Chemical compatibility of geomembranes in presence of synthetic landfill leachate

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ABSTRACT: The paper describes an experimental study performed on different geomembranes immersed in a synthetic landfill leachate in order to evaluate the ageing processes. Seven different geomembranes were tested (3 HDPE, 2 PVC, 1 VLDPE and 1 modified polyethylene); in order to accelerate the ageing processes geomembrane samples were immersed in two steel tanks filled with a synthetic test liquid at a temperature of 50°C and 70°C respectively. Degradations after 4 weeks, 8 weeks and 12 weeks of immersion have been evaluated by subjecting the different types of geomembranes to chemical, physical and mechanical tests.

1 INTRODUCTION

Evaluating the behaviour of geomembranes in contact with leachate is rather an uncertain challenge because of the difficulties in reproducing the typical conditions of a landfill bottom where the contact between leachate and geomembrane could take place. Furthermore, this contact, often developing in the real conditions of a landfill for more than seventy years, has to be reduced to a reasonable laboratory duration.

This paper describes an accelerated ageing procedure developed in order to evaluate the degradations produced by leachate chemical action.

The experimental research described hereafter has been carried out at the Environmental and Sanitary Engineering Laboratory of the University of Palermo and at the Special Materials Laboratory of ENEL Spa Research Centre on Hydraulics and Structures in Milano.

2. THE LEACHATE CHEMICAL ACTIONS ON GEOMEMBRANES

At the bottom of a landfill the contact with leachate could produce on geomembranes the following main degradation mechanisms, often resulting in a reduction of efficiency and durability of barrier systems:

a) Swelling: a long contact with liquids can cause the geomembrane swelling due to absorption; swelling does not necessarily imply material failure, but is an important alarm–bell to be considered (Koerner et al., 1990).

b) Bond scission; it includes the different chemical actions by which leachates can degrade geomembranes: methatesis, oxidation, solvolysis, dissolution (Koerner and Richardson, 1987).

c) Extraction: organic compounds of leachates can produce a solvent action on geomembranes with consequent extraction of additives and relaxation of links resulting in a general change of chemical, physical and mechanical properties (Koerner and Richardson, 1987; Cazzuffi et al., 1990; Koerner et al., 1990).

The chemical resistance to leachate is a primary requirement for the durability of any liner system, because geomembranes could be in constant contact with leachate during the long mineralization period of wastes.

Usually a geomembrane in a landfill works into a large range of temperatures. During winter, in continental climate area, temperature can fall more than 50°C below zero; during summer an exposed black geomembrane can reach 90°C. A thermoplastic material softens when heated and becomes harder if temperature falls. In any case, extreme conditions of temperature can produce undesirable effects. Since waste decomposition, both aerobic and anaerobic, is an exothermic process, temperature in a landfill can

keep between 40°C and 60°C for many years. As a result all chemical leachate actions are accelerated and dangerous synergistic effects of degradation mechanisms can be produced (Koerner et al., 1990; White and Verschoor, 1990; Gray, 1990; Collins, 1993).

3. ACCELERATED AGEING

An accelerated ageing test executed by immersion is an useful tool for the evaluation of geomembranes long-term behaviour in presence of leachate. This kind of ageing test is based on the two following basic parameters: the test liquid temperature and the test liquid composition.

3.1 *Test liquid temperature*

Temperature has a direct influence on chemical reaction rate (Koerner et al., 1992). A temperature increase accelerates the chemical reactions and allows to simulate the long–term conditions in shorter periods more suitable to laboratory research. Too high temperatures may produce the thermodegradation of immersed materials and cause effects that go beyond those of a mere accelerated ageing.

3.2 *Test liquid composition*

As test liquid, a real leachate or a synthetic one may be employed.

Choosing a real leachate entails some operative difficulties, because the leachate composition depends on the hydrological budget of the landfill and on the age, nature and management conditions of wastes. Although COD or other typical compound concentrations reach with time fairly foreseeable values, leachate characteristics are anyhow extremely variable. As a result it is impossible to perform a reproducible test using a real leachate, especially at elevated temperatures. Microbiological activity makes any laboratory experience even more difficult.

A synthetic leachate allows to eliminate any obstacle to test reproducibility, nevertheless the test results may be referred to real landfill conditions only with a great deal of caution, because of the difference between real leachates and any synthetic test liquid.

In the past, when chemical resistance of geosynthetics was tested by immersion in synthetic test liquid, a water solution of a single acid or basic inorganic compound was used (Lord et al., 1988;

Mathur et al., 1994); in other cases the test liquid was a water solution of a single synthetic organic compound or simply a pure organic reagent (Rad and Acar, 1984; Lord et al., 1988; Tisinger, et al., 1990; Müller and Müller, 1993).

With a few exceptions (Cassidy et al., 1992; Müller and Müller, 1993) the typical chemical action of a real leachate, due to the presence of several different compounds, had generally been disregarded.

4. MATERIALS AND PROCEDURE

Seven different geomembrane samples were tested:
- three types of high density polyethylene geomembranes (named HDPE–A, HDPE–C and HDPE–S, respectively);
- one type of modified polyethylene geomembrane (named PE–m);
- one type of very low density polyethylene geomembrane (named VLDPE);
- two types of polyvinyl chloride geomembranes (named PVC–M and PVC–T, respectively).

The research has developed with the following three stages:
1) ageing of materials by immersions at constant temperatures;
2) testing of aged materials;
3) examination of aged materials test results and comparison between aged and unaged materials properties.

Temperatures of 50°C and 70°C were chosen for the immersions. The first one (50°C) is the higher ageing temperature prescribed by EPA 9090 testing procedure; 70°C was chosen in order to obtain a greater acceleration of ageing. In fact, when climate is particularly warm, geomembranes may work at about 50°C for long periods of the year, for example the temperature of a leachate produced in some Asiatic landfills has sometimes reached 60°C (Overmann et al., 1993). It is clear that in this cases a temperature of 50°C can in no way contribute to the acceleration of ageing.

Both chosen test temperatures are low enough for avoiding any risk of thermodegradation.

The test liquid was prepared by mixing water with methylethylketone, chloroform, tannic acid, benzene, phenol and formaldehyde (Table 1).

These organic compounds may often be found in leachate compositions (Öman and Hynning, 1991; Andreottola and Cannas, 1992). In order to make the test liquid preparation easier, only compounds with good solubility were considered. For any utilised compound, a concentration higher than that one

Table 1. Test liquid composition

Compound	Concentration in the test liquid (mg/l)
methylethylketone	3700
chloroform	3350
tannic acid	2000
benzene	700
phenol	220
formaldehyde	150

usually found in a real leachate composition was chosen. In this way a COD concentration of about 10000 mg/l was reached. It has to be noted that an higher value of COD, typical of the first years of leachate production, could be unsuitable for a research on long-term behaviour of geomembranes.

Geomembranes samples of 0.33 m x 0.12 m were put in metal holders and immersed in two steel tanks; a cover avoided any gas–escape; the two tanks had the following characteristics:

- A-Tank: incubation temperature of 50°C; test liquid volume and samples area in the ratio of 26.80 l/m²;
- B-Tank: incubation temperature of 70°C; test liquid volume and samples area in the ratio of 37.80 l/m².

Mixing devices kept the test liquid in constant movement in order to avoid any stagnation and the consequent stop of geomembranes–test liquid interactions.

The high temperatures of incubation favoured chemical reactions which generated some oxidation products hard to identify. The very confused spectra of two HPLC (high pressure liquid chromatography) analysis, performed on test liquid after 18 and 53

days, gave a further confirmation about test liquid changes in the long run.

Three immersion stages were programmed, of 4, 8 and 12 weeks respectively. In order to assess the degradation level at the end of each immersion period, the following tests were performed on the different geomembrane samples:

- weight;
- thickness;
- tensile test (according to UNI 8202/8, equivalent to ISO R 527, using a strain rate of 50 mm/min);
- water vapour permeability (according to UNI 8202/23, equivalent to ASTM D 1653-method B, condition C);
- thermogravimetric analysis (according to UNI 8698, equivalent to ASTM E 1131);
- hardness Shore A (according to UNI 4916, equivalent to ISO R 868).

In order to make a comparison between aged and unaged materials, the tests were performed also on virgin samples.

5. TESTS RESULTS

5.1 *Weight*

A general increase in weight has been registered. It has to be attributed to test liquid absorption. This process has been nearly always increasing with time and incubation temperature (Fig. 1).

Registered weight changes of aged samples reflect the material nature: all HDPE samples have increased in weight less than 1%; PE–m and VLDPE increases
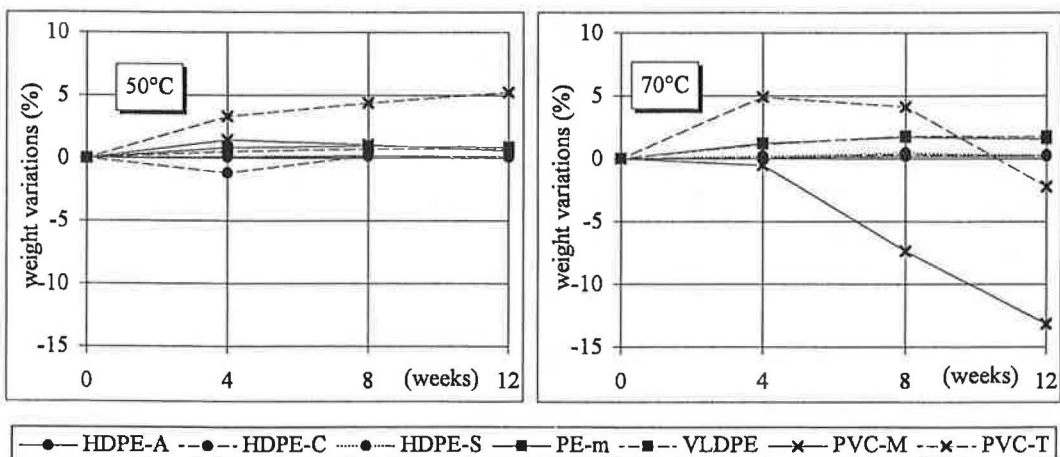

Fig. 1. Weight variations vs. time for geomembrane samples

have been rather regular and similar in quantity and trend: the weight increase for both materials has been more considerable than in the case of HDPE, even if lower than 2%.

Aged PVC samples suffered a decrease in weight due to the solvent action of test liquid and to the consequent extraction of additives. Weight decreases after 12 weeks at 70°C have reached about 3% and 13% for PVC–M and PVC–T respectively. A simple visual examination of aged PVC samples has revealed the loss of plasticizers resulting in a sensible stiffening of materials. The additives loss of PVC geomembranes has been confirmed by thermogravimetric analysis and also by water vapour permeability test (see 5.3 and 5.5).

5.2 Thickness

Because of the test liquid absorption all the samples increased their thickness, even if of a scarce quantity.

The roughness of some geomembranes made the measurement not very significant, but anyway valid from a qualitative point of view.

The PVC–T suffered the greatest increase in thickness: +2,4% and +3,4%, after 4 weeks of immersion, at 50°C and 70°C, respectively. For this material, because of the perfectly smooth surface, the result has to be considered quantitatively valid. Moreover, it is remarkable that the same product experienced also the greatest weight increase, particularly at 50°C.

5.3 Water vapour transmission rate (WVT)

The test liquid solvent action can be shown by determining the water vapour transmission rate (WVT). In particular the extraction mechanisms which could be hidden by the weight increase due to the absorption can be pointed out.

WVT (units: $g/m^2 \cdot d$) is the mass of water vapour passing per unit area of geomembrane per unit period of time under specific pressure conditions.

As illustrated in Fig.2, HDPE-A and HDPE-S have exhibited the greatest variations with increasing WVT of about 300% and 350% at 50°C and 70°C respectively.

HDPE–C data show a strange opposite trend; in fact, this geomembrane has lightly decreased in permeability. The small decrease could be probably due to the intrusion of small particles in the geomembrane porosity.

After 12 weeks of ageing at 70°C the WVT value of PVC–T and PE–m has doubled, lower increases have been observed on VLDPE (+60%) and PVC–M (+15%).

Geomembrane samples exhibited a general increase of water vapour permeability that could be probably due to plasticizers and/or other additives extraction resulting in a density reduction of materials.

The conductivity (coefficient of permeability) of aged geomembranes has also been obtained on the basis of the calculations proposed by Giroud (1984). After 12 weeks of immersion all the aged samples, at both temperatures, have kept their conductivity
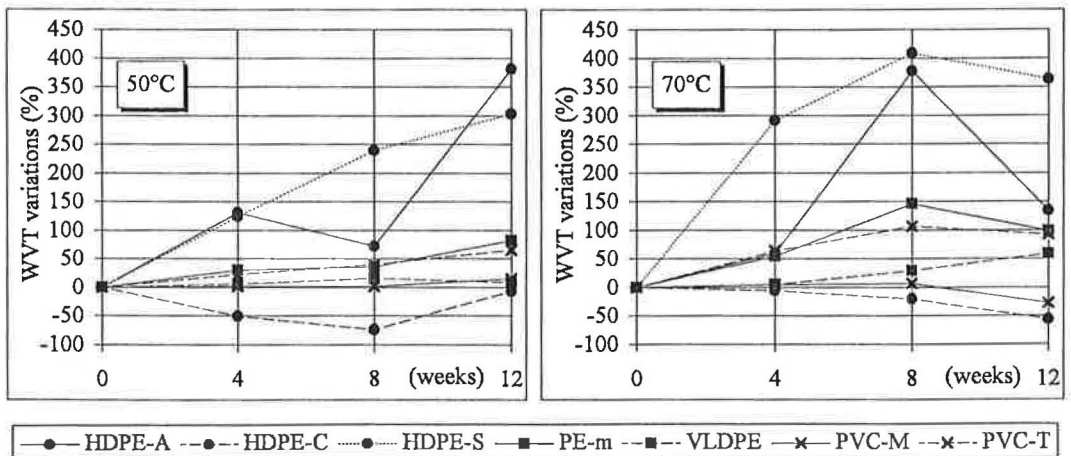

Fig.2. Variations of water vapour transmission rate (WVT) vs. time for geomembrane samples

lower than 10^{-13} m/s. It must be noted that the conductivity of aged HDPE, PE–m and VLDPE has kept about one order of magnitude lower than unaged PVC.

5.4 *Tensile properties*

The tensile test pointed out a general decrease of strength even if test results have a rather confused trend (Fig.3).

The HDPE–A geomembrane changed its tensile breaking strength more than all the other materials, after 8 weeks of ageing it has been observed a decrease greater than 40%.

The decreases of tensile breaking strength of all the other materials are lower than 20%.

Tensile breaking strains have lowered, exhibiting with the corresponding strength increase a general stiffening of materials. Only PE–m and VLDPE registered an increase of tensile breaking strain. This

response is probably due to the presence of absorbed test liquid into the polymer microstructure.

Tensile elongation is mostly due to dislocations within the amorphous portion of polymers, which is probably less resistant than the crystalline one. Moreover, strains depend on the presence of low molecular weight chains, easier to deteriorate than the high weight ones. These are the reasons why, in order to evaluate the durability of polymeric geomembranes, the results in terms of strain have generally been considered more useful than those ones in terms of strength (Koerner et al., 1992). These considerations seem to be confirmed by the significant increases of tensile strain values experienced by PE–m and VLDPE aged samples; these two materials are less crystalline than HDPE. In the case of PVC, the plasticizers extraction, which caused a sensible stiffening of materials, probably restrained increases of strain.

It has been demonstrated that failures of HDPE geomembranes are governed by the yield strain on
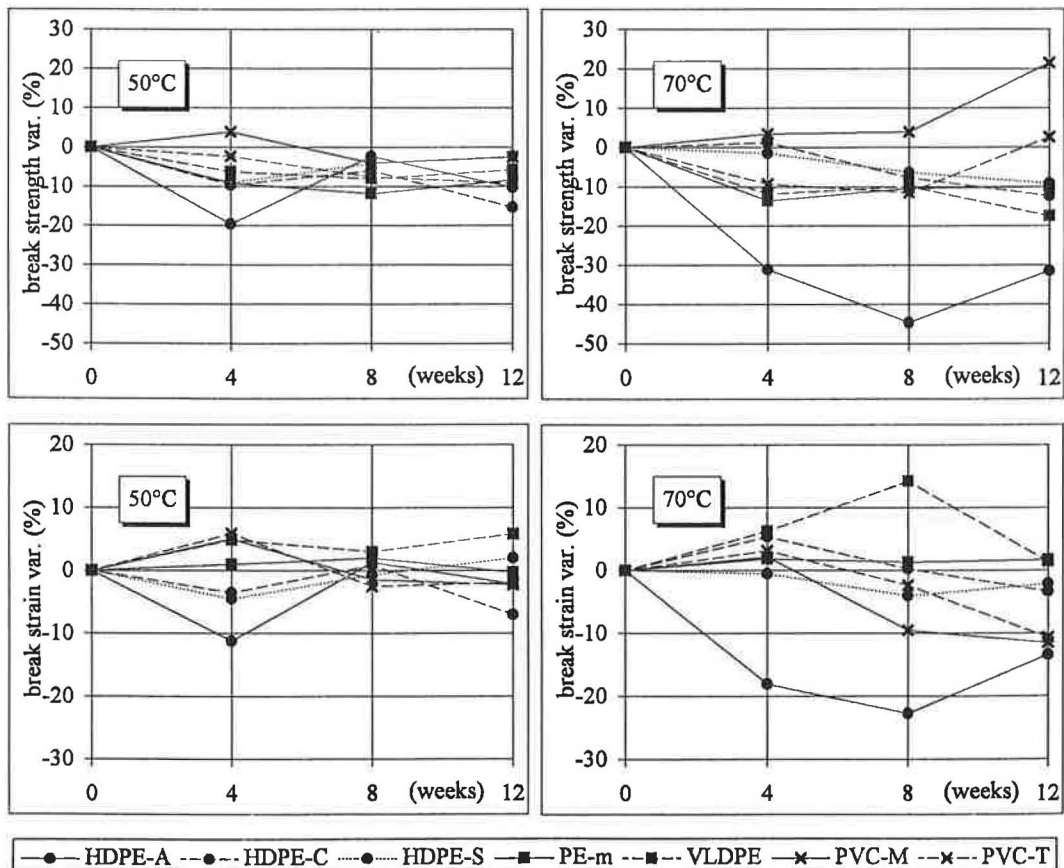

Fig.3. Variations of tensile properties at break vs. time for geomembrane samples

the order of 10% (Giroud, 1994). For this reason, the yield behaviour of the three HDPE aged geomembranes was also considered (Fig.4): a light reduction (<5%) of strength values has been noticed, while the corresponding strain values has increased. The HDPE–A geomembrane has experienced the greatest strain increase after 4 weeks (+22%), but gave the same results of the other two HDPE geomembranes after 12 weeks (strain increase of about 8%).

5.5 *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis (TGA) allows to assess the composition of a material by means of its loss in weight during heating at a controlled (constant) rate in a inert or oxidising atmosphere.

From the observation of TGA curves it results that thermodegradation of all the aged geomembrane samples has started at a lower temperature in

comparison with the thermodegradation of the virgin samples. This kind of behaviour is rather evident for all of the tested geomembranes and is caused by the presence of absorbed test liquid in the polymeric microstructure and also by a possible loss of antidegradants whose usual content is about 1÷2% of weight.

The three durations of ageing do not seem to have significantly differentiated the TGA results.

Curves show the reduction of heat–resistance of every aged material. Distillation of aged PVC, VLDPE and PE–m has started more than 100°C earlier than corresponding unaged samples. By the first 200°C of heating weight decrease of aged PVC has kept under 5%, it has been less appreciable for PE–m, VLDPE and HDPE geomembranes. The TGA has shown a lower heat–resistance of PVC geomembranes compared to PE products.

The TGA curves of HDPE, VLDPE and PE–m aged samples retain the same shape of those obtained from virgin samples, but weight reduction occurs and
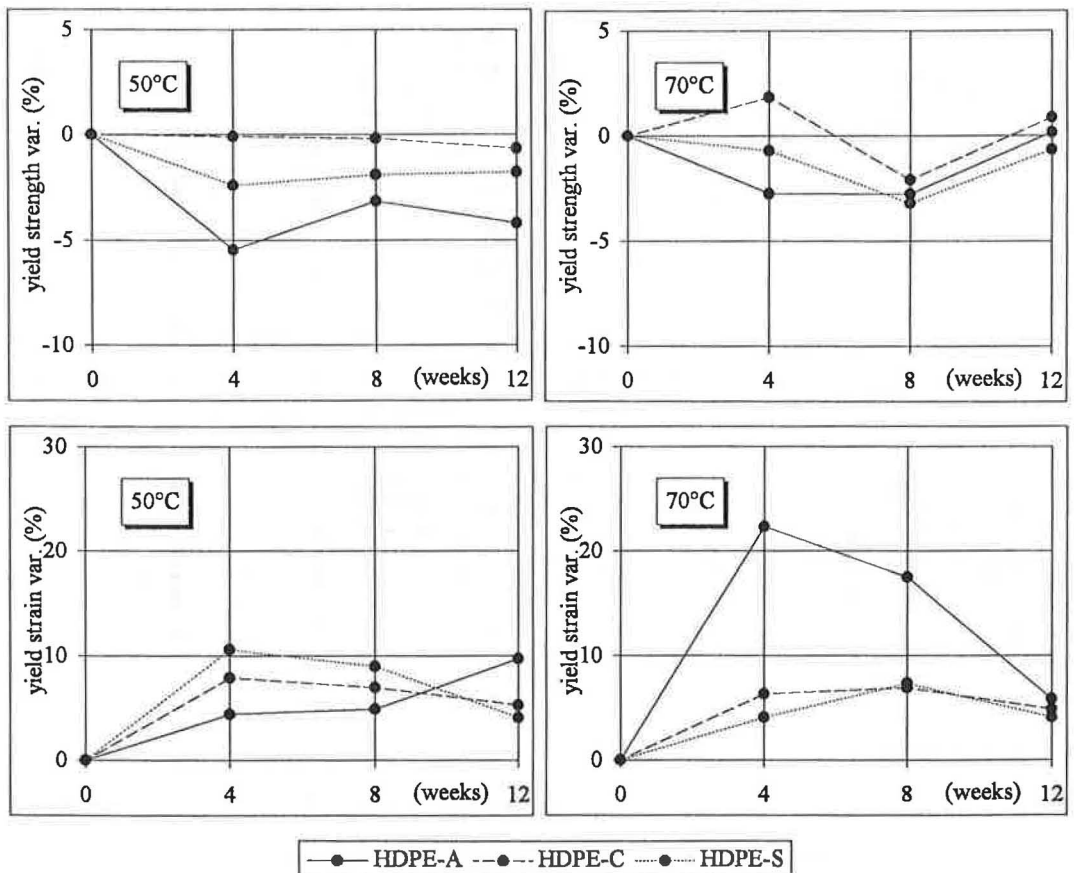

Fig.4. Variations of tensile properties at yield vs. time for HDPE geomembrane samples

proceed earlier on aged samples. The greatest of these differences (about 30°C) is observable on aged HDPE–S samples. In any TGA emphasised that HDPE, VLDPE and PE–m have not suffered significant modification of their composition.

A sensible alteration of both PVC materials has been demonstrated by the shape difference between the curves of aged and virgin samples. It must be noted that PVC geomembranes usually have a quite varied composition in comparison to PE products. The content of additives and fillers mixed with the pure PVC may reach 50% of weight of the final product, while the content of added ingredients in HDPE geomembranes do not exceed 10÷15% of weight (Cazzuffi et al., 1990). Because of their characteristics, PVC geomembranes could be sensible to chemical degradation mechanisms and the TGA has given a further confirmation of this.

5.6 Hardness

Usually, polymeric geomembranes age by becoming harder; this kind of reaction can be particularly strong for polymeric compounds containing plasticizers (PVC). In fact, plasticizers in PVC can migrate to the surface over time and leave the inner polymeric structure: the geomembrane increase in hardness because its resulting structure only consists of resin, fillers and residual plasticizers (Koerner et al., 1992).

After 12 weeks of ageing, the most of tested material have increased their hardness (Fig.5). This behaviour is mostly due to the plasticizers extraction.

In particular, the PVC–M sample, aged at 70°C, has exhibited the greatest hardening (+16%). While

the hardness increases have been of about 1% for HDPE geomembranes.

The few cases of softening could be due to the presence of absorbed test liquid in the microstructure, since softening has been observed on those materials which have exhibited the greatest weight increases.

6. EVALUATION OF THE LONG-TERM DEGRADATION

In order to extrapolating from durations of the accelerated ageing, performed by immersion at 50°C and 70°C, the corresponding time that would be required to obtain, at a lower temperature (25°C), the same kind of degradation observed on aged samples, the *Arrhenius modelling* has been utilised.

This procedure is based on the accelerating effect of temperature on chemical reactions. Every chemical reaction is in fact a specific function of temperature characterised by a value of activation energy (*Eact*).

On the basis of test results performed on samples that have undergone high temperature accelerated ageing, the *Arrhenius modelling* allows to determine the time that would be necessary to produce the same ageing effect at a lower temperature (Koerner et al., 1992).

The *Arrhenius modelling* has been applied to tensile and hardness test results of the seven types of geomembranes.

In particular, for the HDPE–A tensile strength test results, about 50 years would seem to be the longest simulated ageing time. This means that, according to *Arrhenius modelling* calculations, 12 weeks of immersion in the utilised test liquid at a temperature
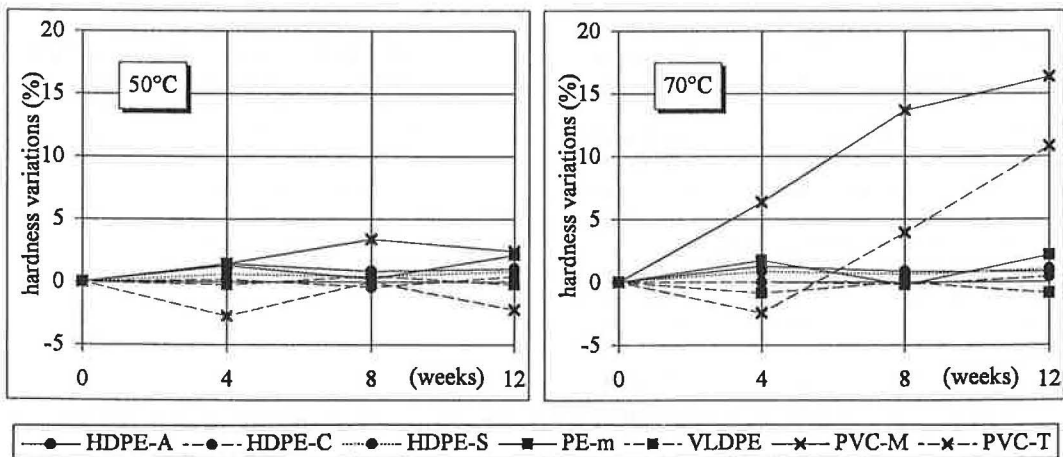

Fig.5. Hardness variations vs. time for geomembrane samples

of 70°C produce a decrease of HDPE–A tensile strength that could be obtained after about 50 years of immersion in the same liquid at 25°C.

7. CONCLUSIONS

The accelerated ageing test performed seems to be valid, in fact, degradation of materials has generally increased with temperature and immersion time, thus confirming the accelerating effect of high temperatures on chemical reactions.

Moreover, the selection of a synthetic test liquid reveal this accelerated ageing test as well reproducible.

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