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# Comparison of the oxidative resistance of various polyolefin geotextiles

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## Abstract

Data are reported from oven aging in circulating air and water immersion tests at 80°C on various polyolefin (polyethylene (PE) and polypropylene (PP)) needle-punched nonwoven geotextiles (GTnws) and the results of these long-term tests are compared with the oxidative resistance of high-density PE geomembranes (HDPE GMs) described in a preceding paper (Polym. Degr. Stability 79(1) (2003) 161). Polyolefin fibers used in geotextiles are typically less stabilized, have a very high surface-to-volume ratio and an oriented morphology compared with HDPE GMs. Therefore, significant differences in the oxidation behavior of these products are expected which may affect their durability. Two general results can be obtained from our measurements: Firstly, while the lifetime of the HDPE GM is essentially determined by the slow loss of stabilizers, for all GTnws a rapid reduction in the oxidative induction time (OIT) and, as we conclude, in the amount of stabilizer was observed during water immersion and air aging. Secondly, the mechanical property degradation of the GTnws depended strongly on the oxidation conditions: the induction period prior to the degradation was much longer for immersion in water than for oven aging in circulating air. After antioxidant depletion, an induction time of the oxidation reaction, which depends on the draw ratio of the stretched fibers and the oxygen supply, might substantially contribute to the induction period of the mechanical property degradation of GTnws. For one PP GTnw product, a sudden reduction in the mechanical strength occurred after onset of degradation which continued rapidly until complete deterioration. For other PP samples as well as for all PE GTnws the reduction in mechanical strength proceeded slowly. Best fits were obtained by modeling the degradation process of the PE GTnws by a second-order kinetic. Using an activation energy of 60 kJ/mol (Geotextiles, Geomembranes and Related Products, Balkema, Rotterdam, 1990; Conference Proceedings of the Sixth International Conference on Geosynthetics, Industrial

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Fabrics Association International (IFAI), Atlanta, USA, 1998, pp. 683–690; Clay Geosynthetic Barriers, Balkema, Lisse, The Netherlands, 2002, pp. 87–96), lower limits of the half-life of the degradation at worst case field conditions were obtained in the range 30–83 years. Some decades have to be added for the overall induction time. However, under field conditions with limited oxygen supply, the expected service lifetime might be at least half an order of magnitude longer.

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## 1. Introduction

Field experience over several decades shows that the oxidative degradation of geotextiles made of appropriately selected polyolefin resins is not relevant for normal service lifetimes, which are about 30 years (Raymond and Giroud, 1993). However, there are very large differences in the oxidation stability of the various products available on the market. The oxidative resistance depends strongly on the resin, the morphology, the stabilizer package and the product design. Such differences become relevant when the geotextiles are functional part of building structures that have to perform over a very large time (100 years), as in the case of liner and capping systems for landfills or contaminated land, where needle-punched nonwoven geotextiles (GTnws) are used as protection, reinforcement or filtration layers or as filter and packaging components of geosynthetic clay liners and geocomposite drains. Especially in capping systems, the long-term slope stability might be impaired by the degradation of the functionally integrated and shear stress bearing geotextiles due to the reduction of their internal shear strength (Seeger et al., 2000; Thies et al., 2002).

In a preceding paper, the oxidative resistance of high-density PE geomembranes (HDPE GMs) was studied (Mueller and Jakob, 2003). The oxidative behavior of these products seems to be well understood (Sangam and Rowe, 2002; Mueller and Jakob, 2003) and may therefore set a frame to study and compare the oxidative resistance of polyolefin GTnws. The oxidative resistance of HDPE GMs is characterized by a time period during which the antioxidant package protects the GM from degradation by oxidative processes. The length of this period, before the oxidative degradation of the mechanical properties sets in, is essentially determined by the duration of antioxidant depletion due to migration processes, which are quite independent from the conditions of the oxidative attack. Therefore, estimation of expected service lifetimes was based on the estimation of antioxidants depletion times. Recently, it was suggested to apply this concept to the evaluation of the durability of various geotextiles made of polyolefin materials (Hsuan, 2002; Hsuan and Koerner, 2002). This approach was questioned by Thomas, who found no induction time at all studying the oxidative degradation of a polypropylene (PP) GTnw in air oven aging at elevated temperature (Thomas, 2002). In various studies on the oxidative resistance of geotextiles, it was found that the material degradation

behavior strongly depends on the special oxidation condition in the experiment and seems to be more complex than the behavior of HDPE GMs (Wisse, 1982; Wisse et al., 1990; Horrocks and D'Souza, 1992; Salman et al., 1998; Schröder et al., 2000; Vink and Fontijn, 2000; Hsuan, 2002; Thomas, 2002). In comparing geotextiles materials with HDPE GMs, it is important to note that there are two significant differences in the material properties beside the differences in the structure of the basic polymers. Firstly, polyolefin fibers and slit films used in geotextiles are less stabilized compared to HDPE GMs. It is true that the components of the stabilizer package are quite similar (at least a combination of phosphite and phenolic antioxidants), but the amount of stabilizer is typically at least half an order of magnitude lower. Secondly, the morphology is different. Part of the manufacturing process of fibers as well as slit films is a cold drawing process following the extrusion. The fibers and films are thereby stretched and oriented. Their draw ratio is defined as relative increase in length during cold drawing. The various products vary in degree and homogeneity of the orientation but a draw ratio of  $\geq 5$  is typically achieved. It is well known that orientation might strongly influence not only the stress crack resistance but also the oxidation process (Emanuel and Buchachenko, 1987; Popov et al., 1991).

The relevant aspects of the degradation process of polyolefin geotextiles, i.e. the relative importance of stabilization, morphology and resin properties for the induction time and oxidation rate and their dependence on oxygen partial pressure and supply, is still unclear. It is therefore difficult to find a common experimental basis for a durability assessment and the question of the oxidative resistance of polyolefin geotextiles and its testing is still highly controversial: What are the relevant chemical and physical aging mechanisms in the fibers that give rise to the degradation of the tensile properties of the geotextiles? To which extent does an appropriate chemical stabilization of fibers contribute to their long-term behavior? How can service lifetimes be reliably extrapolated? How long are these expected service lifetimes compared with HDPE GMs? What are the best test methods to select products with high oxidative resistance at ambient temperatures and normal service conditions?

For this reason long-term oven aging tests (forced air circulation) and immersion tests in water were performed for a variety of different commercially available needle-punched polyethylene (PE) and PP GTnws. The oven aging tests in circulating air were carried out at 80°C for typically 2 years, in some cases up to 3 years, and at 120°C for about half a year. The temperature of the immersion in water was in all cases 80°C and the immersion period 1–2 years. An aging and immersion temperature of 80°C was chosen because detailed long-term data for the oxidative resistance of HDPE GMs were available at that temperature (Mueller and Jakob, 2003). About 80°C is the highest temperature from which Arrhenius extrapolation to room temperature is in many cases possible, as it is known from PE pipe pressure tests (Koch et al., 1988) and oven aging tests for PP resins (Glass, 1988; Gijnsman et al., 1993; Achimsky et al., 1997; Gugumus, 1999). 120°C aging temperature was chosen to force the sample far into the oxidative degradation process, to determine whether there is any induction time still left and to assess the

extent of deterioration. The change in the mechanical properties (specially 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 oxidative induction time (OIT) values (which reflects the change in the amount of stabilizer) were monitored during the aging. The objective of these experimental studies is to clarify the relative importance of antioxidant depletion time, induction period of the oxidative reaction and the duration of the mechanical property degradation for the service lifetime of polyolefin GTnws at 80°C and to compare it with the behavior of HDPE GMs at that temperature. Various polyolefin GTnws were tested to identify the aspects which are common to these fiber-based products. In this way, the reported results might contribute to answers to the above-mentioned questions.

## 2. Experimental

### 2.1. Sample properties

The experiments were performed on four different needle-punched PP GTnws products (samples P9, P12, P16, P27), which were commercially available from four manufacturers and on eight needle-punched PE GTnws products (samples P4, P5, P14, P17 and P20 (same fiber resin as P17 but higher fiber titer), P23, P35 and P36 (same fiber resin as P35 but smaller fiber titer)) which were made available by three manufacturers. Tables 1 and 2 show characteristic values of the fiber properties (strength and titer) as well as the GTnw tensile properties: maximum tensile force normalized to the mass per area (tensile strength) and elongation at maximum tensile force. The titer of the fibers was in the range of 7–17 dtex. The mass per area and the thickness were about 1200 g/m<sup>2</sup> and 10 mm, respectively, with the exception of sample P36 which had a mass per area of 400 g/m<sup>2</sup>.

Since high concentration of additives might cause problems during manufacturing of fibers (extruding through a small hole spinneret, cooling and stretching),

Table 1

Initial mean values of strength and titer of the PP fibers as well as of tensile strength normalized to mass per area and elongation at strength of PP GTnw samples (machine direction (MD) and cross machine (XMD)), that were used as reference for the aged samples

| Sample | Initial mean values of some properties of the reference samples |                    |  |                                  |
|--------|---|--------------------|--|----------------------------------|
|        | Fiber strength (cN/dtex)  | Fiber titer (dtex) | Strength normalized to mass per area (Nm <sup>2</sup> /g) (MD/XMD) | Elongation at break (%) (MD/XMD) |
| P9     | 2.5   | 11                 | 43/22  | 71/119                           |
| P12    | 3.3   | 17                 | 31/70  | 152/74                           |
| P16    | 5   | 7                  | 68/89  | 74/67                            |
| P27    | 3.3   | 16                 | 36/68  | 95/64                            |

Table 2

Initial mean values of strength and titer of the PE fibers as well as of tensile strength normalized to mass per area and elongation at strength of the PE GTnw samples (machine direction (MD) and cross machine (XMD)), that were used as reference for the aged samples

| Sample | Initial mean values of some properties of the reference samples |                    |  |                                  |
|--------|---|--------------------|--|----------------------------------|
|        | Fiber strength (cN/dtex)  | Fiber titer (dtex) | Strength normalized to mass per area (Nm <sup>2</sup> /g) (MD/XMD) | Elongation at break (%) (MD/XMD) |
| P4     | 2.2   | 17                 | 24/43  | 122/99                           |
| P5     | 2.2   | 17                 | 19/39  | 159/98                           |
| P14    | 2.4   | 9 and 17           | 24/43  | 122/99                           |
| P17    | 2.7   | 7                  | 25/48  | 126/79                           |
| P20    | 2.4   | 16                 | 28/38  | 137/114                          |
| P23    | 2.7   | 9 and 17           | 30/55  | 104/98                           |
| P35    | 2.5   | 16                 | 23/33  | 180/120                          |
| P36    | 3   | 7                  | 32/51  | 120/90                           |

antioxidants are mixed into fiber resins essentially for the purpose to protect it from oxidation in the extrusion process. The details of the stabilizer package are normally not published by the resin manufacturers. Information has been given to the authors for most of the samples but has to be treated confidential. However, it may be said, that the fiber resins are typically stabilized with only few hundred ppm for each component of phenolic and phosphite antioxidants. In addition, all PE GTnws 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 GTnws, the UV stabilization was achieved by carbon black for P12 and by a considerable amount of chemicals (hindered amine light stabilizers (HALS)) for P9, P16 and P27. There are large differences in the initial OIT values (Table 3) and no correlation was found between the height of the initial OIT value and the amount of antioxidants comparing the different resins. Differences in the UV stabilizer and other additives and to a minor extent differences in the intrinsic properties of the resin (e.g. amount of catalyst residues, details of the polymer structure) as well as in the manufacturing process with its oxidative stress can strongly influence the effectiveness of the antioxidants and therefore can trigger the differences in the height of the initial OIT values.

## 2.2. Experimental procedures

The following experimental methods were used:

1. oven aging (forced air circulation) and immersion in hot de-ionized water,
  2. tensile tests,
  3. differential scanning calorimetry (DSC) measurement of high-temperature OIT values and melting curves.
1. For the oven aging, the specimens were aged in a thermostatically regulated Heraeus UT 6760 oven. The dimensions of the working chamber were

Table 3

Initial OIT values for various PE and PP GTnws measured at OIT-testing temperature  $T_m = 150^\circ\text{C}$  (Cu pan) and  $170^\circ\text{C}$  (Al pan)

| Sample |     | OIT (min) at |            |
|--------|-----|--------------|------------|
|        |     | 150°C (Cu)   | 170°C (Al) |
| PP     | P9  | —            | 49         |
|        | P12 | —            | 12         |
|        | P16 | —            | 4          |
|        | P27 | —            | 18         |
| PE     | P4  | 43           | —          |
|        | P5  | 13           | —          |
|        | P14 | 210          | —          |
|        | P20 | 30           | —          |
|        | P23 | 23           | 29         |
|        | P35 | 39           | 48         |
|        | P36 | 47           | —          |

52 cm × 100 cm × 132 cm with a working chamber volume of 689 l. The aging temperature was achieved and maintained by controlled heating of the working chamber walls. The air exchange took place via two open air channels (3 cm diameter) on top and bottom of the back wall. An air ventilation fan in the ceiling of the working chamber forced internal circulation. According to the technical data of this oven, there were 10 air changes per hour and a fresh air quantity of approximately 10 m<sup>3</sup>/h. The temperature variation (with closed flaps) was ± 1°C. Square specimens of 50 cm × 40 cm were cut out of the GTnw rolls at randomly distributed locations. The fiber lubricant (avivage) was removed from the GTnw sheets. To achieve this, the sheets were immersed for 24 h in ethanol, put on a grid in a fume hood to drain off the alcohol and to dry them in room climate. The sheets were then hung up on three rows of grids in the preheated oven. For the water immersion test of the GTnws, strips for the tensile test were put in closed glass flasks filled with de-ionized water. The flasks were placed in a regulated oven at (80 ± 1)°C. The flasks were opened and shaken every 4 weeks. The water was changed every 3 months.

- For the testing of the tensile properties of the GTnw, DIN EN 29073-3 (1992) was followed, using 50 mm wide and 250 mm long strips which were punched out of the GTnw sheets in machine direction (MD) and cross machine direction (XMD). The tensile strength is defined as maximum tensile force achieved during the test. Using the test results the relative value,  $\delta F_B(t) = F_B(t)/F_B(0)$ , of the tensile strength normalized to the mass per area and the relative value,  $\delta \varepsilon_B(t) = \varepsilon_B(t)/\varepsilon_B(0)$ , of the elongation at tensile strength as a function of the aging time  $t$  was determined.
- For the high-temperature OIT measurement by DSC, a Perkin-Elmer DSC 7 was used. The procedure followed essentially ASTM D 3895 (2002) with the exception

of the OIT testing temperature  $T_m$ , i.e. the temperature at which the OIT value was measured, and the sample preparation technique. The OIT testing temperature was chosen as low and therefore as close to the melting temperature as possible. The OIT values of the PP GTnws were typically measured at  $T_m = 170^\circ\text{C}$  in open Al pans, those of the PE GTnws at  $T_m = 150^\circ\text{C}$  in open Cu pans. Cu pans were chosen at  $T_m = 150^\circ\text{C}$  to accelerate the oxidation with the intention to achieve OIT values short enough to be practicable in the experiment. The process for the specimen preparation was as follows: a small cylinder (3 mm diameter) was punched out of the GTnw sheet. A small plate-like heap of fibers was cut from the middle section of the cylinder. Since it is very difficult to perform well-defined and small scattering OIT measurements on such a spatially inhomogeneous heap of fibers, the specimen was put in a closed Al pan, heated up to  $180^\circ\text{C}$  in nitrogen atmosphere and re-cooled to ambient temperature in the DSC. The change in melt enthalpy during aging or immersion was determined from this first DSC melting curve. The pellet from the re-cooled molten material was then used for the OIT measurement. With this preparation technique, the specimen is melted twice before the OIT measurement is carried out. Therefore, it was checked whether the number of melting influences the OIT value. Using this procedure of melting twice, e.g., an initial OIT value of  $(24 \pm 4)$  min ( $T_m = 175^\circ\text{C}$ , Al Pan) was found for sample P9 and an OIT value of  $(14 \pm 4)$  min ( $T_m = 150^\circ\text{C}$ , Cu Pan) for sample P36 after 90 days of oven aging. Melting the specimen a third time before the OIT measurement, the OIT value stayed in the same range: 28 min for one specimen of sample P9 and  $(14 \pm 2)$  min for sample P36. Therefore, melting the pellets twice did not significantly change the OIT value. The scattering of OIT data from geotextiles is rather broad. In most cases, each data point is the mean value of at least three single measurements. The standard deviation was typically 15–20% (e.g. Fig. 5). From these measurements the relative OIT value,  $\delta\text{OIT}(t) = \text{OIT}(t)/\text{OIT}(0)$ , as a function of the aging time  $t$  was obtained. Especially for the above-mentioned stabilizer package, it is expected that the OIT is roughly proportional to the antioxidant concentration with some proportionality constant specific for a given resin and measurement condition (Howard, 1973; Gray, 1990; Mueller and Jakob, 2003). Therefore, the change in relative OIT values might be used to monitor the change in the level of antioxidant concentration during the aging or immersion of the samples.

### 3. Results

Table 3 shows the initial OIT values of the GTnw samples used for the air oven aging and immersion tests in water. These OIT values are comparable in length with OIT values of HDPE GMs measured at much higher temperatures of typically  $200^\circ\text{C}$  or  $210^\circ\text{C}$ . Assuming that the OIT value increases at least by a factor of two if one reduces  $T_m$  by  $10^\circ\text{C}$ , OIT values of the GTnws are typically one order of magnitude smaller than those of HDPE GMs when measured at the same temperature (see Table 2 in Mueller and Jakob, 2003). Even for the fiber resins of

sample P9 and P14, with the highest OIT values, the level of oxidation stability in the OIT measurement is well below that of the poorest HDPE resin studied by Mueller and Jakob (2003). The oxidative resistance of the fiber resins as determined in an OIT measurement is obviously much lower than that of HDPE resins. This result reflects to some extent the considerably smaller amount of antioxidants present in fiber resins compared with HDPE resins for geomembranes.

Figs. 1–3 show the OIT reduction curves—i.e. the change in the relative OIT value with time—during oven aging of PP and PE GTnws at 80°C. The OIT value

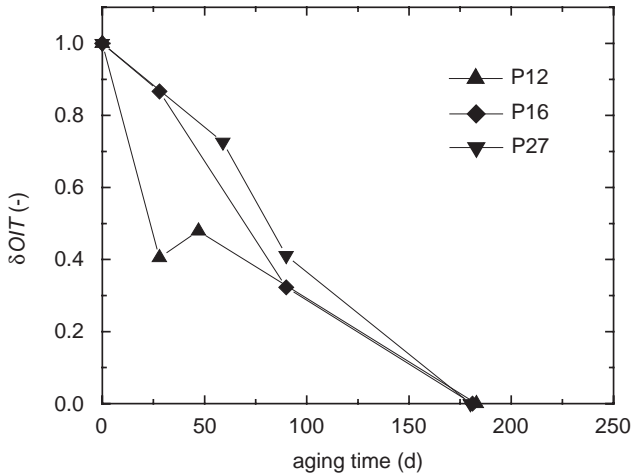


Fig. 1. Change of the relative OIT value  $\delta OIT$  with time of the PP GTnws P12, P16 and P27 during oven aging in air at 80°C. The OIT values were measured at  $T_m = 170^\circ\text{C}$  with Al pans.

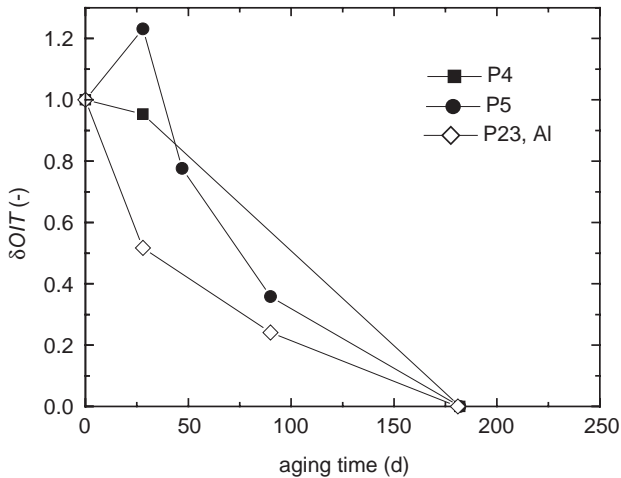


Fig. 2. Change of the relative OIT value  $\delta OIT$  with time of the PE GTnw samples P4, P5 and P23 during oven aging in air at 80°C. Closed symbols: the OIT values were measured at  $T_m = 150^\circ\text{C}$  with Cu pans. Open symbols: at  $T_m = 170^\circ\text{C}$  with Al pans.



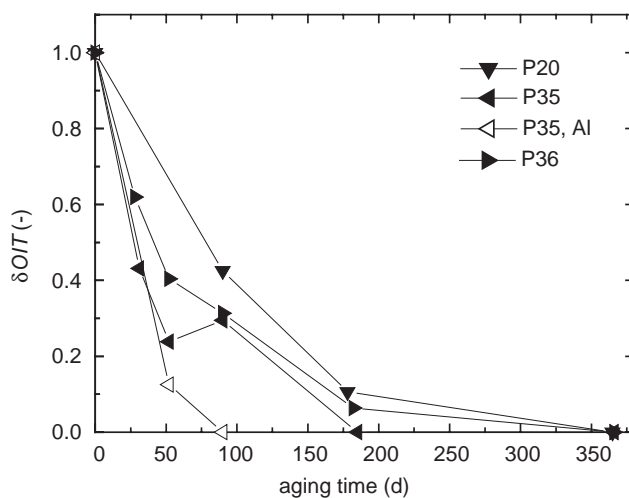


Fig. 3. Change of the relative OIT value  $\delta OIT$  with time of the PE GTnw samples P20, P35 and P36 during oven aging in air at  $80^{\circ}\text{C}$ . Closed symbols: the OIT values were measured at  $T_m = 150^{\circ}\text{C}$  with Cu pans. Open symbols: at  $T_m = 170^{\circ}\text{C}$  with Al pans.

decreases rapidly: After half a year of air oven aging, no OIT value could be measured at  $T_m = 170^{\circ}\text{C}$  (Al pans) and the OIT values at  $T_m = 150^{\circ}\text{C}$  (Cu pans) were near the detection limit. A similar behavior of the change in OIT value was found for immersion in water at  $80^{\circ}\text{C}$ . The OIT value measured at  $T_m = 170^{\circ}\text{C}$  (Al pans) was zero after 90 days of water immersion for P23, after 180 days of water immersion for P12 and at the latest after 360 days of water immersion for P16. As an example, the time dependence of the relative OIT value of P14 during air oven aging and water immersion is compared in Fig. 4. Fig. 5 shows the change of the absolute OIT value measured at  $T_m = 175^{\circ}\text{C}$  (Al pans) of sample P9 during water immersion together with the typical standard deviations of the OIT measurements.

Sample P9 (Fig. 5) is the one PP GTnw and sample P14 (Fig. 4) is the one PE GTnw, which behave slightly different than the other samples. The initial level of oxidation stability of both products is very high (Table 3) compared with the other GTnws. Even after 2 years of oven aging or immersion in water, the OIT value of P14 was still about 9–14 min, when measured at  $T_m = 150^{\circ}\text{C}$  with Cu pans. After about 580 days of immersion in hot water, the OIT value of P9 was still 5 min even with  $T_m = 175^{\circ}\text{C}$  (Al pans). Analyzing these data one has to keep in mind that in a thermoanalytical measurement at  $150^{\circ}\text{C}$ , just above the melting point of PE, the processes to achieve thermal equilibrium and the oxidation itself proceed very slowly. At such a low OIT testing temperature, OIT values below about 5 min are not conclusive. However, beside this experimental limitation the data show clearly that there remains a certain level of oxidation stability quite independent of the aging time for samples P9 and P14. The components and amount of the stabilizer package of samples P9 are not significantly different from those of P16 or P27. The same is valid for P14 compared to other PE GTnw samples. Taking the specification of the

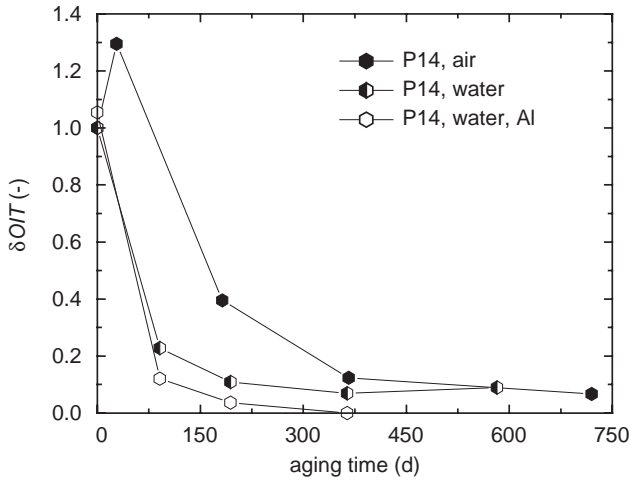


Fig. 4. Change of the relative OIT value  $\delta OIT$  with time of the PE GTnw sample P14 during oven aging (closed hexagon) and during immersion in water (half closed hexagon and open hexagon) at  $80^{\circ}\text{C}$ . The OIT values during air aging were measured at  $T_m = 150^{\circ}\text{C}$ , Cu pans, and those during water immersion at  $T_m = 150^{\circ}\text{C}$ , Cu pans (half closed hexagon) as well as at  $T_m = 170^{\circ}\text{C}$ , Al pans (open hexagon).

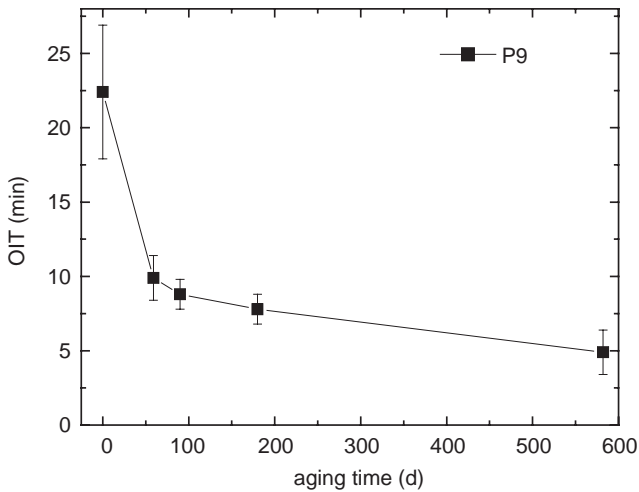


Fig. 5. Change of the absolute OIT value ( $T_m = 175^{\circ}\text{C}$  with Al pans) with time of the PP GTnw sample P9 during immersion in water at  $80^{\circ}\text{C}$ . The corresponding standard deviations are indicated.

resin manufacturers as reliable, one would have to suppose that the very high initial OIT value and therefore also the “residual” OIT value after aging of these samples is due to an “intrinsic” oxidation stability of the resins (small amount of catalyst residue, high molecular mass and narrow distribution, other additives) and possibly very low oxidative stress during manufacturing.

Assuming that the change in relative OIT value reflects the change in the amount of antioxidants, one can estimate the antioxidant depletion time constant from the OIT reduction curves in Figs. 1–5, which is roughly 80 days for polyolefin GTnws oven aged in air or immersed in water at 80°C. In sharp contrast to such short antioxidant depletion times observed for the GTnw, the long-term antioxidant depletion time constant for HDPE GMs was found to be about 6 years (Mueller and Jakob, 2003). For HDPE GMs the length of the period, during which the antioxidant depletion process takes place, is the main part of the overall induction period prior to the mechanical property degradation. If the same relation held for GTnws, one would expect that their induction times prior to mechanical degradation are likewise very short at 80°C aging or immersion temperature: about 0.5 years.

The mechanical property degradation (tensile strength and elongation at tensile strength) of the PP GTnw during air oven aging at 80°C and 120°C and immersion in hot water at 80°C is shown in Fig. 6 for sample P9, Fig. 7 for sample P12, Fig. 8 for sample P16 and Fig. 9 for sample P27. Sample 9 has a very high oxidative resistance. There is no indication of a change in the mechanical properties, neither during oven aging at 80°C nor during immersion in hot water at 80°C. On the other hand, sample P12 is obviously quite sensitive to oxidation. The mechanical property degradation proceeds rapidly at 120°C oven aging temperature. At 80°C, there seems to be an induction time of about 1 year after which the sample loses all its mechanical strength within a few weeks by oxidation. A similar behavior is observed for immersion in water, however, with a degradation rate of the mechanical strength that is considerably smaller than in air oven aging. Sample P16 shows likewise no induction time at 120°C oven aging and a rapid degradation of mechanical strength at such a high aging temperature. At 80°C, there is an indication of an induction

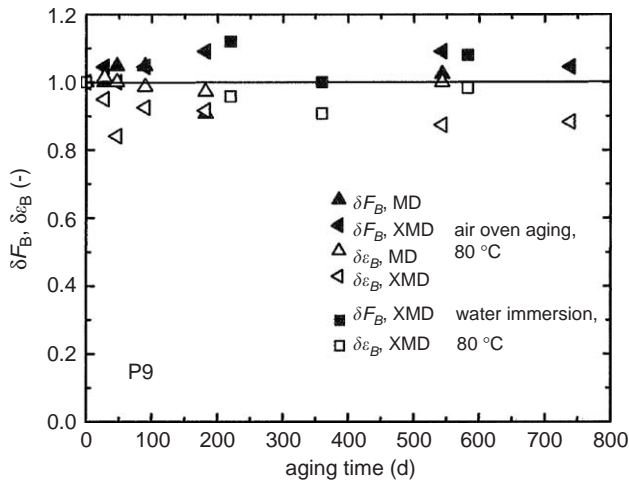


Fig. 6. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PP GTnw sample P9 during air aging and immersion in water at 80°C. Specimen were taken in MD and XMD. For the immersion in water only specimen taken in XMD were used.

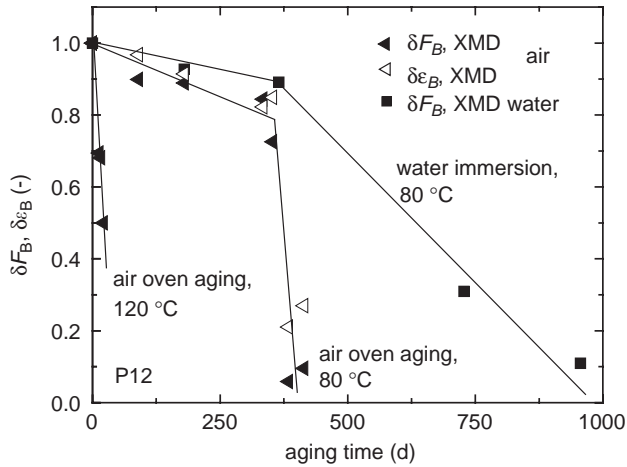


Fig. 7. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PP GTnw sample P12 during air aging at 80°C and 120°C and immersion in water at 80°C. Specimen were taken in MD and XMD. For the immersion in water only specimen taken in XMD were used.

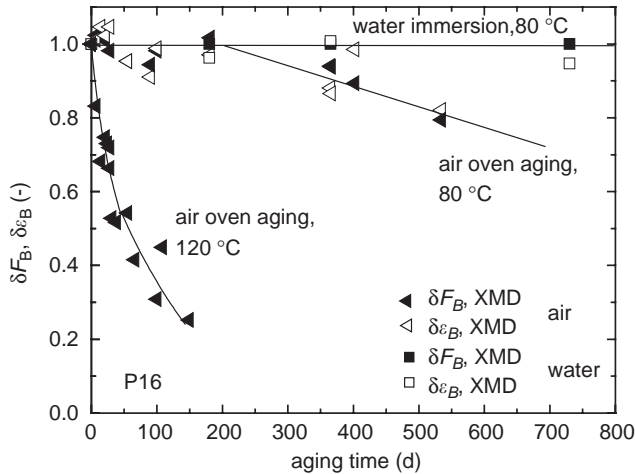


Fig. 8. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PP GTnw sample P16 during air aging at 80°C and 120°C and immersion in water at 80°C. Specimen were taken in MD and XMD. For the immersion in water only specimen taken in XMD were used.

time after which the degradation proceeds much slower than compared with the rate of sample P12. For the immersion in water at 80°C, the degradation process of the mechanical properties proceeds even much slower than for aging in air: no significant change of tensile strength or elongation at tensile strength is observed after 2 years of immersion. Sample P27 behaves similar to sample P16: low degradation rate of the mechanical properties for oven aging at 80°C, which makes it difficult to decide

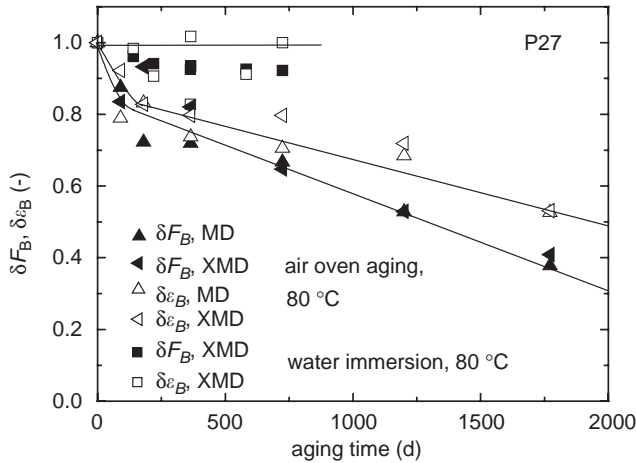


Fig. 9. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PP GTnw sample P27 during air aging and immersion in water at 80°C. Specimen were taken in MD and XMD. For the immersion in water only specimen taken in XMD were used.

whether there is a short induction time, and essentially no change of the mechanical properties for immersion in hot water.

For the PE GTnw, a slow and continuous decrease in tensile strength is observed in the long run during oven aging at 80°C (Fig. 15 gives an overview). In this respect the behavior of all of the PE GTnws seems to be quite similar, independent of their initial OIT values. After 1 year aging time, the tensile strength is about two-thirds of the initial value and after 2 years roughly one-half. Closer inspection of the data reveals that the mechanical degradation does not start right from beginning at 80°C. Fig. 10 (sample P4), Fig. 11 (sample P5) and Fig. 12 (sample P14) show that there are induction times of the mechanical property degradation. For samples P20 (Fig. 13) and P23 (Fig. 14), the data are not conclusive. The example of sample P20 (Fig. 13) demonstrates that at 120°C air oven aging, a rapid deterioration of the PE GTnws occurs within a few weeks. The results from the immersion tests in hot water for samples P20 (Fig. 13), P23 (Fig. 14) and samples P35 and P36 (Fig. 15) show that the time period prior to the onset of degradation is much longer and the oxidation rate much slower in water than in air, as was the case for the PP GTnw. Table 4 summarizes these time periods to the degradation process at 80°C, as read from the figures of the change in mechanical properties versus aging time.

To describe the time dependence of the mechanical degradation of the PE GTnws, as shown in Fig. 15, one may assume a first- or a second-order kinetic of the tensile strength degradation process (Salman et al., 1998; Thomas, 2002). In a first-order kinetic, the logarithm of the relative tensile strength  $\delta F_B(t) = F_B(t)/F_B(0)$  is a linear function of the aging time  $t$ ; whereas the integration of a second-order kinetic reaction equation gives a linear relation with aging time for the inverse of the relative

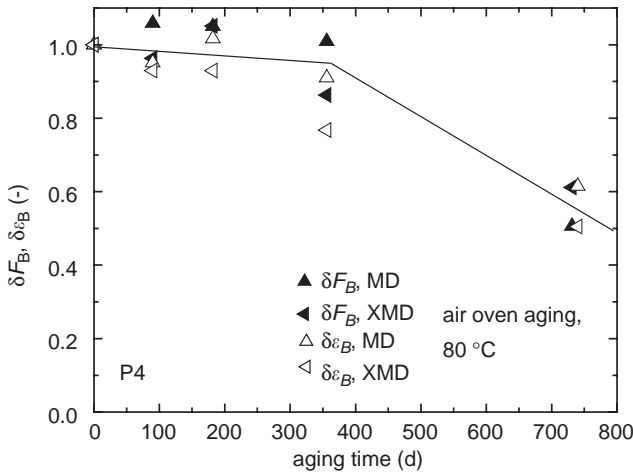


Fig. 10. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PE GTnw sample P4 during air aging at 80°C. Specimen were taken in MD and XMD.

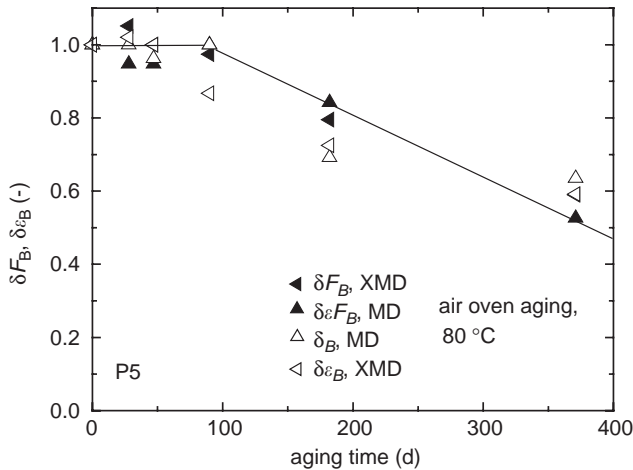


Fig. 11. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PE GTnw sample P5 during air aging at 80°C. Specimen were taken in MD and XMD.

tensile strength:

$$\frac{1}{\delta F_B(t)} - 1 = kt, \tag{1}$$

$k$  is the degradation rate of the relative tensile strength and the half-life is then simply given by  $t_{1/2} = 1/k$ . Best fits to the data are obtained assuming a second-order kinetic for the degradation process of the tensile strength and elongation at break

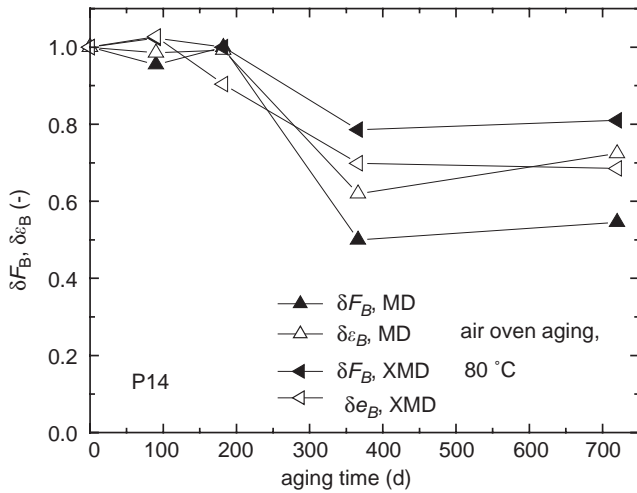


Fig. 12. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PE GTnw sample P14 during air aging at 80°C. Specimen were taken in MD and XMD.

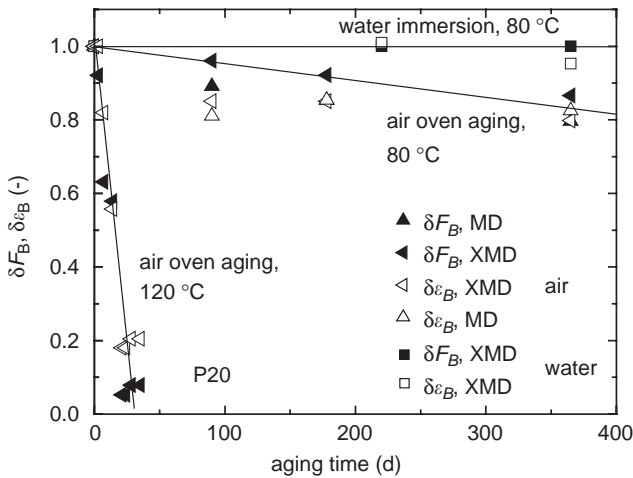


Fig. 13. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PE GTnw sample P20 during air aging at 80°C and 120°C and immersion in water at 80°C. Specimen were taken in MD and XMD. For the immersion in water only specimen taken in XMD were used.

(Fig. 16). However, such conformance does not mean that the underlying microscopic oxidation process itself follows a simple second-order kinetic. From the slopes of the lines in Fig. 16, one obtains degradation rates of 0.0035 per day for sample P5, 0.0061 per day for sample P17 and 0.0022 per day for sample P36.

All PE GTnw samples showed a gradual change in melt enthalpy. For PE resins an aging temperature of 80°C lies in the temperature range where small crystallites

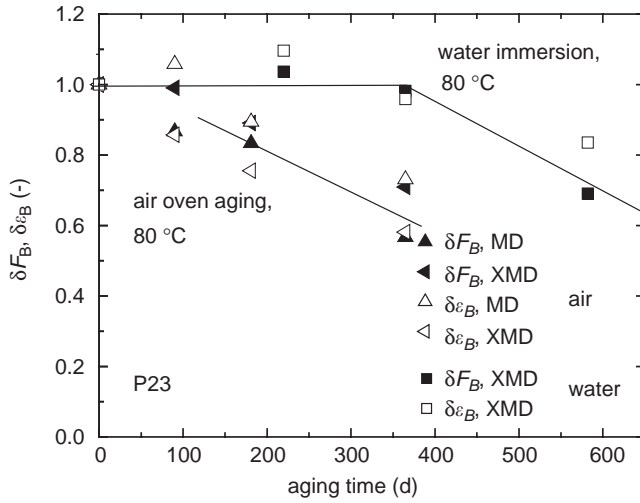


Fig. 14. Change in the relative tensile strength  $\delta F_B$  and the corresponding elongation  $\delta \epsilon_B$  with time of the PE GTnw sample P23 during air aging and immersion in water at 80°C. Specimen were taken in MD and XMD. For the immersion in water only specimen taken in XMD were used.

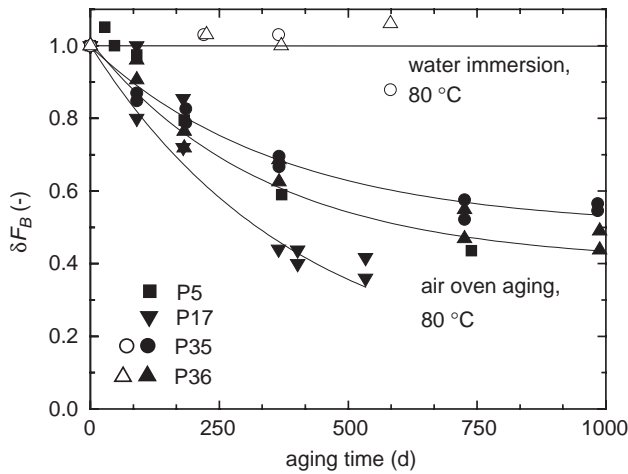


Fig. 15. Overview of the change in the relative tensile strength  $\delta F_B$  with time of PE GTnw samples P5, P35, P36 and P17 during air aging and water immersion at 80°C. The specimen were taken in XMD. Different symbols indicate different samples. Closed symbols are used for air aging and open symbols for immersion in water.

begin to melt and some recrystallization occurs. The rising of a small and broad peak at about 110°C is characteristic for the melting curve of aged PE samples. The effect is well known as so-called “memory effect” from thermal treatment of semicrystalline PE polymers treated not too far from their melting temperature. Fig. 17 shows,



Table 4

Induction period to the onset of the mechanical strength degradation during oven aging and water immersion as estimated from Figs. 6–15

| Sample |     | Induction period (days) at 80°C |                    |
|--------|-----|---------------------------------|--------------------|
|        |     | Air oven aging                  | Immersion in water |
| PP     | P9  | > 720                           | > 739              |
|        | P12 | 360                             | 300                |
|        | P16 | > 180                           | > 739              |
|        | P27 | 0 ?                             | > 739              |
| PE     | P4  | 360                             | —                  |
|        | P5  | 90                              | —                  |
|        | P14 | > 200                           | —                  |
|        | P20 | ?                               | > 582              |
|        | P23 | 100                             | 360                |
|        | P35 | < 100                           | > 582              |
|        | P36 | < 100                           | > 582              |

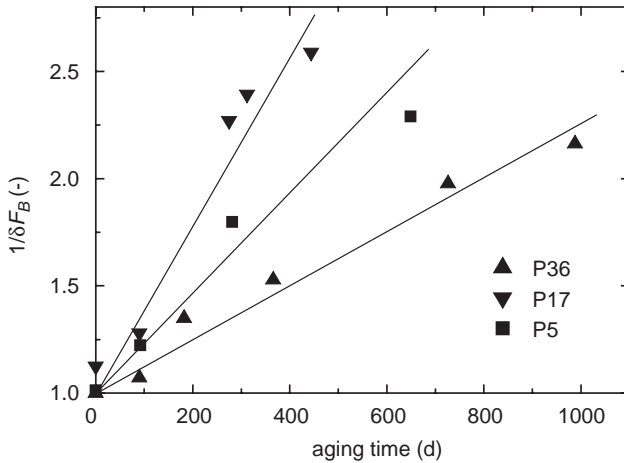


Fig. 16. Plot of the inverse of the relative tensile strength ( $1/\delta F_B$ ) versus aging time  $t$  according to Eq. (1). The data for P17, P36 and P5 were taken from Fig. 15.

as an example, the change in the crystallinity of samples P5, P14, P35 and P36 as a function of aging time. The crystallinity was calculated from melt enthalpies assuming the literature value of 293 J/g for fully crystallized PE. The change in crystallinity was most significant within the first 200 days of aging and after 2 years the overall increase in crystallinity was about 15–20%. The increase of crystallinity of the fibers has not reduced the mechanical strength of the GTnw, because the

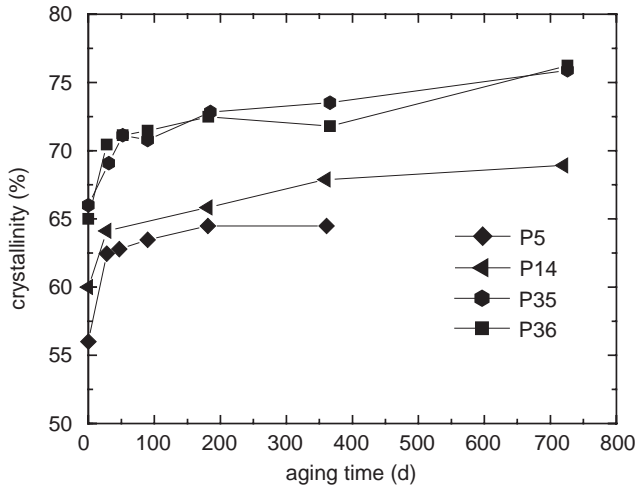


Fig. 17. Change of the crystallinity of PE GTnw samples P5, P14, P35 and P36 during air oven aging at 80°C.

changes in the mechanical properties were only very small during that initial time period. No change in melt enthalpy and therefore in the crystallinity was found for all of the PP samples.

## 4. Discussion

### 4.1. Antioxidant depletion

The first important experimental finding is that the OIT reduction time of PP and PE GTnws is in all cases very short and in the range of several months compared to several years for HDPE GMs. For the discussion, it is crucial that the change in OIT value monitors the antioxidant depletion process and gives the base for at least a rough estimate of the antioxidant depletion time. This assumption is for all effective purposes established for the commonly used stabilizer package which is a combination of a phenolic and phosphite antioxidant (Howard, 1973; Gray, 1990; Mueller and Jakob, 2003). Typically, such composition of a phosphite and a hindered phenol is used as main part of the antioxidant package of the basic resin for most of the polyolefin geosynthetics available on the market and it is the antioxidant package of the studied GTnws. The PP GTnws P9, P16 and P27 were, in addition, UV stabilized with a considerable amount of hindered amine light stabilizers (HALS). Since HALS have an antioxidant capability, which is most effective at temperatures below 120°C (Fay and King, 1994), the reduction of an OIT value, which is measured above the PP melting point at 170°C, does not necessarily correlate with the depletion of this type of stabilizer. On the other hand, it was found

that oxidative induction temperatures of LDPE samples correlated with the amount of HALS (Haider and Karlsson, 2001). The depletion of HALS is a very complex process since not only stabilizer migration but also chemical modification of the molecule, its chemical degradation and the migration of the degradation products contribute (Dudler, 1993; Malik et al., 1994; Malik et al., 1998; Haider and Karlsson, 2001). However, three arguments may be given in favor of applying the following discussion tentatively to the HALS containing samples too: leaching tests on LDPE films with commonly used high molecular HALS have shown that a considerable amount of stabilizer was depleted at 80°C within some months, even with low liquid-to-solid ratio and no water changes, and that the extrapolated depletion time at room temperature is in a range expected for high molecular phenolic stabilizers (Haider and Karlsson, 1998); the behavior during aging and immersion of at least P16 and P27 is indeed similar to all other samples; further on, the depletion of HALS seems to proceed more rapidly during storage in water than in air (Haider and Karlsson, 2001), as it is the case for the phenolic and phosphite antioxidants (Mueller and Jakob, 2003).

Under normal conditions (ambient oxygen pressure), antioxidants are lost by migration, dissolution, evaporation and extraction (Moisan, 1985; Smith et al., 1992). The antioxidant depletion time  $t_{AO}$  is defined as the time period required for the depletion of antioxidants by these migration processes (Hsuan and Koerner, 1998; Sangam and Rowe, 2002). After the antioxidants concentration has fallen below a critical value, the auto-catalytic oxidative chain reaction is no longer inhibited. However, there is an additional time period until the oxidative chain reaction gains speed and finally deteriorates the macroscopic properties. The induction time  $t_{Ox}$  is defined as this time period prior to the mechanical property degradation under field or aging conditions in a material, that has already lost its antioxidants, (Hsuan and Koerner, 1998; Sangam and Rowe, 2002). Therefore, the expected service lifetime  $t_L$  of a HDPE GM was estimated on the basis of

$$t_L = t_{AO} + t_{Ox} \quad (2)$$

and the experiments with HDPE GMs have shown that  $t_{AO} \gg t_{Ox}$  (Mueller and Jakob, 2003). The depletion time  $t_{AO}$  due to the stabilizer migration depends on the geometry of the basic components of the geosynthetic. The ratio of the depletion time of a fiber to that of a geomembrane may therefore be estimated by comparing the geometric parameter (Müller, 2001b). The typical diameter of a fiber is of the order of  $10^{-5}$  m. The typical thickness of a geomembrane is of the order of  $10^{-3}$  m. The overall rate of the loss of antioxidant from a geosynthetic is proportional to its surface area. The total amount of stabilizer in the geosynthetic is proportional to its volume. Therefore, the depletion time is proportional to the ratio of volume to surface, namely to the diameter in case of the fiber and to the thickness in case of the GM. The ratio of the antioxidant depletion time of the fiber to that of the GM is then  $(10^{-5} \text{ m})/(10^{-3} \text{ m}) = 10^{-2}$ . This consideration underestimates the ratio to some extent, since each fiber is entangled in a dense plane fiber heap forming the GTnws. It was shown that the antioxidant depletion time at 80°C for HDPE GMs are several years (Mueller and Jakob, 2003). Therefore, it can be expected that the antioxidant

depletion time  $t_{AO}$  at 80°C is at most a few weeks for fibers and to some extent higher for a GTnw. These theoretical expectations are confirmed by the OIT reduction data. The OIT induction times for the GTnw are several month (Figs. 1–5) as expected and even shorter OIT reduction times of several weeks were indeed observed for fibers in single-fiber long-term tensile tests ((Seeger et al., 2002), the complete results of these single fiber tests will be published elsewhere). Therefore, the commonly used simple model for interpretation of aging data of polyolefin geomembranes (and pipes), according to which the induction time  $t_{Ox}$  of the auto-oxidation reaction of the unstabilized polymer is much smaller than the antioxidant depletion time  $t_{AO}$  and the service lifetime  $t_L$  is essentially determined by the latter, is obviously not applicable to geotextiles made of fibers and probably not applicable to geotextiles made of slit films too.

#### 4.2. Induction time and half-life of mechanical property degradation

Closer inspection of our data reveals further differences in the oxidation behavior. The second important experimental finding is that the reduction to essentially zero of the OIT value after 0.5 years during water immersion at 80°C for the PP GTnws and the PE GTnws is not accompanied by a sudden change in the mechanical properties (last column of Table 4). This is in remarkable contrast to the behavior of the HDPE GMs. When their level of OIT value had fallen to zero, which needed at least about 6 years of immersion in 80°C hot water, an oxidation process readily started which led to brittleness of the GM after some additional years (Mueller and Jakob, 2003). But also for oven aging in air of the GTnws, the induction period with respect to the onset of mechanical property degradation seems to be longer than the antioxidant depletion time, at least for some of the samples. The oxidative degradation of samples P4, P12 and P16 started not earlier than after about 360 (Fig. 10), 360 (Fig. 7) and >180 days (Fig. 8), respectively, while the OIT value had dropped to zero at the latest after 180 days (Figs. 1 and 2).

After the onset of degradation, the reduction of the tensile strength of PP GTnw samples P9, P16 and P27 proceeded very slowly for oven aging in air at 80°C. For immersion in water no relevant change in the mechanical properties of these samples was seen during the whole testing periods. The same behavior was observed for the PE GTnws. Only the behavior of PP GTnw sample P12 was different at 80°C: within a few months after the onset of degradation this geotextile has lost all its mechanical strength. The fibers had completely disintegrated to fragments. At 120°C oven aging temperature, all studied samples showed a pronounced decrease of the tensile strength and elongation at break, which started immediately from the beginning of the oven aging.

Two conclusions have to be drawn from these observations:

1. After the antioxidant depletion, the oxidation process of the GTnw samples strongly depends on the rate of oxygen supply. This follows from the large difference in the oxidation behavior during air oven aging and immersion in water. The concentration of oxygen in air at atmospheric pressure is of the order

of 10 mmol/l. The oxygen solubility in polyolefins in contact with air at atmospheric pressure is of the order of some tenth of millimole per liter or a few ten parts per million over a broad temperature range (Van Krevelen, 1994; Epacher et al., 2000). With such low oxygen concentration the oxidation process should be indeed controlled by the rate of oxygen supply due to gas penetration. The solubility of oxygen in pure water at 80°C is likewise very low: only 0.16 mmol/l or 5 ppm (Tromans, 1998). Therefore, one expects that a surface layer of high oxygen content is formed on the samples in contact with air and oxygen is more readily available in contrast to samples immersed in water. This might be especially relevant for the fibers due to the large surface. In addition, the aqueous environment might strongly influence the behavior of oxygen dissolved in immersed samples: e.g. the oxygen solubility increased but the oxygen diffusion coefficient decreased markedly in crosslinked PE immersed in water (Matsui et al., 2002).

- $t_{Ox}$  is comparable (oven aging) or even larger (water immersion) than  $t_{AO}$  or the corresponding OIT reduction time, i.e. there seems to be some intrinsic oxidation stability of the fibers even in a state where antioxidants have been lost and zero OIT value is found in the high-temperature OIT measurement in the molten state. It was already mentioned that the PP and PE fibers used in a GTnw are normally cold drawn during the manufacturing process. Since  $t_{Ox}$  is defined as induction time of the oxidative reaction well below melting temperature, its length might be strongly influenced by the so-called structural stabilization (Emanuel and Buchachenko, 1987) due to the morphological changes in stretched fibers. It is known that oriented polyolefin polymer films show indeed a marked increase in oxidation stability (Popov et al., 1991). Within the auto-oxidation process, that follows after some induction time  $t_{Ox}$ , the relevant radical initiators for new reaction chains are produced by a bimolecular decomposition of hydroperoxids. However, this decomposition reaction only takes place when a certain amount of hydroperoxid concentration has been already produced and accumulated. Production and accumulation of hydroperoxids during the induction period  $t_{Ox}$  as well as the auto-catalytic oxidation are most effective with high molecular mobility of macromolecules, oxygen and reaction products. Due to the morphological changes in stretched polyolefin polymers the mobility of macromolecule segments, oxygen as well as of reaction products might be strongly reduced. The diffusion coefficients of gases are indeed considerably lower in oriented than in isotropic samples. In stretched films it was observed that the hydroperoxide yield with respect to a given amount of oxygen consumed in the oxidation process is strongly reduced and likewise the rate of hydroperoxid formation as measured by ESR technique (Popov et al., 1991). Therefore, it can be expected that the induction time  $t_{Ox}$  of stretched PP and PE fibers increases with the draw ratio  $\lambda$ .

Likewise, the oxidation rate and therefore the rate of mechanical property degradation is reduced in oriented samples. Expressing the degradation rate by the half-life of the tensile strength  $t_{1/2}$ , i.e. the time it takes for the GTnw to lose half its

tensile strength, much higher half-lives for oriented than for isotropic fiber materials can be expected. A high rate of oxygen supply  $r_{O_2}$  acts in the reversed direction: decreasing the induction time and increasing the oxidation rate. Therefore, the induction time  $t_{Ox}$  and the half-life  $t_{1/2}$  of mechanical strength degradation are sensitive functions of  $r_{O_2}$  and  $\lambda$ .

#### 4.3. Assessment of service lifetimes of geotextiles

To predict the service lifetime of a GTnw accurately under field conditions, it would be necessary to know these functions  $t_{Ox}(r_{O_2}, \lambda)$  and  $t_{1/2}(r_{O_2}, \lambda)$  and their temperature dependence. The lack of data and understanding of the relative contributions of the various chemical and physical mechanisms behind the deterioration of polyolefin geotextiles is still too large for an accurate description of the functional relationship. However, a credible estimate of  $t_{1/2}$  in field conditions might be obtained by a pure “phenomenological” modeling of the data for the time dependence of the degradation with a simple kinetic law and an Arrhenius law for the temperature dependence of the degradation rate involved. Likewise, an estimate of  $t_{AO}$  might be obtained assuming an Arrhenius law for the temperature dependence of the rate constant of stabilizer migration (Mueller and Jakob, 2003). Such an approach looks only for a consistent parameterization of the data. It does not intend to clarify the chemical reaction and physical processes behind the deterioration or migration processes. The degradation rate  $k$  at 80°C of the relative tensile strength was obtained for some of the materials by fitting the aging data with a second-order kinetic law according to Eq. (1) (Fig. 16). Assuming an Arrhenius law for the temperature dependence and an “apparent” activation energy, the degradation rates at ambient temperatures can be calculated. An estimate of the half-life of the mechanical strength  $t_{1/2}$  at ambient temperatures is then easily obtained, since for second-order kinetics:  $t_{1/2} = 1/k$  (see Eq. (1)). Table 5 shows the estimates for a range of apparent activation energies found in the literature for the mechanical property degradation of PP GTnw (Wisse et al., 1990; Salman et al., 1998; Thomas, 2002). A similar analysis might be performed for the antioxidant depletion (Mueller and Jakob, 2003). With activation energies for the migration process in a range of

Table 5

Half-lives  $t_{1/2}$  at 20°C of mechanical strength degradation (time to lose 50% of tensile strength after degradation has started) of PE GTnw samples calculated from the degradation rate  $k$  at 80°C (Fig. 16) assuming different activation energies

| Reaction rate $k$ at 80°C ( $d^{-1}$ ) | Half-life $t_{1/2}$ at 20°C (year) |           |           |
|--|------------------------------------|-----------|-----------|
|  | 50 kJ/mol                          | 60 kJ/mol | 70 kJ/mol |
| 0.0022                                 | 40                                 | 83        | 165       |
| 0.0061                                 | 15                                 | 30        | 60        |

60–100 kJ/mol one obtains at least some decades for  $t_{AO}$  of GTnws at ambient conditions.

To estimate the expected service lifetime, one has to determine such apparent activation energy of the mechanical property degradation and of the migration process. Thomas (2002) performed air oven tests with a PP-GTnw at temperatures between 70°C and 100°C and measured the degradation of the tensile properties. Best fits to the data were obtained with a second-order kinetic law, as is the case for our measurements at 80°C. The temperature dependence of the rate constant followed an Arrhenius law and an activation energy of about 49 kJ/mol was obtained. Salman et al. (1998) measured oxidation stability via the induction time, defined as the period of oven aging when no statistically significant change in tensile strength is observed. According to our notation this time is equivalent to  $t_{AO} + t_{OX}$ . For their samples P-3 and P-4, they observed a strong dependence of the induction time on the temperature and partial oxygen pressure. For oven aging in circulating air, the induction time of P-3 was vanishing for temperatures  $\geq 80^\circ\text{C}$ , while in diluted air with 8% O<sub>2</sub> the induction time was about 400 days at 80°C. An induction time ( $t_{AO} + t_{OX}$ ) at ambient temperature of 50 years in circulating air and 240 years in diluted air (8% O<sub>2</sub>) was extrapolated. The mechanical property degradation, which starts after the induction time, was modeled by a first-order kinetic and an activation energy of 61 kJ/mol and a half-life at ambient temperature and circulating air of  $t_{1/2} = 38$  years was obtained. These findings for PP GTnws agree with our results for PP GTnws as well as PE GTnws. From the large differences in the time periods to the onset of mechanical property degradation between air oven aging and immersion in water at 80°C (Table 4), one may conclude that under field condition with limited oxygen supply, the induction time  $t_{OX}$ —and therefore the service lifetime too—might be at least half an order of magnitude larger than in circulating air.

#### 4.4. Testing of the oxidative resistance

It is obvious that especially the oxidative resistance of PP GTnws differs considerably with various market-available products. Therefore, an appropriate test method to select geotextile products with high oxidation stability at ambient temperatures and normal service conditions would be suitable. For HDPE GMs testing procedures and specifications have been established to assess the oxidation stability. The GM-13 standard from the Geosynthetic Research Institute requires an initial standard (Std) OIT value at  $T_m = 200^\circ\text{C}$  of 100 min or a high-pressure (HP) OIT value of 400 min at  $T_m = 150^\circ\text{C}$  and  $p_{O_2} = 38$  bar. The reduction in Std-OIT value must be less than 45% or in HP-OIT less than 20% in 90 days oven aging at 85°C. The certification of the Federal Institute for Materials Research and Testing (BAM) (Müller, 2001a) for GMs requires an initial OIT value at  $T_m = 210^\circ\text{C}$  of > 20 min and an OIT value of > 10 min after an oven aging at 80°C for 0.5 years. Continuing the aging for 1 year, the relative change in OIT value,  $\delta\text{OIT}$ , between 0.5 and 1 year must be less than 30%. It is also necessary to establish testing procedures and requirements for polyolefin GTnws used in long-term applications. For the time being the requirements have still to be tentative. In the BAM certification for GTnws

used as protection layer for GMs in landfill liner and capping systems, it is required that during an oven aging test at 80°C for 1 year, no significant change in tensile strength (reduction <20%) should occur.

Oven aging not close to the melting temperature requires long testing time. It was therefore suggested to test with high oxygen pressure. However, the results have to be interpreted with caution. Under high oxygen pressure, the stabilizers are rapidly consumed by oxidative reactions and the hydroperoxid formation and oxidative degradation are strongly accelerated. On the other hand, high pressure has minor influence on the stabilizer migration processes. Therefore,  $t_{1/2}$  and  $t_{Ox}$  are considerably reduced, while the depletion time due to migration  $t_{AO}$  remains constant or is possibly increased. Within the interpretation scheme described above, the failure time in an aging test at high oxygen pressure is therefore essentially determined by the short high-pressure values of  $t_{1/2}$  and to some extent of  $t_{Ox}$  (including antioxidant consumption under specific test conditions). The high-pressure test neglects completely antioxidant migration effects because the stabilizers are consumed by oxidative reactions within a time period short compared with  $t_{AO}$ . Brittleness of GTnws as well as of HDPE GM samples is indeed achieved in high-pressure tests at 80°C within a few weeks (Schröder et al., 2000). Whereas antioxidant depletion by migration at that temperature requires a few months for GTnws and a few years for HDPE GMs. For HDPE GM the service lifetime is determined by an extremely large value of  $t_{AO}$ . In the high-pressure test, a sample of a poorly chemically stabilized but highly stretched monofilament fabric or slit film fabric might therefore perform as good or even better than a chemically well-stabilized geomembrane sample, while in normal pressure oven aging and therefore in “real life” performance, the service lifetime of the GM might possibly be an order of magnitude larger than that of the fabric. It is therefore not possible to compare the oxidative resistance of different geosynthetics under field condition by doing a ranking according to the failure time in high-pressure tests as it is not possible to qualify oxidative resistance by high-temperature initial OIT values (Mueller and Jakob, 2003). As described,  $t_{AO}$  is generally very small for polyolefin GTnws stabilized with a package of phenolic and phosphite antioxidants. Therefore, high-pressure tests might only be applied to compare the oxidative resistance within such a product group.

## 5. Conclusions

Experimental data from air oven aging and immersion in hot water of polyolefin GTnws show that the time period to the onset of mechanical property degradation exceeds the antioxidant depletion time  $t_{AO}$  determined by the OIT value reduction. This applies, in particular, to water immersion testing where mechanical properties remain constant much longer than in air oven aging in spite of the rapid antioxidant depletion. Therefore, it may be assumed that the induction time  $t_{Ox}$  of the oxidation process itself is an important factor for service lifetime of polyolefin GTnws made of stretched fibers, because of structural stabilization effects. The data of mechanical



strength degradation of GTnws in air oven aging may be fitted by a second-order kinetic and characterized by the half-life  $t_{1/2}$ . Both the induction time  $t_{Ox}$  as well as the half-life  $t_{1/2}$  should depend on the draw ratio  $\lambda$  of the stretched fibers and on the rate of oxygen supply  $r_{O_2}$ . Summarizing the above consideration, we postulate the following equation for service lifetime of polyolefin GTnws:

$$t_L = t_{AO} + t_{Ox}(r_{O_2}, \lambda) + t_{1/2}(r_{O_2}, \lambda) \quad (3)$$

instead of Eq. (2), which applies to HDPE GMs. The experimental data for the PE and PP GTnws show that  $t_{AO} \leq t_{Ox}$  and  $t_{AO} \leq t_{1/2}$ . The extent of  $t_{Ox}$  and  $t_{1/2}$  of being greater depends on the oxidative environment conditions and on the draw ratio of the stretched fibers. The service lifetime  $t_L$  of a GTnw is therefore not only determined by  $t_{AO}$  but to a large extent by  $t_{Ox}$  and  $t_{1/2}$  unlike HDPE GMs. For HDPE GMs  $t_{AO}$  is extremely long and therefore  $t_L \approx t_{AO}$ . For a GTnw  $t_{AO}$  is normally two orders of magnitude shorter than  $t_{AO}$  of a HDPE GM. Therefore, very long expected service lifetimes of GTnws, comparable with those of HDPE GMs, are expected to be only achieved with products made of well-stabilized and well-oriented fibers under field conditions ensuring limited oxygen supply.

The terms “well-stabilized” and “poorly stabilized” are used quite often in the discussion of the oxidative resistance. Their meaning for the GTnws is now clearer. A well-protected GTnw not only incorporates an antioxidant package in combination with carbon black or chemical UV stabilizers providing a high initial OIT value and a low depletion rate—it is also made of highly and homogeneously oriented fibers.

Polyolefin geosynthetics have been used in geotechnical applications for about 30 years. Data from excavated polyolefin materials after about 5–20 years of field service are available, (e.g. Raymond and Giroud, 1993; Mannsbart and Barry, 1997). In nearly all cases only the appearance, the mechanical and hydraulic properties and some material properties (MFR, density, crystallinity) were determined and these properties were unchanged in many cases. However, after 5–20 years of application, polyolefin GTnws are still somewhere within the overall induction period (antioxidant depletion time and induction time of the oxidation reaction). As a result, unchanged mechanical or hydraulic properties of such excavated materials cannot be used to extrapolate further service life with regard to oxidation. Therefore, it is an important task for assessment of oxidative resistance under actual field conditions to measure the antioxidant depletion that has taken place and to determine the oxidative environment to which the geosynthetics are subjected in various geotechnical applications.

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