Durability of polyolefine geosynthetics under elevated oxygen pressure in aqueous liquids

H.F. Schroeder, H. Bahr, P. Herrmann, G. Kneip, E. Lorenz and I. Schmuecking
Federal Institute for Materials Research and Testing (BAM), Berlin, Germany

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ABSTRACT: Immersion testing under elevated oxygen pressure ensures the simultaneous action of oxidation reaction and elution of additives. Elevated oxygen pressure and temperature have to be balanced to give reaction conditions under which oxygen diffusion is not rate limiting. These are the conditions thought to prevail in constructions designed with geosynthetics. Under the preliminary conditions of tests given, in contrast to the oventest used before, a screening of geosythetics with respect to resistance to oxidation is found though clearly the surface to volume ratio is of importance for simultaneous leaching of additives. A general application as a standard test for screening the resistance to oxidation seems to be feasible. Some promising results are presented. A research project is being launched to scrutinise conditions of tests and to validate the method and its possible abilities for assessments of oxidative design life of geosynthetics.

1 INTRODUCTION

Lifetime of polyolefins generally is limited by their sensibility to oxidation. In geotechnical constructions applying geosynthetics in essential long-term-functions it is therefore necessary to know the oxidative durability of these construction products, especially if they cannot be repaired or exchanged without serious impact on the construction. A reasonable test method is urgently needed, but actually does not exist (Zweifel 1997a).

Current oventests, like NEN 5132, Nov. 1992 and ENV ISO 13438: 1999, are useful for certain comparative purposes for screening of similarly constructed materials having constituent components of similar dimensions as e. g. tape yarns. Problems arise with the screening of geoproducts with very different surface to volume ratio at the high temperatures used.

Oxidation induction time (OIT)-tests usually working near or above the melting point of the polyolefins have other problems. At these temperatures only parts of the stabiliser systems are working, or other components which like organic phosphites are not relevant at working temperatures of geosynthetics (Zweifel 1997b) may have a large impact. Therefore interpretation has to be done with caution. Further the high temperature used has a large impact on the oxidation mechanism. Therefore this method is not able to assess lifetime of geosythetics either.

Since most geosynthetics shall be or are rather stable, the testing of long time stability has to resort to accelerated conditions. These usually include higher concentrations or pressures of the active chemical species involved in the oxidation reactions and/or higher temperatures. Finally the lifetime of the stabiliser system may be shortened by e. g. leaching of additives into the surrounding phases (Calvert, Billingham 1979). This is an important aspect to be taken into account.

The excessive use of higher temperatures to accelerate oxidative chain reactions may be rather critical since the single reactions are accelerated due to their activation energy which may cause a considerable distortion of the relevant events compared to normal working temperatures. Basic physical processes and transition modes of polymers accompanying and making possible chemical reactions may be changed too, e. g. by enlarged free volume. So diffusion often has a lower activation energy than chemical reactions. This may result in adulteration of oxidative reactions by lim-

ited oxygen diffusion at elevated temperature and invalidity of test results since the general opinion prevails that oxygen saturation is given for the practical application (Zweifel 1997c). The sensitivity to degradation of a geoproduct is then found to depend stronger on the relation of its surface area to volume than on kind of stabilisation. This often holds if testing is performed at higher temperature. Regarding the cross section of the materials tested by such a procedure strangulated by oxygen diffusion, profiles of typical surface reactions are found as they are realistic e. g. for photo-oxidation. The influence of the applied pressure has to be considered separately for the effect of pressure alone and for the component directly involved here: oxygen.

Usually the general effect of pressure can be considered to be comparatively less grave for reactions with condensed materials, having less enlarging influence on free volume than elevated temperatures. But its physical effects have to be considered too for e. g. leaching of additives, in order to avoid adulterations.

The other intended effect of enlarged oxygen concentration in the immersion is to be considered too. Comparing the concentration of oxygen in air, the concentration of oxygen in water is rather low. To achieve the same concentration of oxygen in water at 80 ^{o}C as in ambient air, the application of Henry's law tells (D'Ans Lax 1967), that about 20 bars of pure oxygen have to be applied. These problems mentioned are some of the inherent general problems of accelerated tests.

Further geosynthetics often are in contact with humid or aqueous ionic surroundings which influence the hydrolysing stability of e. g. stabilizers and the elution of additives. These important simultaneous influences cannot be easily taken into account by actual oven testing because of the high temperatures used. But these influences have to be taken into account too.

Therefore an oxidation test for geosythetics should work under elevated gradients of oxygen to minimize sufficiently limitations by oxygen diffusion and simulate additive elution by the presence of an appropriate aqueous liquid phase. This can be achieved by working under elevated oxygen pressure. The acceleration achieved can be used to work at markedly lower temperatures than used at usual oven testing at atmospheric conditions in line with ENV ISO 13438: 1999. The extent of the accelerating effect should be clearly limited by the amount achieved by saturating the oxidation chain reaction with oxygen. This effect should be bigger for compact materials than for materials with a high ratio of surface to volume. But the additional effect of additive elution under pressure which should remain proportional to the surface of the specimens tested should be kept in mind. It will additionally limit oxidation resistance of materials.

A research project has thus been launched with the first objective to find out conditions for a standard procedure which can be used to screen of the oxidative stability of polyolefin geoproducts possessing different ratios of surface to volume, like e. g. nonwovens and geogrids. This project is open to industrial co-operation and sponsoring to facilitate a rapid and harmonised progress. The first object is a general testing standard for geosythetics. At the time being the draft standard prENV 13438 rev. has been worded. If this is achieved the further potential of the method for lifetime- assessment of polyolefin geoproducts in soil shall be tested.

The research is still in an early stage by limiting autoclave capacity. But starting results on some typical materials donated by industry are thought to be promising and are presented here for discussion. The results given concentrate on mechanical testing after exposure to oxidative conditions. In the future we intend to further extend these studies to the fate of stabilisers involved (Zeynalov et al. 2000). Both aspects together will enable us to make more stringent interpretations of results than are possible at the time being.

2 EXPERIMENTAL

2.1 Materials

The materials are donated. Only products made from isotactic PP or PE-HD are regarded. Most of them are rather near or identical to commercial grades, others like the differently stretched tape yarns are research grades, i.e. specially manufactured for testing purposes. The difference to commercial products refers mainly to the additives used. Further details are given in Table 1.

Table 1. Materials used

CODE	Kind of geosynthetics	Material Data
NW01	geotextile	PP-Nonwoven, staple fibres, needle-punched, basically stabilised (phenol type)
NW02	geotextile	PP-Nonwoven, staple fibres, needle-punched, normally stabilised
NW03	geotextile	PP-Nonwoven, filaments, needle-punched, normally stabilised
YT06	geoyarn	PP-tape yarn, 1100 dtex, basically stabilised (phenol type), stretch ratio 1: 6
YT09	geoyarn	Same yarn as YT06, But stretch ratio 1: 9
YT12	geoyarn	Same yarn as YT06, But stretch ratio 1: 12
YT20	geoyarn	PP-tape yarn, 1100 dtex, carbon black, normally stabilised (hals type),
YT00	geoyarn	PP-tape yarn, 1100 dtex, recycled product
GM01	geomembrane	PE-HD-membrane, certified material for waste disposals in Germany, fully stabilized, carbon black
GM02	geomembrane	PE-HD- membrane, certified material for waste disposals in Germany, fully stabilized, carbon black
GG01	geogrid	PE-HD-geogrid, fully stabilized, type 1
GG02	geogrid	PE-HD-geogrid, fully stabilized, type 2

2.2 Methods

Tensile testing of nonwovens, gauge length: 200 mm, width of specimens: 50 mm was executed in line with ISO 10319 with a constant velocity of the drawing clamp of 200 mm/min.

Tensile testing of tape yarn, gauge length: 100 mm, with a constant velocity of the drawing clamp of 50 mm/min. At least sixteen specimens were tested for each exposure time.

Tensile testing of the geogrid type used was done with specimens containing the strand of one rip and one central knot within the gauge length: 100 mm and constant velocity of the drawing clamp of 25 mm/min. The failure occurred near the knot, containing the clearly less stretched material. At least five specimens were tested for each exposure time.

Tensile testing of geomembranes was performed with specimens of type 5 A in line with DIN EN ISO 527-2 and constant velocity of the drawing clamp of 50 mm/min.

2.3 Immersion Testing at atmospheric oxygen pressure

Exposures at atmospheric pressure were executed in well stirred thermostats made from stainless steel with a working volume of about 22 l. A schematic view of the equipment is shown in Figure 1. The local and timely constancy of temperature was about ± 0,5 K . Oxygen was introduced into the immersion using a fine frit gas bubbler with a rate of at least 100 ml/min and a flowmeter. To get different concentrations of oxygen, oxygen and nitrogen were mixed in different parts. The grade of oxygen and nitrogen was 5.0 (meaning ≥ 99,999 volume % O_2 respectively N_2). In this

experiment the following mixtures of Oxygen and Nitrogen (volume %/volume %) were used: Pure Oxygen (100/0), synthetic air (79/21)and synthetic mixture (50/50). (Care was taken to avoid direct contact of gas bubbles with immersed specimens. The oxygen content was measured with an Oximeter of type OXI 96 of the manufacturer WTW using a Clark electrode and a flow cell in a cooled bypass.

Specimens were vertically clamped and parallel to each other without marked tension. The distance between the specimens was at least 1 cm. Specimens and reference specimens were pretreated in the same way by tensionless immersion for one hour at immersion test temperature.

The immersion medium 0,01 M $NaHCO_3$ was adjusted with 1 n NaOH to pH 10,0 with a freshly calibrated glass electrode before the test. This medium was chosen to have a defined pH and in line with Henry et al. 1992. The medium may be changed due to special considerations. For tests at neutral conditions e. g. NaH_2PO_4 solutions adjusted to pH 7,00 might be used.

2.4 Immersion Testing at elevated oxygen pressure

Exposures at elevated pressure were executed according to prENV 13438 rev. in stirred autoclaves made from high graded stainless steel with a working volume of about 7 l. A photographic view of the autoclaves is shown in Figure 2. The local and timely constancy of temperature was better than ± 0,5 K . Constancy of pressure was better than ± 0,5 bar, days of specimens extraction or installation excluded. For the 24 hours after initial installation of testing pressure or after extraction of specimens the pressure was constant within ± 2,0 bar.

The pressure and temperature are continuously monitored at least every 10 minutes. The free space above the liquid was somewhat bigger than 20 % of its volume.

The pressure release or application is done steadily within about five minutes. The total time for depressurising and specimen extraction or loading and pressurising did not exceed 30 minutes.

Specimens were installed in specimen holders made from high graded stainless steel. Yarns were wound round a cylindrical coil of about 6 cm diameter, made from fine stainless steel wire mesh, under constant tension of 50 cN. After exposure specimens were rinsed in deionized water and conditioned and tested according to or in line with ENV 12226.

After completion of all exposures of one test series the vessel and its equipment were carefully cleaned of any remaining residues.

2.5 Oventesting at atmospheric air pressure

Testing was done in forced draught air ovens for PP-materials at 110 ^{o}C with a timely and local temperature constancy of ± 1,0 K. The temperature was monitored at least every 10 min. Tensile testing was done as described before.

3 RESULTS and DISCUSSION

3.1 Testing at atmospheric oxygen pressure

Figure 3 shows the results of the exposure of a commercial PP staple fibre and needlepunched nonwoven NW01, being only basically stabilised, at 90 ^{o}C to aqueous solutions of 0,01 M $NaHCO_3$ with adjusted content of solute oxygen. It is clearly seen, that maximum tensile force of the nonwoven is declining after an induction phase, which clearly depends on the amount of solute oxygen. Taking the time until a residual maximum tensile force of 90 % is reached as induction time, figure 4 shows, that no proportionality of the reciprocal of this parameter to oxygen concentration is found, but rather a trend to saturation at higher oxygen concentrations is seen. This is a result which is to be commonly expected from the prevailing ideas of oxidation of polyolefins by a

radical chain mechanism (Zweifel 1997d). The diagram shows the big influence of oxygen concentration on the lifetime of basically stabilised nonwovens.

It is to be expected and we have the results, that the induction time is depending on the composition of the aqueous system.

For the nonwoven material, being basically stabilised with a hindered phenol stabiliser, we clearly found a better resistance in more acid than in more alkaline media (Schroeder et al. 1999). This resistance found is probably resulting from stabilizer elution on pH of the liquid.

Studies in aqueous immersions at atmospheric oxygen pressure are interesting for systems, where geosythetics with a large surface to volume ratio, as is valid for many fibre products, are predominantly exposed to liquid media. In these cases, depending on temperature, the oxidation reaction can be found to be in an kinetic regime and not in a regime governed by oxygen diffusion.
To be more sure that oxygen diffusion is not rate limiting, studies at higher oxygen pressure are appropriate.

3.2 Testing at elevated oxygen pressure

Effect of stretching:
In Figure 5 the results of testing the oxidative resistance of three research grade tape yarns YT06, YT09 and YT12 are given in order to demonstrate the effect of stretching. It is important to know that the yarns are made from the same only basically stabilised PP-material and manufactured in the identical way except for final stretching.

Figure 5 shows that obviously there exist different induction times dependent on the extent of stretching which are followed by an oxidative degradation being different in rate too.

A certain amount of stretching, which effects molecular orientation in the amorphous regions, seems to be optimal with regard to resistance to oxidation. (The crystalline districts of semicrystalline materials like PE and PP are usually thought to be impermeable to oxygen. This effect is rather well known (Billingham 1990). The rate of oxidation is depending on the concentration of oxygen dissolved in the material. The transport process of oxygen is depending on the product of this oxygen concentration and affiliated diffusion constant of oxygen, being is called permeability. If the transport of oxygen is not rate limiting, obviously the solubility of oxygen in the tape yarn has been minimised by stretching. Overstretching was achieved here at a stretch ratio 1:12. It obviously leads to premature failure by formation of crazes.

Therefore the effect of optimal stretching on solubility of oxygen should determine the relative durability for otherwise identical materials.

Influence of specimens dimensions:
The selection of the appropriate kind of specimens may be an important question. For durability testing the surface to volume ratio of specimens is important for the process of elution of antioxidants. Generally for identical materials and for the same kind of exposure, elution should be proportional to the surface of the specimens.

As Figure 6 shows, we observed indeed that plates of the geomembrane with the dimension 12 cm by 12 cm by 2,5 mm and dumbbell specimens of type 5 A according to DIN EN ISO 527-2 cutted from the same plates differed in time until residual failure load of 80 % just in the amount expected by surface difference.

These different specimens of the same geomembrane material were simultaneously exposed in the same autoclave.

This shows that extraction of antioxidants is an important process during the oxidation test in immersions.

It is therefore proposed to chose the form of specimens as near as possible to application or to consider the effects of different size of test specimens and the materials as they are applied in constructions.

Further results of oxidation testing:
The results are summarised in Table 2. It is seen, that a differentiation between differently stabilized and differently orientated materials seems to be possible. If materials of the specimens are not homogeneous in orientation, a clear tendency is observed, that the failure will occur in the less stretched area.

Table 2. Results of oxidation tests in autoclaves

CODE	Temperature °C	Oxygen Pressure bar (aqueous medium/pH)	Induction time t(80% residual failure load) days
NW01	80	50 (0.01M $NaHCO_3$/pH 10)	9
NW02	80	50 (0.01M $NaHCO_3$/pH 10)	12
NW03	80	50 (0.01M $NaHCO_3$/pH 10)	43
YT06	80	50 (0.01M $NaHCO_3$/pH 10)	10,5
YT09	80	50 (0.01M $NaHCO_3$/pH 10)	12,5
YT12	80	50 (0.01M $NaHCO_3$/pH 10)	5,5
YT20	80	50 (0.01M $NaHCO_3$/pH 10)	45
YT00	80	50 (0.01M $NaHCO_3$/pH 10)	5,5
GM02	80	50 (0.01M $NaHCO_3$/ pH 10)	>35
GG01	80	50 (0.01M $NaHCO_3$/pH 10)	32
GG02	80	50 (0.01M $NaHCO_3$/pH 10)	34

It is known that for the compact materials tested, the exposure time at the same temperature in the actual oven test would be some years to reach the same amount of damage. For YT00 the oventest at 110 °C still gave an induction time of 42 days.

The typical type of curve of degradation of mechanical strength for hindered phenol stabilised materials is already given in Figure 5 and 6. For HALS stabilised materials this decay is more gradual.

At the time being these testing conditions given in table 2 are provisionally proposed as draft screening testing conditions in prENV 13438 rev. until further research provides better evidence for others. Further tests are running with e. g. known materials like PE 100. We intend to build up sufficient autoclave capacity to be able to perform systematic testing to get the profound knowledge needed for a standard for screening and possible assessments of lifetimes.

4 CONCLUSIONS

A new immersion test method and provisional testing conditions for screening oxidative resistance of geosynthetics are presented, which may be able to perform accelerated testing of oxidative resistance of polyolefin geosynthetics to oxygen and simultaneous leaching of additives. The methods is able to distinguish between differently stabilised materials, between different stretch ratios

and different types of specimens size. The testing temperatures are markedly lower than for air draught ovens, especially for compact materials. The induction times range from a few days to about 40 days at 80 ^{o}C and 50 bars oxygen.

Thus it is expected to be promising and feasible to further develop and validate this method to a testing standard.

It is supposed that for compact materials like geomembranes and geogrids at the usually high testing temperatures used in oven tests the rate of oxidation is limited by oxygen diffusion. The test results for these materials under these oven conditions cannot be seen therefore to be useful for screening the behaviour for practical purposes.

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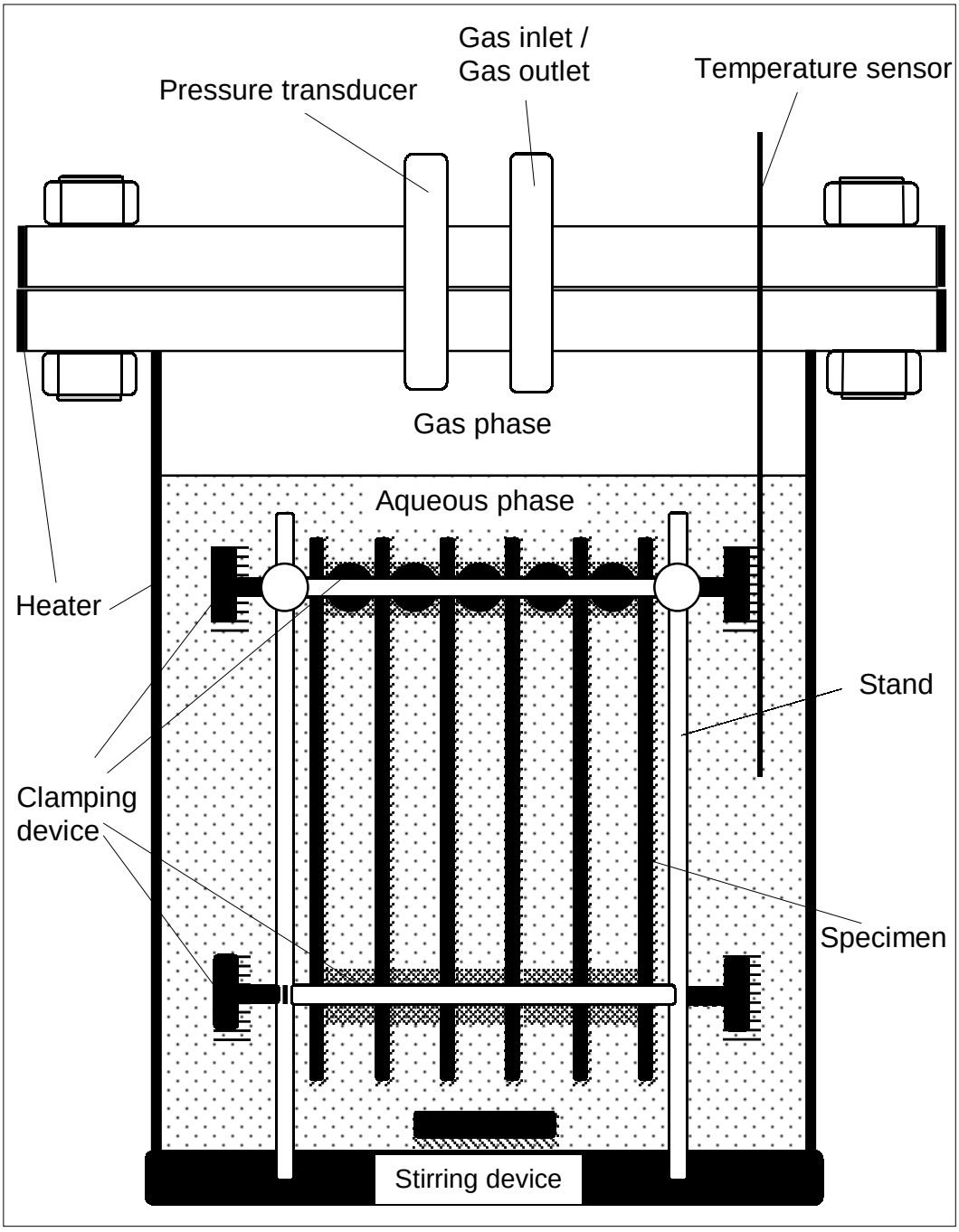

Figure 1. Scheme of autoclave for testing oxidative resistance

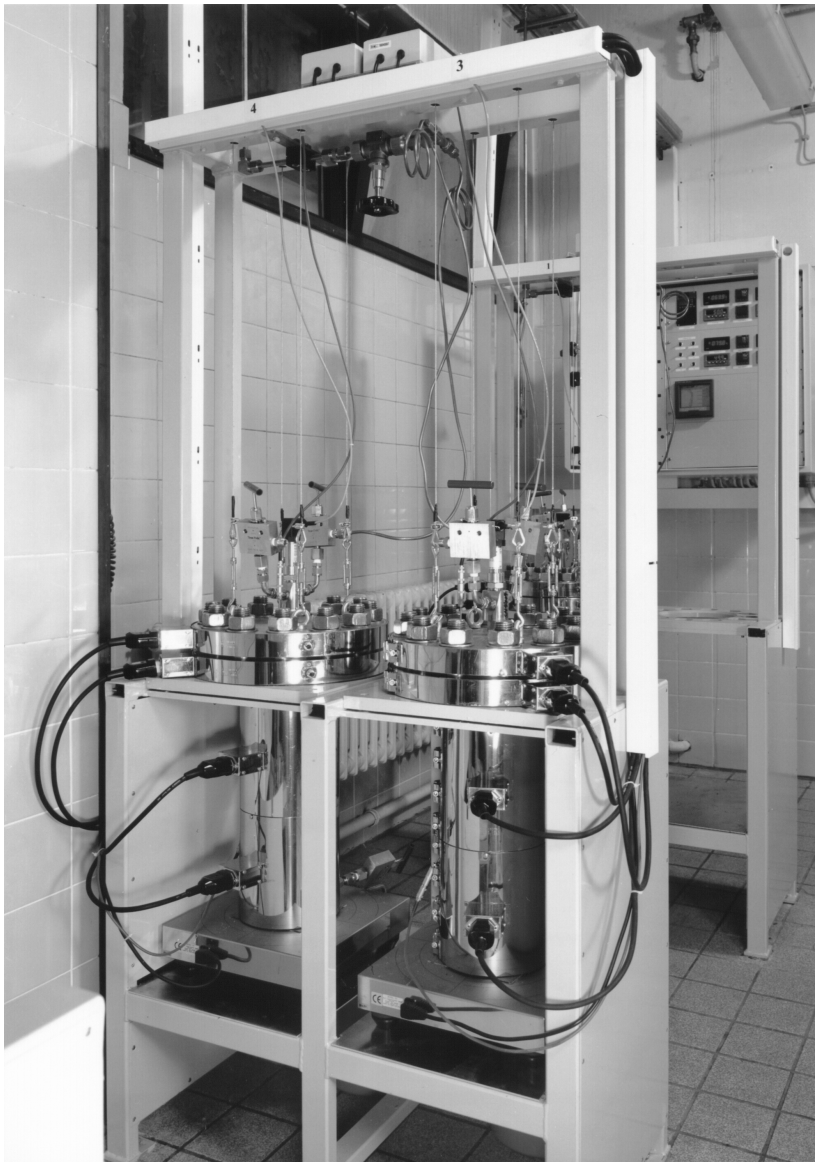

Figure 2. View of two autoclaves of the actual oxidative testing apparatus showing details of installations

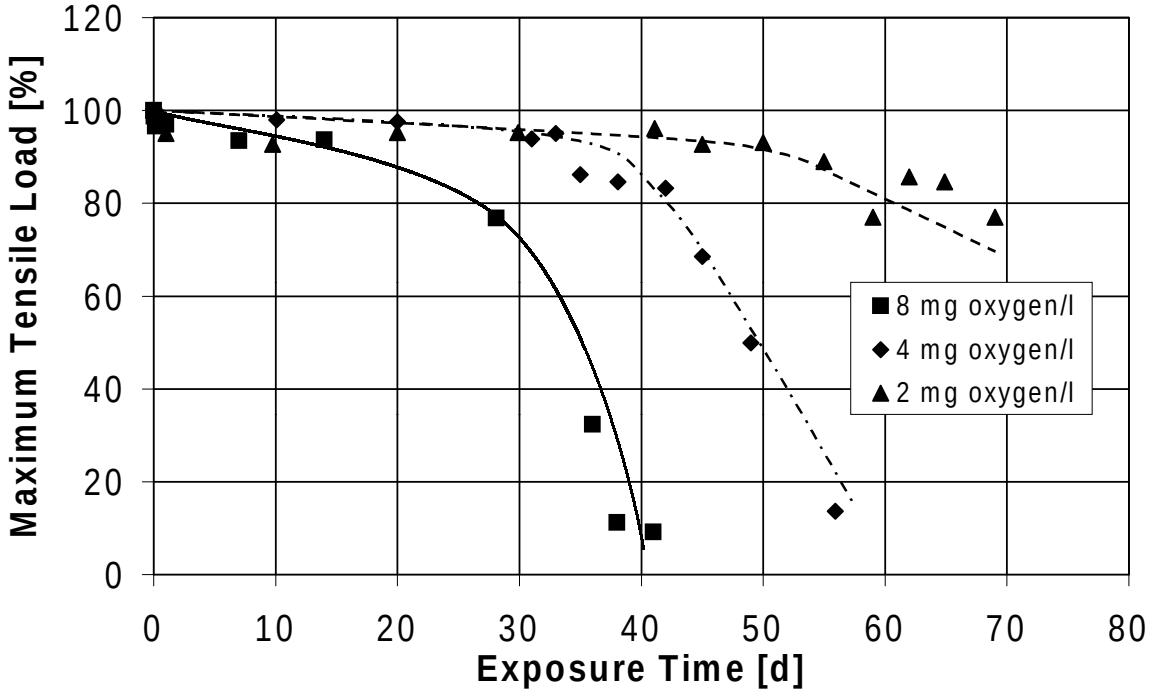

Figure 3. Change of maximum tensile load of nonwoven NW01 immersed at 90 °C under atmospheric conditions in a diluted solution of sodiumbicarbonate at different oxygen concentrations

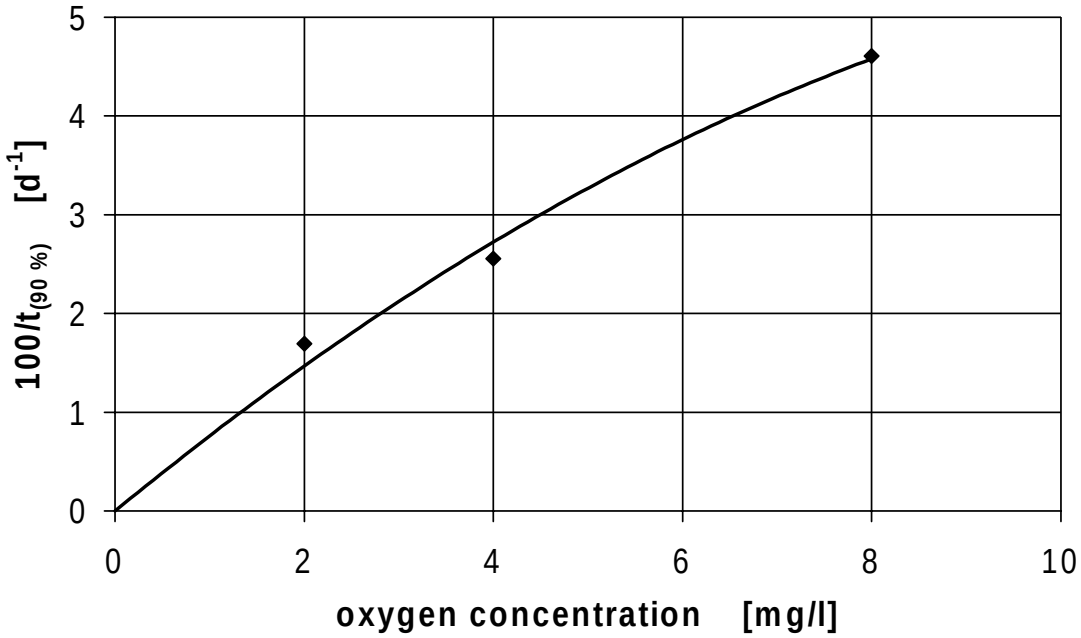

Figure 4. Dependence of reciprocal induction time t (90% residual tensile load) on oxygen concentration at atmospheric conditions for the basically stabilized nonwoven NW01 at 90 °C.

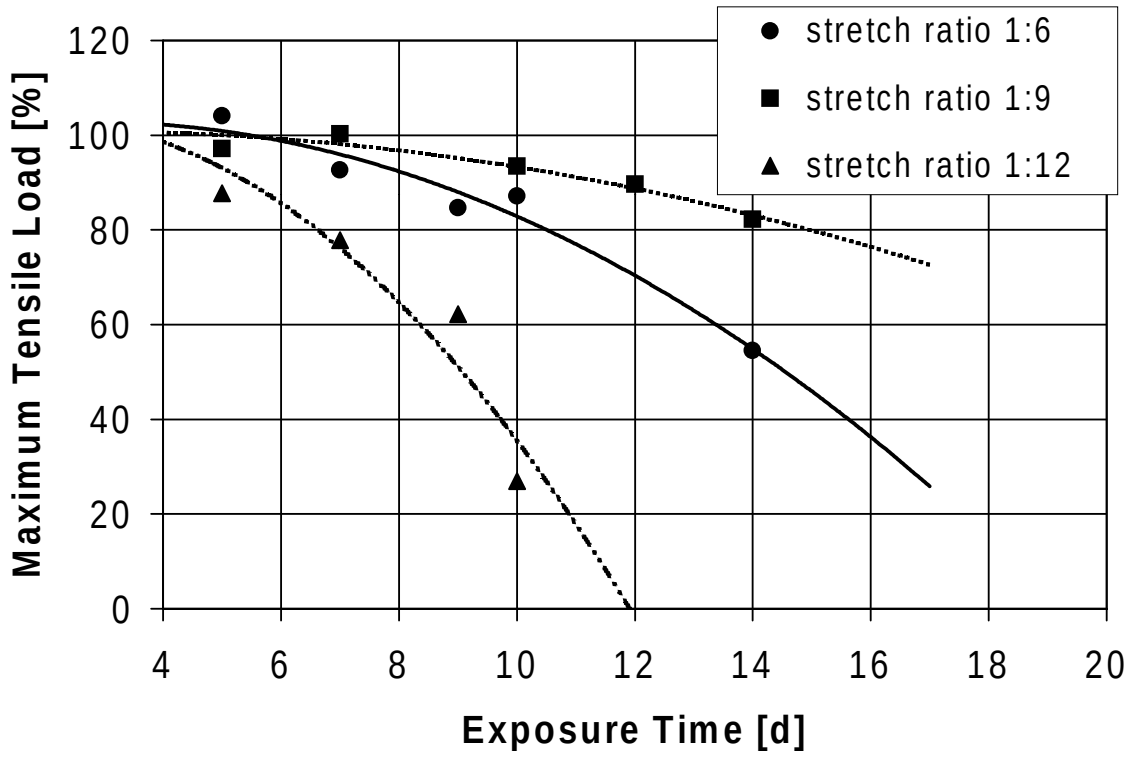

Figure 5. Effect of stretch-ratio on oxidative durability of the basically stabilized PP-tapeyarn YT06 – YT12

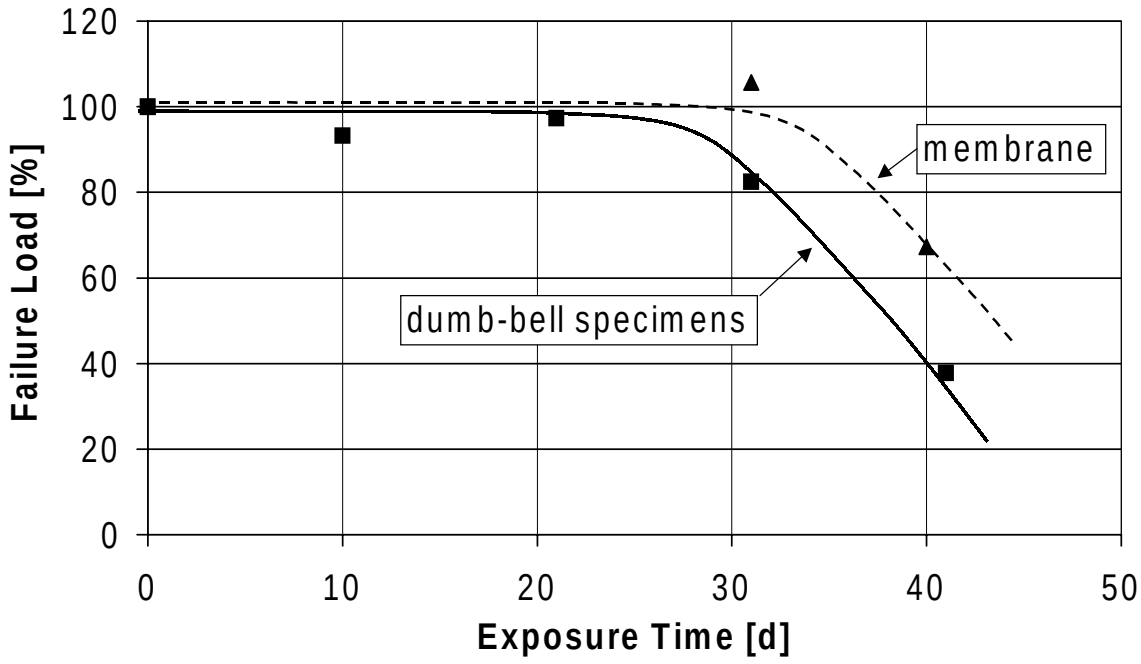

Figure 6. Dependence of failure load of a PE-HD-geomembrane on oxidative immersion exposure in neutral solution to 20 bar oxygen at 80 °C