	-1,0

<b>70 °C Chloride ions, Black material, Cross direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	-0,16	-0,23	-0,8
6	+0,05	0,00	-1,0
9	-0,02	-0,12	-0,9
12	-0,09	-0,18	-1,0

<b>80 °C Chloride ions, Black material, Length direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	-0,27	-0,31	-1,3
6	+0,16	-0,06	-1,1
9	+0,07	-0,00	-1,7
12	-0,05	+0,17	-2,0

<b>80 °C Chloride ions, Black material, Cross direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	-0,12	+0,13	-1,3
6	-0,02	+0,11	-1,8
9	+0,07	-3,83	-1,7
12	+0,07	+0,03	-0,9



<b>90 °C Chloride ions, Black material, Length direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	0,00	-0,05	-1,9
6	+0,06	+0,09	-2,8
9	+0,35	+0,07	-3,1
12	-0,22	+0,22	+4,1
<b>90 °C Chloride ions, Black material, Cross direction</b>			
<b>Time (months)</b>	<b>Dimensional change (%)</b>		<b>Weight change (%)</b>
	<b>Length</b>	<b>Cross</b>	
3	-0,12	-0,15	-1,9
6	+0,05	-0,05	-2,7
9	+0,16	+0,12	-3,2
12	+0,19	+0,30	+8,3

Table 2: Tensile properties of the geomembranes

<b>70 °C Metal ions, Black material, Length direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
3	13,1	185	83	130
6	11,9	148	57	79
9	12,0	160	61	45
12	12,7	159	65	81
<b>70 °C Metal ions, Black material, Cross direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
3	12,2	182	73	42
6	11,5	149	55	31
9	11,5	151	54	26
12	12,1	158	60	42

<b>80 °C Metal ions, Black material, Length direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
3	11,1	152	54	40
6	10,3	133	41	47
9	11,0	131	43	64
12	11,7	124	43	36
<b>80 °C Metal ions, Black material, Cross direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
3	10,8	140	47	25
6	10,2	133	40	21
9	10,0	116	33	26
12	10,5	116	36	39

<b>90 °C Metal ions, Black material, Length direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
3	9,2	129	35	18
6	9,9	120	36	56
9	11,9	141	51	62
12	7,5	61	15	68
<b>90 °C Metal ions, Black material, Cross direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
3	9,3	131	36	21
6	10,0	122	38	54
9	11,4	137	48	75
12	6,9	61	15	48

<b>70 °C Chloride ions, Black material, Length direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
3	14,7	250	136	466
6	15,7	228	129	876
9	15,0	251	141	501
12	15,4	242	133	497

<b>70 °C Chloride ions, Black material, Cross direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
3	14,3	230	118	393
6	15,1	216	118	557
9	14,4	224	116	399
12	14,9	224	116	392

<b>80 °C ions, Black material, Length direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
3	14,7	234	126	549
6	15,0	224	118	646
9	14,6	222	115	527
12	14,8	213	108	439

<b>80 °C Chloride ions, Black material, Cross direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
3	14,1	225	114	461
6	10,9	187	86	379
9	14,9	210	108	675
12	14,5	207	102	448

<b>90 °C Chloride ions, Black material, Length direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
3	14,5	211	110	564
6	15,1	187	97	717
9	14,6	188	92	543
12	14,5	179	87	426
<b>90 °C Chloride ions, Black material, Cross direction</b>				
<b>Time Months</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
3	13,9	205	101	439
6	14,9	191	96	987
9	14,6	185	89	415
12	13,9	186	85	108

<b>50 °C Synthetic diesel oil, Black material, Length direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
7	19,1	72	76	1 684
14	12,8	76	79	1 521
21	22,2	68	78	1 747
28	22,0	53	63	1 847
35	17,5	41	50	2 383

<b>50 °C Synthetic diesel oil, Black material, Cross direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
7	20,5	86	87	1 340
14	16,6	77	78	1 459
21	21,1	62	67	1 513
28	19,3	74	81	1 573
35	22,2	73	83	1 838

<b>60 °C Synthetic diesel oil, Black material, Length direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
7	21,4	80	87	3 064
14	20,9	29	35	1 984
21	32,6	7	12	2 932
28	21,4	13	17	2 467
35	21,6	12	16	2 291

<b>60 °C Synthetic diesel oil, Black material, Cross direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
7	21,4	80	86	1 845
14	23,0	65	74	1 988
21	30,7	6	9	2 781
28	15,9	11	14	2 433
35	27,9	9	12	2 450

<b>70 °C Synthetic diesel oil, Black material, Length direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,9	253	128	645
7	23,3	27	35	2 613
14	34,5	6	10	3 188
21	32,4	5	7	3 869
28	33,8	5	8	3 146
35	38,3	4	6	3 539
<b>70 °C Synthetic diesel oil, Black material, Cross direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	13,8	249	121	566
7	21,2	25	32	2 088
14	30,6	11	16	2 268
21	31,6	6	9	3 355
28	32,5	5	8	3 167
35	35,5	5	6	3 539

<b>50 °C Synthetic diesel oil, Grey material, Length direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	14,5	211	114	678
7	11,5	24	26	1 786
14	13,5	42	45	1 758
21	14,8	24	26	1 694
28	13,5	33	39	2 064
35	14,4	38	41	1 547

<b>50 °C Synthetic diesel oil, Grey material, Cross direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	14,0	217	117	512
7	13,4	29	31	1 451
14	10,6	58	56	1 206
21	10,8	33	33	1 629
28	11,7	50	50	1 241
35	12,8	48	48	1 247

<b>60 °C Synthetic diesel oil, Grey material, Length direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	14,5	211	114	678
7	11,8	32	35	1 429
14	13,8	52	53	1 487
21	17,0	24	29	1 588
28	14,0	32	38	1 595
35	13,0	30	34	2 024

<b>60 °C Synthetic diesel oil, Grey material, Cross direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	14,0	217	117	512
7	12,2	34	35	1 239
14	14,2	71	71	1 108
21	15,5	32	35	1 524
28	20,6	43	48	1 394
35	16,1	40	44	1 372



<b>70 °C Synthetic diesel oil, Grey material, Length direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	14,5	211	114	678
7	22,7	64	74	1 803
14	22,6	69	82	1 673
21	23,0	22	26	1 667
28	33,8	5	8	3 146
35	23,9	69	83	1 911
<b>70 °C Synthetic diesel oil, Grey material, Cross direction</b>				
<b>Time weeks</b>	<b>Stress at break MPa</b>	<b>Strain at break %</b>	<b>Energy at break J</b>	<b>Modulus MPa</b>
0	14,0	217	117	512
7	22,2	84	91	1 275
14	23,1	91	102	1 413
21	20,9	36	40	1 481
28	22,1	78	85	1 597
35	23,1	75	86	1 465

