

# Comparison of oxidation stability of various geosynthetics

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**ABSTRACT:** Data from oven aging (in air) and immersion tests in water on HDPE-geomembranes (GM) and on polyolefin (PE, PP) nonwoven geotextiles (GTnw) are reported and the results of these long-term tests are compared. Most of the GTnw are poorly stabilized compared with the GMs. The service time of the GM is essentially determined by the slow loss of stabilizers, while for the GTnw a rapid reduction in the amount of stabilizer was observed. Even after the loss of stabilizers some oxidation stability remained which may be attributable to the structural stabilization of the strained and oriented fibres. For PP-GTnw samples a sudden reduction in the mechanical strength occurred after some aging time after which the oxidation continued rapidly until complete deterioration. For the PE-GTnw the reduction in mechanical strength starts immediately but proceeds very slowly. We attribute this to morphological changes and not to oxidative degradation.

## 1 INTRODUCTION

It is generally accepted that the oxidative degradation of geosynthetics made of polyolefin resins (PP, PE) is not relevant for normal service times, which are about 30 years. However, there are very large differences in the oxidation stability of the various products available on the market. The oxidation stability depends strongly on the resin, the morphology, the stabilizer package and the product design. Such differences become relevant when the geosynthetics are integral part of building structures which have to perform over a very large time (100 y), as is the case for geomembranes (GM), bentonite mats (GCL), nonwoven geotextiles (GTnw), geocomposite drains (GCD) and geo-grids (GG) in landfill liner systems. Especially in the capping system the long-term slope stability might be impaired by the degradation of the geosynthetics due to the loss of the internal shear strength (Seeger et al. 2000). While for polyethylene pipes and polyethylene GMs well founded estimates of the service times are possible, there is still a lack of data and understanding of the relevant aspects for non-woven geotextiles (GTnw) used e.g. as protection layers or as components of GCLs and GCDs: How important is an appropriate stabilization of fibres for their long-term behaviour? What does “appropriate” mean for fibres? What does the intrinsic oxidation stability of the oriented fibres (structural stabilization) contribute to the overall service time? How long is this service time compared with HDPE-GMs? What are the best test methods to select products with high oxidation stability at ambient temperatures and normal service conditions?

We performed long-term oven aging tests (gravity air convection) and immersion tests in water for a variety of different commercially available PE-GTnw as well as PP-GTnw and HDPE-GMs. The oven aging and immersion temperature was in all cases 80°C. This temperature was chosen because it is the highest temperature from which Arrhenius extrapolation to ambient temperatures is possible for PE. For PP however, Arrhenius extrapolations generally overestimate considerably service times at ambient temperatures (Gugumus 1999). The change in the mechanical properties (especially stress and strain at break which is the most sensitive mechanical property with respect to oxidative degradation), melt flow rate (MFR) and density and the change in high temperature OIT values (which reflect the change in the amount of stabilizer) was monitored during the aging.

It is hoped that these measurements would give indications of the answers to the above mentioned questions.

## 2 THEORY

In the following a simplified picture of oxidation and stabilization is given. The chemistry and physics of the processes involved are quite complex but in principle to a large extent well understood. A detailed discussion can be found elsewhere (Emanuel, Buchachenko 1987; Kamiya, Niki 1978; Gugumus 1999, references therein). The oxidative degradation of PE and PP is initiated by the formation of free radicals. The formation is due to peroxides, oxygenated compounds (formed during the processing of the polymer) and catalyst residues in combination with oxygen. UV and high energy radiation will also produce free radicals and free radical initiators. In principle free radicals are also initiated thermally and mechanically. Once free radicals are formed and oxygen is available, a chain reaction can start. Within each propagation cycle of the chain reaction, hydroperoxides are formed. The decomposition of the hydroperoxides initiate new chain reactions. Eventually each chain reaction is terminated. The termination reaction leads to a decomposition of the polymer chain. To some extent cross linking might occur in the early stage.

Oxidative degradation is therefore an auto-accelerated process (autoxidation). After a certain induction period  $t_1$  with no significant changes in the polymer properties, the degradation rate increases rapidly, the molecular weight distribution is shifted towards lower values, the material becomes brittle and loses finally all mechanical resistance. Since at the beginning the reaction rate at ambient temperatures is very low the induction time  $t_1$  is quite large. Depending on the amount of free radical sources and the sensitivity of the polymer to oxidation the induction time might range from a few years to some decades.

Antioxidants are mixed into the polymer to protect it from oxidation. These are either compounds which trap free radicals and prevent reaction chain initiation or which decompose hydroperoxides, therefore preventing them to form free radicals and new reaction chains. Usually a combination of both types of antioxidants are used. Each antioxidant has a temperature range in which it functions most effectively. There are antioxidants which have their effective temperature range at higher temperature and are used as processing stabilizers (phosphites) and there are others which have their most effective temperature range at ambient temperature (HALS) or over a wide range of temperature (hindered phenols) and which are used as long-term stabilizers to provide protection during the low temperature service time.

Typically a composition of a phosphite and a hindered phenol is used as antioxidant package for most of the geosynthetics available on the market. In addition HALS or carbon black are added as the UV stabilizer component. The concentration of the antioxidant components might range from several hundred ppm (mg/kg) to a few thousand ppm.

It is well known that under normal conditions (ambient oxygen pressure) antioxidants are not consumed by the very slow oxidation process but are lost by migration, dissolution, evaporation and extraction (Smith et al. 1992). These antioxidant depletion processes depend strongly on the environmental conditions. If after a certain induction time  $t_2$  of antioxidant depletion the antioxidant concentration has fallen below a critical value, the autoxidation with induction time  $t_1$  will start. Therefore the service time  $t_L$  of a geosynthetic might be written as

$$t_L = t_1 + t_2 \tag{1}$$

The oxidation stability at high temperature (above the melting point) can be directly measured using thermoanalytical methods. By the thermoanalytical measurement the time interval (oxidative induction time, OIT) to the onset of exothermic oxidation of a polymer at a specified OIT testing temperature  $T_m$  in a specified oxygen atmosphere is determined. It is neither possible to extrapolate from OIT values (measured at high temperatures) the induction times at ambient temperature nor is it permissible to classify the oxidation stability of different resins and products according to small

differences in their OIT values. However the change in OIT values might be used to monitor the change in the level of stabilization. Especially for the above mentioned stabilizer package the OIT value is roughly proportional to the antioxidant concentration with some specific proportionality constant for a given resin (Howard 1973; Gray 1990). This concept was used for example to estimate the induction time  $t_2$  of HDPE-GMs (Hsuang, Koerner 1998).

### 3 EXPERIMENT

8 commercially available HDPE-GMs (samples 1 and 48 (same resin), 12 and 136 (same resin), 82, 123, 139, 146) from 5 manufacturers were tested. The GMs were 2.5 mm thick and used e.g. in landfill lining systems. In all cases the UV stabilization was effected by carbon black with a typical content of 2.5 wt.-%. Concerning the nonwoven geotextiles 4 PP-GTnws, (samples P9, P12, P16, P27) from 4 manufacturers and 6 PE-GTnws (samples P4, P5, P14, P20, P23, P35, P36) from 3 manufacturers were tested. The titre of the fibres was typically about 15 dtex, the mass per area and the thickness typically about 1200 g/m<sup>2</sup> and 10 mm. All PE-GTnw were UV-stabilized by carbon black with a typical carbon black content in the range of 0.5-1 wt.-%. In the case of PP-GTnw carbon black as well as chemicals were used for the UV stabilization.

The following experimental methods were used:

1. Oven aging (gravity convection)
2. Immersion in water
3. Tensile test, melt flow rate (MFR) and density
4. DSC measurement for high temperature OIT values and melting curve

1. The specimens were aged in thermostatically regulated ovens with gravity convection via two open air channels. For the GTnw a Heraeus UT 6760 oven (working chamber volume 689 l) was used, which has an internal air ventilation by a fan. According to the technical data of this oven there were 10 air changes per h and a fresh air quantity of about 10 m<sup>3</sup>/h. The temperature variation (with closed flaps) was about  $\pm 1^\circ\text{C}$ . The GMs were tested in a Heraeus T 5110 E oven (working chamber volume 258 l). Technical data concerning the oven's air changes per h and fresh air quantity are not available. However both quantities are substantially lower than for the UT 6760. The temperature variation (with closed flaps) was about  $\pm 3^\circ\text{C}$ . Square sheets of width 50·40 cm<sup>2</sup> (GTnw) and 30·40 cm<sup>2</sup> (GM) were cut out of the samples. The fibre lubricant (avivage) was removed from the GTnw specimens. To achieve this, the specimens were immersed for 24 h in ethanol, put on a grid to drain off the alcohol and to dry them. The specimens were hung up on the grids in the preheated oven.

2. For the water immersion test of the GMs, tensile test specimens of type 1B according to EN ISO 527-3:1995 were put in closed glass flasks filled with de-ionized water. The flasks were placed in a regulated oven at  $(80 \pm 1)^\circ\text{C}$ . The flasks were opened and shaken every 4 weeks, the water was changed every 3 months.

3. The tensile properties of the GMs were tested according to the above mentioned EN ISO 527-3. Specimens of type 1B were punched out of the sheets which had been taken from the oven and cooled off in the standard climate (23/50). For the testing of the tensile properties of the GTnw, we followed DIN EN 29073-3:1992. In this case strips 50 mm wide and 250 mm long were punched out of the sheets. The melt flow rate and the density were tested according to DIN ISO 1133:1991 and DIN 53479:1976, method A, using strands from MFR measurements.

4. The procedure of the high temperature OIT measurement by differential scanning calorimetry is described in ASTM D 3895-95. A Perkin Elmer DSC 7 was used. In case of the GMs a small cylinder (3 mm diameter) was punched out of the geomembrane. A small plate was cut from the middle section of the cylinder. This plate was used for the OIT measurement. For the GTnw we

proceeded with the same method. However the small plate of fibres was put in a closed Al-pan, heated up to 180 °C and cooled to ambient temperature in the DSC. The pellet of molten material was then used for the OIT measurement (see appendix-1). The OIT value was determined using open Al- as well as Cu-pans. Cu-pans were chosen to accelerate the oxidation: we wanted to achieve an OIT testing temperature  $T_m$  as close to the melting temperature as possible with OIT values short enough to be practicable in the experiment.

## 4 EXPERIMENTAL RESULTS

### 4.1 HDPE-geomembranes

Figure 1 shows the relative change of the OIT value,  $\delta\text{OIT}$ , of GM sample 1 and 48 (same resin and same GM-manufacturer) and sample 12 during the oven aging in air at 80°C. Sample 1 and 48 are poorly stabilized as can be seen from the initial absolute OIT values (Tab. 1). The OIT value slowly decreases, but even after 8.4 years of aging in air an OIT value can still be measured at 180°C OIT testing temperature  $T_m$ . None of the samples show any significant change neither in the tensile properties or in the melt flow rate.

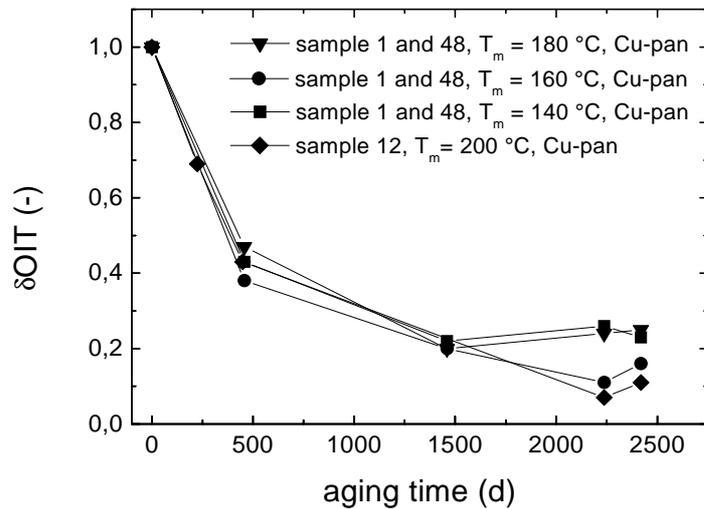


Figure 1. Relative change of the OIT value,  $\delta\text{OIT}$ , of GMs at different OIT testing temperature  $T_m$  during aging in air at 80°C. Cu-pans were used for the OIT measurement.

Table 1. Initial OIT value of the HDPE-GM samples at  $T_m = 160^\circ\text{C}$ ,  $180^\circ\text{C}$  and  $200^\circ\text{C}$ . Cu-pans were used in all cases

Sample	OIT (min) at $T_m$		
	160 °C	180 °C	200 °C
1	61	7	-
48	72	13	-
12	-	-	19
82	-	113	7
123	-	56	8
136	-	123	24
139	-	203	15
146	-	46	13

Figure 2 shows an Arrhenius plot of the inverse absolute OIT testing temperature ( $1/T_m$ ) versus the logarithm of the OIT values for GM sample 48 after two oven aging times: 6 y (sample 48a) and 8.4 y (sample 48b), and after about 8.2 y of immersion in liquid hydrocarbons at room temperature (sample 48c). For each aging condition the data follow a Arrhenius line with the same slop (activation energy) as the data for the initial sample. However, the lines are shifted parallel to each other to lower OIT values according to the severity of the aging condition (stabilizer evaporation and dissolution during aging and extraction due to hydrocarbons). This clearly indicates that the change in OIT value can be interpreted as proportional to the change in stabilizer content.

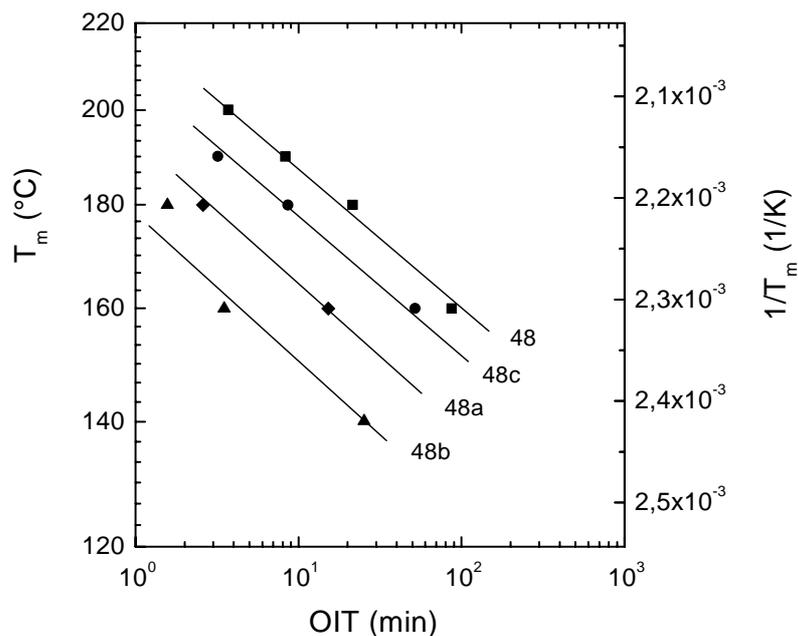


Figure 2. Arrhenius plot of the inverse absolute OIT testing temperature ( $1/T_m$ ) versus the logarithm of the OIT values, (48): initial values, (48c): immersion in liquid hydrocarbons for 8.2 y, (48a): oven aging at 80°C for 6 y, (48b): for 8.4 y.

The behaviour during the immersion in water is different from that in the oven aging. Figure 3 and 4 show  $\delta$ OIT as a function of the immersion time in the de-ionized water for sample 82, 123, 136, (Fig. 3) and 146, 139 (Fig. 4). Sample 136 was made of the identical resin as sample 12.

At the beginning the OIT value decreases rapidly for all samples. However, at the latest after 200 d the curve levels off and the further decline in oxidation stability is only minimal. Dependent on the height of the initial OIT value the initial decrease is quite pronounced (e.g. sample 139). However the remaining OIT value itself after 982 d is quite similar for the samples shown in Figure 3 and 4. At  $T_m = 180^\circ\text{C}$  it is 9 min (136), 7 min (82), 7 min (123), 5 min (139) and 8 min (146). For all these samples there was no change observed in the tensile properties and no change in melt flow rate or density.

Sample 1 and 48 are obviously made of poorly stabilized resins compared with the other resins tested. The initial OIT value is extremely low (Table 1). For the GMs made of this resin the rapid decrease in OIT value continues (Fig. 5). After about 2 y of immersion in water no OIT value was measurable. Even at  $T_m = 140^\circ\text{C}$  the OIT value was practically zero. From that time on the oxidative degradation proceeded. The sample became brittle. A drastic reduction in the elongation and

stress at break was observed. Yet, at that time there was no change in yield stress and strain and therefore the field performance of the GM would not have changed. However, for the time being (4.4 y of immersion) the elongation at break is now as low as about 6%. The change of  $\epsilon_B$  was accompanied by a reduction in the melt flow rate indicating cross linking as the main early degradation effect. The same oxidative behaviour (Fig. 5) was observed in pipe pressure tests at 80°C with pipes made of this resin (Koch et al. 1988).

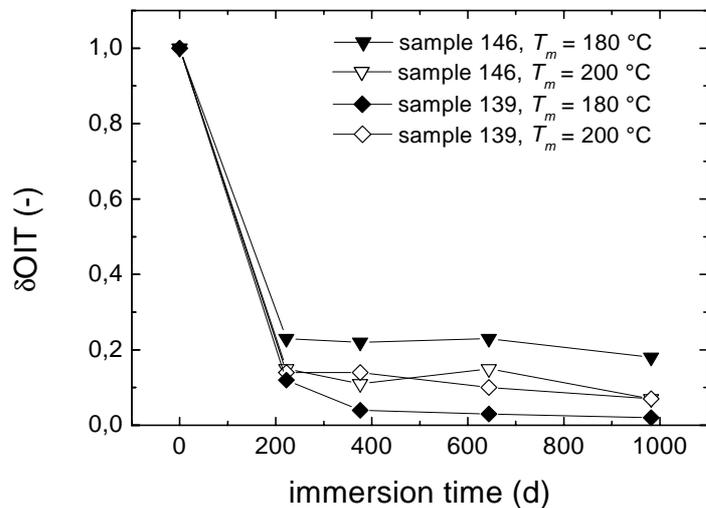
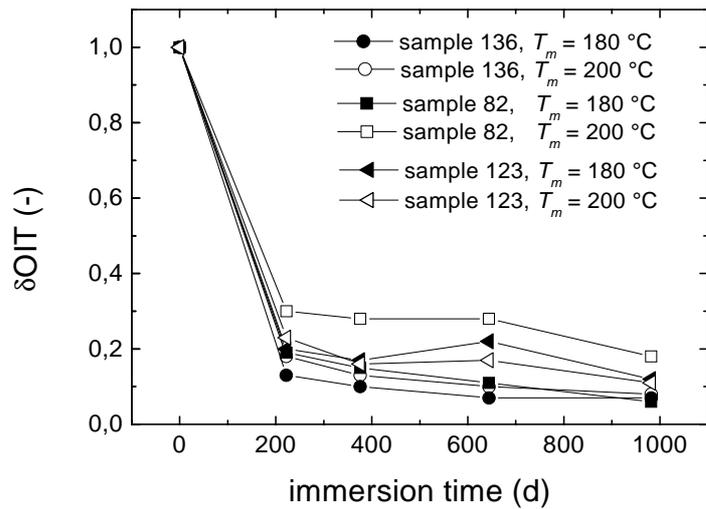


Figure 3 and 4. Relative change of the OIT value,  $\Delta OIT$ , of GMs at different OIT testing temperature  $T_m$  during immersion in water at 80°C. Cu-pans were used for the OIT measurement.

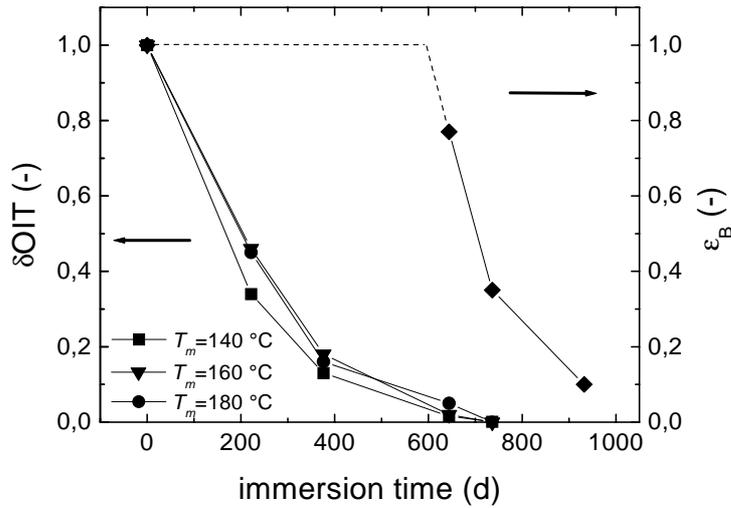


Figure 5. Relative change of the OIT value,  $\delta\text{OIT}$ , of sample 48, measured at different OIT testing temperatures  $T_m$ , and relative change of the elongation at break,  $\delta\epsilon_B$ , during immersion in water at  $80^\circ\text{C}$ .

#### 4.2 Nonwoven geotextiles

Table 2 gives the initial OIT values of the GTnw samples used for the oven aging and immersion tests in water. OIT values of the PP-GTnw were measured at  $T_m = 170^\circ\text{C}$  in Al-pans, these of the PE-GTnw at  $T_m = 150^\circ\text{C}$  in Cu-pans.

Table 2. Initial OIT values for the various PE- and PP-GTnw tested. The OIT-testing temperature and the pans used are indicated

Sample	OIT (min) at $T_m$	
	150 °C (Cu)	170 °C (Al)
PP	P12	-
	P16	4
	P27	18
PE	P4	43
	P5	13
	P20	30
	P35	39
	P36	47
	P14	215
	P23	23
		29

Obviously the OIT values for the GTnw are much lower than the OIT values for the GM: to obtain comparable times one has to reduce the OIT testing temperature from  $200^\circ\text{C}$  to  $150^\circ\text{C}$  (Cu-pans) and from  $210^\circ\text{C}$  to  $170^\circ\text{C}$  (Al-pans). Assuming that the OIT value increases a factor of 2 if one reduces  $T_m$  by  $10^\circ\text{C}$ , the OIT value of the GM is at least one order of magnitude larger than for the GTnw. Even for the best fibre resin found, P14, the level of oxidation stability in the OIT-measurement is much lower than that of the worst HDPE resin, P48, studied. Also, the behaviour in the aging testing is quite different, even if we keep in mind that the ovens used are different and the aging conditions for the GTnw was more severe than that for the GMs (see appendix-2).

Figure 6 and 7 show the change in the OIT value of the PP- and PE-GTnw during oven aging. For all but one sample the OIT value decreases rapidly. After half a year of aging no OIT value could be measured at  $T_m = 170^\circ\text{C}$  (Al-pans), see appendix-3. The data measured at  $T_m = 150^\circ\text{C}$  (Cu-pans) indicate essentially the same behaviour. However, in the thermoanalytical measurement the processes to achieve thermal equilibrium and the oxidation proceed very slowly at  $150^\circ\text{C}$ . At such a low OIT testing temperature OIT values below about 10 min are not conclusive. Beside these experimental problems there seems, however, to remain a low level of oxidation stability at least for some samples. This might be due to the intrinsic oxidation stability of the unstabilized resins. The low level is quite independent of the aging time.

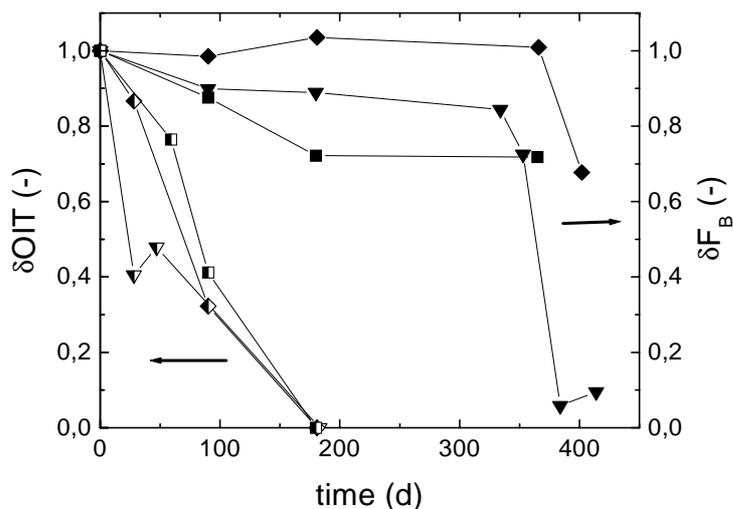


Figure 6. Relative change of the OIT value,  $\delta\text{OIT}$ , of the PP-GTnw samples, P12 (triangle), P16 (rhombus) and P27 (square), and relative change of their tensile strength,  $\delta F_B$ , during aging in air at  $80^\circ\text{C}$ .

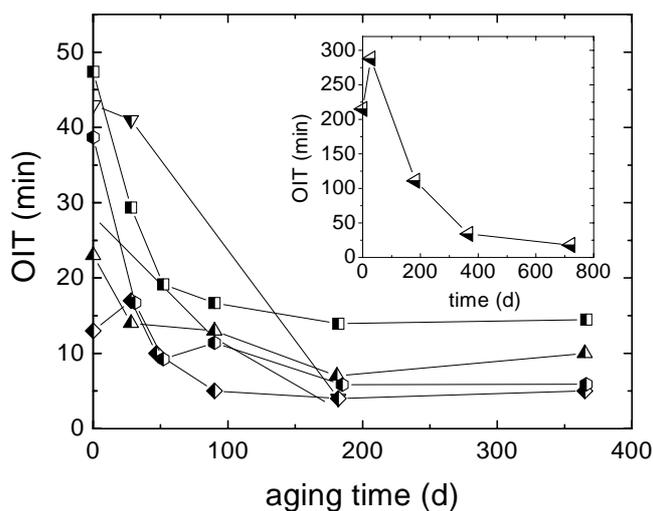


Figure 7. Relative change of the OIT value,  $\delta\text{OIT}$ , of the PE-GTnw samples, P4 (triangle upside down), P5 (rhombus), P14 (rotated triangle, small inserted figure) P20 (circle), P23 (triangle), P35 (hexagon) and P36 (square), during aging in air at  $80^\circ\text{C}$ .

Sample 14 is the one PE-GTnw which behaves differently than the others. The initial level of oxidation stability is very high and decreases slowly. Even after two years of aging the OIT value is 18 min ( $T_m = 150^\circ\text{C}$ , Cu-pan), higher than the initial value of some other PE fibre materials.

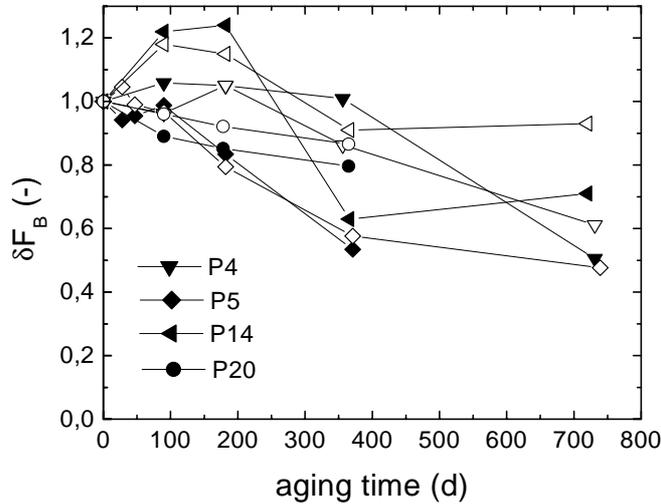


Figure 8. Relative change of tensile strength,  $\delta F_B$ , of the PE-GTnw samples P4, P5, P14 and P20 during aging in air at  $80^\circ\text{C}$ . Filled symbols mark tensile strength in the machine direction, open symbols in the cross machine direction.

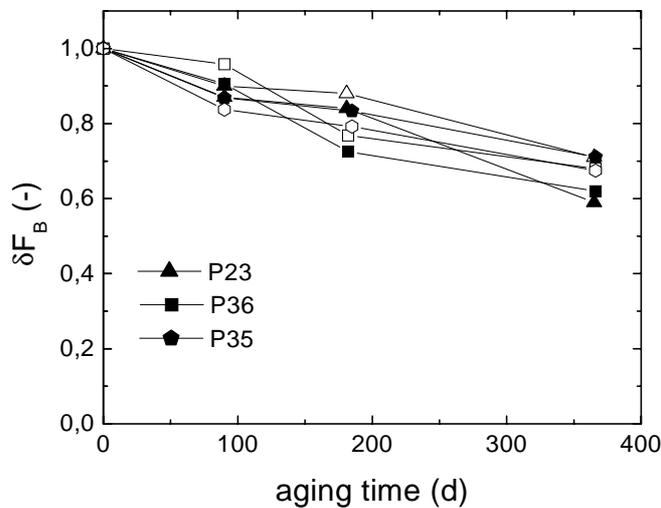


Figure 9. Relative change of tensile strength,  $\delta F_B$ , of the PE-GTnw samples P23, P35 and P36 during aging in air at  $80^\circ\text{C}$ . Filled symbols mark tensile strength in the machine direction, open symbols in the cross machine direction.

Reduction to essentially zero of the OIT value during aging is not accompanied by a sudden change in the mechanical properties of the GTnw. For the PP-GTnw the tensile strength remains on the initial level (Fig. 6). Not until 1 y after the OIT value had dropped to zero, the oxidative dete-

rioration of sample P12 and P16 started. Within a few months these geotextiles have then lost all mechanical strength. The fibres have completely disintegrated to fragments. However, for PP-GTnw sample P9 no change of the tensile strength was found after 739 d of oven aging.

For the PE-GTnw a slow and continuous decrease in tensile strength is observed (Fig 8, 9). In this respect the behaviour of all of the PE geotextiles seems to be quite similar independent of their OIT values. In most cases the decrease starts immediately from the beginning of the oven aging. After 1 y aging time the tensile strength is about two thirds of the initial value and after 2 y about one half.

For all PE-GTnw samples a gradual change in melt enthalpy, determined from the first DSC melting curve of the fibre plate, was observed. A small peak at about 110°C arises in the melting curve. This effect is well known as so called “memory effect” from thermal treatment of semicrystalline polymers not too far from their melting temperature. 80°C is at the beginning of the range where small crystallites begin to melt. Figure 10 shows the relative change in melt enthalpy of samples P4, P5, P14 and P35 as a function of aging time. Assuming a melt enthalpy of 293 J/g for a PE crystal the samples had the following initial cristallinities: 48% (P4), 56% (P5), 60% (P14) and 66% (P35). After 2 y the increase in crystallinity calculated from the change in melt enthalpy is about 15-20%. This recrystallisation might be accompanied by a change in the degree of orientation of the fibres explaining therefore the continuous decrease in strength of the geotextile. No change in melt enthalpy and therefore in the crystallinity was found for the PP samples.

The behaviour of the PP-GTnw samples, P12, P16 during immersion in water was similar to their behaviour in air oven aging.

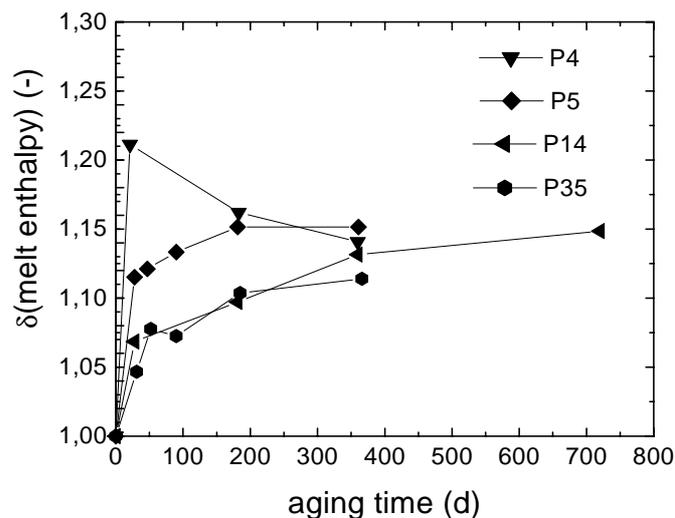


Figure 10. Relative change of melt enthalpy of the fibre plates taken from sample P4, P5, P14 and P35.

## 5 DISCUSSION

In Section 2 of this paper, the commonly used simple model for interpretation of aging data was considered. According to this model the service time  $t_L$  is composed of the induction time  $t_1$  of the autoxidation of the unstabilized polymer and the antioxidant depletion time  $t_2$ . For our discussion it is crucial that the change in OIT value gives at least a rough estimate for the depletion time  $t_2$ . This is for all effective purposes established for the commonly used antioxidant packages.

It is well known that strained or oriented polyolefin polymer films show an increase in oxidation stability. The induction period of autoxidation grows exponentially with the degree of deformation (Emanuel, Buchachenko 1987); this phenomenon is referred to as structural stabilization. Assuming structural stabilization for the oriented fibres of the nwGT, we introduce a third time  $t_3$  which is the increment in induction time of the autoxidation process due to orientation.  $t_1$  is then the induction time of the unstabilized and unoriented material. Instead of Equation 1 we may therefore write:

$$t_L = t_1 + t_2 + t_3 \quad (2)$$

With this model in mind, we may interpret our data tentatively as follows. We may assume that  $t_1$  is quite small for oven aging at 80°C. However, at ambient temperature it might contribute considerably to  $t_L$ , at least of PE resins. For the HDPE-GM  $t_3 = 0$  and  $t_L \approx t_2$ . For the GTnw,  $t_2$  is normally quite small compared with  $t_2$  of the GM. This is because for the GTnw resins the amount of stabilizers (and carbon black) added is considerably lower than for the GM resins and the surface to volume ratio is at least two orders of magnitude larger for the fibres of GTnw than for GM sheets. Essentially all antioxidant depletion processes are accelerated substantially by the increase of this ratio. However, for the GTnw  $t_3$  might contribute substantially to  $t_L$ . Therefore large oven aging times might be achieved if the materials are well stabilized and/or well oriented.

The terms “well stabilized” and “poorly stabilized” were used quite often in this paper. Their meaning for the GTnw is now more clear. One should add not only an antioxidant package in combination with carbon black or chemical UV stabilizers which leads to a high initial OIT value in combination with a small change of OIT value during aging but also produce highly and homogeneously oriented fibres.

On the Sixth International Conference on Geosynthetics Salmen et al. (1998) presented a paper about degradation of PP-GTnw. They measured oxidation stability via the induction time, in their terminology defined as the period of oven aging when no statistically significant changes in tensile strength is observed. According to our interpretation this is equivalent to  $t_2 + t_3$ . For their sample P-3 and P-4 the induction time at oven aging in circulating air was about zero at 80°C. Our samples P12 and P16 show induction times of about 1 y. If the oven aging data are comparable, P12 and P16 were much better stabilized than P-3 or P-4. The oxidation stability of P9 with induction time  $> 2$  y is even higher. The change in the tensile strength of the PE-GTnw was not attributed to oxidation but to morphological changes. If we define therefore significant change by a 50% reduction of tensile strength the induction time of the PE-GTnw would be  $> 2$  y. For the GM we expect the induction time to be  $\gg 2$  y. For P-3, Salmen et al. (1998) extrapolated an induction time ( $t_2 + t_3$ ) at ambient temperature of 50 y adding another 40 y for  $t_1$ . On the same conference G. Hsuang presented oven aging data for  $t_2$  of a typical HDPE-GM, extrapolating 200 y (Hsuang, Koerner 1998). For the poorest stabilized HDPE resin of our study, sample 48, Koch et al. (1988) extrapolated  $> 500$  y of service time at ambient temperature from pipe pressure test data. Obviously these service time extrapolations for ambient temperatures do not fit with the large differences in the oxidation stability of the materials found at 80°C oven aging (e.g. no induction time for P-4, induction times of  $\gg 1$  y for HDPE). Salmen et al. might have been too optimistic (Arrhenius extrapolation overestimates service times for PP) and Hsuan too pessimistic. However, very large service times ( $> 100$  y) might be obtained for (in the above sense) well stabilized GTnw.

For HDPE-GMs test procedures and specifications have been established to assess the oxidation stability. The GR-13 Standard requires an initial OIT value at  $T_m = 200$  °C of 200 min or a high pressure OIT value of 400 min at  $T_m = 150$ °C and  $p_{O_2} = 38$  bar. The reduction in OIT value must be less than 45% in 90 d oven aging at 85°C. The BAM certification (Mueller 1999) for GM requires OIT values at  $T_m = 210$  (200)°C of  $> 10$  min ( $> 20$  min). During an oven aging at 80°C for 1 y the relative change in OIT value,  $\delta$ OIT, between 0.5 y ( $> 10$  min) and 1 y must be less than 30%.

For long-term applications it is also necessary to establish requirements for other geosynthetics. For the time being the requirements have to be still tentative. For the GTnw we suggest that the OIT value at  $T_m = 170$ °C (Al-pans) should be at least 20 min. During an oven aging test at 80°C for

1 y, no oxidative degradation or other significant change in tensile strength (e.g. 50% reduction) should occur.

Oven aging not too close to the melting temperature requires long testing time. It was therefore suggested to test with high oxygen pressure. This is an interesting approach (see conference contribution of H. Schröter and Salmen et al. 1998). However, the results have to be interpreted with care. Within our interpretation model we expect that oven aging at high oxygen pressure obviously measures essentially  $t_3$  (under the specific test conditions) and neglects completely antioxidant depletion effects,  $t_2$ . In the high pressure test a poorly chemically stabilized but oriented monofilament-fabric or slit film-fabric might therefore perform as good or even better than a chemically well stabilized GM sheet, while in normal pressure oven aging and therefore in “real life” performance the service time of the latter might possibly be an order of magnitude larger than the former. However, there is still considerable research on geosynthetics necessary to clarify the relative importance and magnitude of  $t_1$ ,  $t_2$  and  $t_3$ .

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## APPENDIX

1. For GTnw sample P36, 182 d oven aging, it was checked how the number of melting influences the OIT value. For our procedure of melting twice an OIT value of  $(14 \pm 4)$  min was found. Melting the specimen a third time the OIT value was in the same range  $(14 \pm 2)$  min. Melting GM sample 257 once the OIT value was  $(41 \pm 6)$  min, melting twice  $(39 \pm 2)$  min.

2. The HDPE-GMs were aged in an oven with stagnant air while the GTnw in an oven with forced air circulation. However, HDPE-GM sample 257 was also tested with forced air circulation.

The initial OIT value was  $(41 \pm 6)$  min ( $T_m = 200^\circ\text{C}$ , Cu-pans) or  $(41 \pm 2)$  min ( $T_m = 210^\circ\text{C}$ , Al-pans). After 90 d of aging an OIT value of  $(36 \pm 2)$  min respectively  $(34 \pm 2)$  was found. This is a reduction of 12-17 %. Figure 1 shows that in stagnant air the reduction after 90 d of aging was typically 10%.

3. For PE-GTnw sample P23 and P35 the OIT measurement was also performed with Al-pans at  $T_m = 170^\circ\text{C}$ . Under these conditions the reduction of OIT value with aging time is more pronounced than under the conditions  $T_m = 150^\circ\text{C}$ , Cu-pans (Fig. 11). The behaviour is similar to that of the PP-GTnw (Fig. 6).

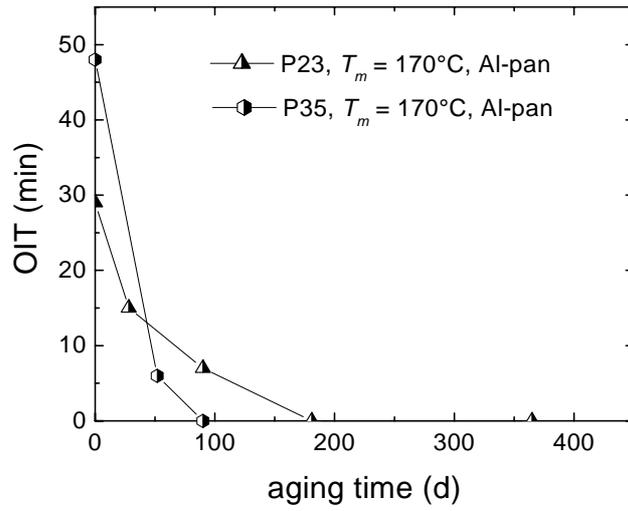


Figure 11. Relative change of OIT value,  $\delta\text{OIT}$ , measured with Al-pans at  $T_m = 170^\circ\text{C}$ , of the PE-GTnw samples P23 (triangle) and P35 (hexagon) during aging in air at  $80^\circ\text{C}$ .