Accelerated ageing of polypropylene geotextiles in autoclaves at elevated temperature and oxygen pressure

S. Hausmann
SKZ German Plastics Center, Wuerzburg, Germany (s.hausmann@skz.de)

H. Zanzinger
SKZ German Plastics Center, Wuerzburg, Germany (h.zanzinger@skz.de)

C. MacKenzie
Kaytech, Atlantis, South Africa (clintm@kaytech.co.za)

C. Els
Kaytech, Atlantis, South Africa (chrise@kaytech.co.za)

ABSTRACT: Oxidation is the dominant ageing process for polypropylene (PP) geotextiles (GTX) not exposed to mechanical stress or UV radiation. Resistance against oxidation depends strongly on temperature. In certain applications like in landfills geotextiles have to fulfil their functions for very long service lives at elevated temperature. In an extensive test program one nonwoven (GTX-N) and two woven geotextiles (GTX-W), all made of PP were subjected to thermo-oxidative ageing in high-pressure autoclave testing (HPAT) at temperatures between 75 °C and 90 °C under elevated oxygen pressures ranging from 200 kPa to 500 kPa. The progressive effect of oxidation was monitored by carrying out tensile tests and by noted changes in oxygen pressure in the autoclave during exposure. A decrease in oxygen pressure can be attributed to consumption of oxygen molecules and therefore oxidation of the polymer. Both - tensile properties and decrease in oxygen pressure - are used to determine times-until-failure. By varying the temperatures and the oxygen pressures in the autoclave, times-until-failure extrapolations to service conditions (e.g. 40 °C, 21 kPa oxygen pressure) were carried out resulting in realistic service lives. The resultant activation energy determined was between 84 kJ/mol and 93 kJ/mol. Additional oven ageing tests were carried out at 90 °C and 110 °C in order to compare both test methods. Depending on the stabilization of the tested GTX their lifetimes varied considerably under the anticipated elevated temperatures occurring in landfills.

Keywords: oxidation, autoclave, elevated temperature, elevated oxygen pressure, polypropylene geotextiles

1 INTRODUCTION

For civil engineering applications longevity of the products installed is a basic requirement. It is essential, especially concerning products difficult to access to be sure they fulfil their function during the whole designed service life. Depending on possible short-term and long-term mechanical stress and on environmental conditions present, the longevity of construction products is related to the construction site specific conditions and their application. Limited to products ideally installed without stress, ambient factors like temperature, contact with other foreign substances, including O_2, water and extremes of pH all have to be taken into consideration.
When it comes to GTX-N and GTX-W, PP is the most commonly used material, which has been proven due to its excellent processability and good mechanical performance of the final

product. Nevertheless PP has weaknesses such as the tendency to chemical reaction with oxygen (= oxidation), which is accelerated at elevated temperatures. Therefore for applications in which permanently high temperature is given the GTXs used must be highly stabilized in order to withstand oxidative attack for the design service life of the civil construction work.
In landfills for municipal solid waste permanent temperature in the waste body as well as at the bottom liner system can reach significantly more than 40 °C (Yoshida and Rowe, 2003), (Mueller, 2007). In landfills for mining and industrial waste temperatures can be even higher (Rowe, 2011).
For application under elevated temperature conditions it is important to understand the performance of the components installed. This work deals with determination of oxidation resistance of three GTXs intended for manufacturing of clay geosynthetic barriers (GBR-C), used for sealing landfills.

2 THERMO-OXIDATIVE DURABILITY OF POLYPROPYLENE

Like other polyolefins, PP is prone to oxidation. Due to the presence of many tertiary C-H bonds, the macromolecules of PP are especially prone to chemical reaction with oxygen when compared to that of polyethylene. As a result chain scission occurs which leads to easier chain disentanglement, crystallisation and subsequently to embrittlement of the polymer. The beginning of embrittlement, change in physical and mechanical properties, can be attributed to the molecular weight falling below a critical value, driven down by chain scission.
In order to prevent the PP molecules from chemically reacting with oxygen long-term stabilizers (= antioxidants) are incorporated. The most common stabilizers are phenolic, amine and phosphitic stabilizers which react with radicals resulting from β-chain scission and thereby interrupt the autocatalytic chain reaction of polymer oxidation. Often more than one type of stabilizer is used in order to achieve a synergetic effect.
From the thermodynamic point of view, the energy barrier of antioxidants to react with oxygen or the radicals formed during the autocatalytic chain reaction is smaller than the one for PP molecules. This energy barrier (= activation energy E_A) is a key factor of the Arrhenius equation (eq. 1) setting in relation reaction kinetic and temperature (T):

$$k = A \cdot \exp\left(-\frac{E_A}{R \cdot T}\right) \qquad (1)$$

k: speed of reaction, A: parameter, R: universal gas constant

To accelerate the ageing process under laboratory conditions, temperature during testing is generally higher than environmental temperature at service. Extrapolation of laboratory test results to service temperature can subsequently be carried out using the Arrhenius equation.

3 REQUIREMENTS IN EUROPE, GERMANY AND SOUTH AFRICA REGARDING OXIDATIVE RESISTANCE OF GEOTEXTILES FOR APPLICATION IN LANDFILLS

For applications where elevated temperature conditions are dominant it’s particularly important for constructors and users alike to know about the performance of the products intended for installation. Depending on the region where the landfill is located different requirements have to be met by GTXs used for separation, filtration or for manufacturing of GBR-C. The specifications defining the required quality regarding oxidation resistance of GTX for usage in landfills in Europe, Germany (location of SKZ testing laboratory) and South Africa (location of Kaytech manufacturing plant) are listed in Tab. 1. Not just the requirements but also the types of laboratory test which need to be performed vary significantly. The mentioned index tests (oven tests and leaching tests) at a single temperature point for a predefined test duration was developed historically based on the Arrhenius-based temperature dependency of time-till-failure. This method assumes that the product has a typical activation energy. Probably due to the variety of different types of PP, activation energy referring to PP oxidation is known to lie in a wide range between 65 and 110 kJ/mol (Wisse and Birkenfeld, 1982 and Wisse et al., 1990). The extensive HPAT test program according to LAGA, BQS 5-5 does not rely on assumptions regarding activation energy, nor the pressure dependency but includes determination of both. In principle all mentioned tests intend to assure service life of the GTX, regarding oxidation, for at least 100 years.

Table 1. Specifications and requirements for geotextiles and geotextile-related products used for separation, filtration or as components for GBR-Cs for landfill applications

Territorial validity	Standard/ Specification	Type of laboratory test	Requirement
Europe	EN 13257+A1 (2015-02)	Leaching in hot water (28 d, 80 °C) followed by oven test (112 d, 100 °C)	$F_{max,res} \geq 50\%$
Germany	BAM Approval Principles [1] (2015-02)	Oven test (1 year, 80 °C) and Leaching test in hot water (1 year, 80 °C)	$F_{max,res}$ and $\varepsilon_{max,res} \geq 50\%/80\%$ [3)4)]
	LAGA, BQS 5-5 [2] (2014-05)	Oven test (28 d, 110 °C) and Leaching test in hot water (56 d, 50 °C)	$F_{max,res} \geq 50\%$
		or: HPAT (80 °C / 5.0 MPa, 2.0 MPa and 1.0 MPa, 70 °C / 5.0 MPa and 60 °C / 5.0 MPa)	≥ 100 years extrapolated service life
South Africa	GRI-GCL3 ASTM D 5721	Oven test (50 d, 60 °C)	$F_{max,res} \geq 50\%$

1) relevant for GTXs used for separation and filtration, 2) relevant for GTXs used for manufacturing of GBR-Cs

3) $F_{max,res}$ and $\varepsilon_{max,res} \geq 50\%$ or 80 % depending on type of stabilizer present in the GTX

4) additional requirements regarding amount of residual stabilizer and crystallinity

4 SAMPLE MATERIAL AND PERFORMED LABORATORY TEST

4.1 *Sample material*

Table 2. Sample material and test conditions

Sample name	Type of polymer	Type of product	Long-term stabilizer(s)	Test conditions	
				HPAT	Oven test
GTX-N-x	PP	nonwoven geotextile	unknown	75 °C / 300 kPa 80 °C / 300 kPa 90 °C / 300 kPa	90 °C [1] and 110 °C
GTX-W-y	PP	woven geotextile (tape)	unknown	75 °C / 300 kPa 80 °C / 300 kPa 90 °C / 300 kPa	90 °C [1] and 110 °C
GTX-W-z	PP	woven geotextile (tape)	phosphite and phenolic primary antioxidant	75 °C / 300 kPa 80 °C / 300 kPa 90 °C / 300 kPa 90 °C / 200 kPa 90 °C / 500 kPa	90 °C [1] and 110 °C

1) prior to oven testing at 90 °C pre-leaching for 28 d in hot water (80 °C) was carried out according to the Harmonized European Standard for GTX and GTX-related products EN 13257: 2014.

One nonwoven (GTX-N-x) and two woven geotextiles (GTX-W-y and GTX-W-z), used for manufacturing of GBR-C, were tested by high-pressure autoclave testing in the accredited laboratory of SKZ in Wuerzburg, Germany. Simultaneously, in the laboratory of Kaytech, Atlantis, and Geosynthetic Laboratory, Pinetown, South Africa oven tests were carried out. The tested samples as well as the applied test conditions are listed in Tab. 2.

4.2 *Oven test*

Oven tests were carried out on all three GTXs following Annex B of EN 13257: 2014, including 28 d pre-leaching at 80 °C in hot water for the 90 °C test only. Deviating from EN 13257: 2014 + A1: 2015 oven temperature was adjusted to 90 °C and 110 °C, based on the current standards when starting the tests (EN ISO 13438: 2004 (110 °C) and EN 13257: 2014 (90 °C)). Test durations were predefined to 14, 28, 56, 112, 224, 448 and 896 days. A forced-ventilation oven (type 1) according to clause 4.1.4 of ISO 188 was used. In order to determine progress of oxidation weekly visual inspection and tensile tests were carried out according to ASTM D6768 on clearly identified specimens from each product being tested. These specimens were tested to 50% of maximum tensile force (F_{max}) and then returned to the oven. This weekly test ensured that the progress of oxidation was not beyond the defined evaluation criteria (≤ 50% $F_{max,res}$) before the predetermined date was reached. Oven tests were stopped after a residual maximum tensile force of less than 50% of the initial value was reached.

4.3 *High-pressure autoclave test (HPAT)*

HPATs were carried out following EN ISO 13438. Deviating from the standard, tests were performed at 75 °C, 80 °C and 90 °C and 300 kPa oxygen pressure on all three GTXs. Test duration was not predefined. Tensile tests were carried out according to EN 29073-3 and EN ISO 13934-1 throughout duration of exposure in order to determine progress of oxidation. HPATs were stopped after a residual maximum tensile force of less than 50% of the initial value was reached. Time-till-failure has been defined as duration of exposure when 50% residual maximum tensile force ($F_{max,res}$) and 50% residual elongation at maximum tensile force ($\varepsilon_{max,res}$) is reached. GTX-W-z was tested additionally at 90 °C / 200 kPa and 90 °C / 500 kPa oxygen pressure.
Oxygen pressure in the autoclave has been recorded continuously and time of pressure decrease evaluated afterwards. Decrease in pressure can be attributed to chemical reaction of oxygen with the polymer and therefore a change in molecular morphology. Since the degree of pressure change is dependent on pressure and temperature during HPAT as well as the autoclave's volume, a time-till-failure criteria applicable to all test conditions must not refer to change in oxygen pressure, but change in quantity of oxygen molecules ($\Delta n(O_2)$). Using the laws of Boyle-Mariotte, Gay-Lussac and the thermal equation of state and taking into account that temperature and volume are constant in the autoclave during HPAT, $\Delta n(O_2)$ can be calculated from change in pressure and the initial HPAT conditions according to equation 2.

$$\Delta n(t) = n(t) - n_0 = \left(\frac{p(t)}{p_0} - 1\right) \cdot \left(\frac{p_0 \cdot V_0}{R \cdot T}\right) \quad (2)$$

p_0: initial pressure, $p(t)$: pressure at time t, n_0: initial quantity of oxygen available (in mol), $n(t)$: quantity of oxygen available at time t, V_0: volume of oxygen in gaseous state

Due to removal of specimens during exposure the quantity of sample material in the autoclave reduces with progressing duration of exposure which must be taken into account. Therefore not $\Delta n(O_2)$ but $\Delta n(O_2)/m$ (m = mass of specimens in the autoclave), is a suitable characteristic referring to the amount of consumed oxygen. For thick specimens surface to volume ratio must be taken into account to. For GTX surface to volume ratio is very high.

Therefore it is anticipated oxygen is available for chemical reaction throughout the whole specimen's cross section. Based on the pressure data, the recorded change in O_2 quantity of 0.05 mmol per gram of specimen material ($\Delta n(O_2)/m$ = -0.05 mmol/g) was determined. This corresponds to $3.0 \cdot 10^{19}$ consumed molecules O_2 per gram PP specimen, which was defined as time-till-failure based on $\Delta n(O_2)/m$. As can be seen in section 5, this criterion for time-till-failure is corresponding well with beginning of loss in mechanical stability. Since oxygen pressure is recorded continuously the graph is a more reliable indicator than $F_{max,res}$ and $\varepsilon_{max,res}$ which are based on a limited number of discrete measured values. Therefore determination of time-till-failure based on consumed oxygen ($\Delta n(O_2)/m$) is much more accurate and solid than time-till-failure based on $F_{max,res}$ and $\varepsilon_{max,res}$. All chosen evaluation criteria ($F_{max,res}$ = 50%, $\varepsilon_{max,res}$ = 50% and $\Delta n(O_2)/m$ = -0.05 mmol/g) were evaluated adapting an exponential decreasing fit (Eq. 3) to the results obtained.

$$y = y_0 + a \cdot \exp\left(-\frac{t}{b}\right) \tag{3}$$

y_0: relative initial value (for $F_{max,res}$ and $\varepsilon_{max,res}$: 100%, for $\Delta n(O_2)/m$: 0), t: exposure time, a, b: parameter

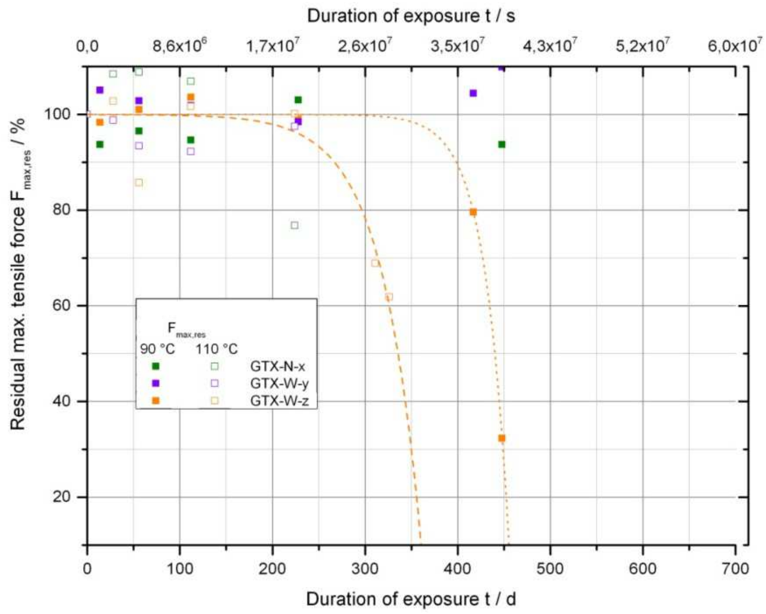

Figure 1. Residual maximum tensile force versus exposure time in the oven – GTX-N-x, GTX-W-y and GTX-W-z

5 TEST RESULTS

5.1 *Oven tests*

In Fig. 1 $F_{max,res}$ test results are shown for all three tested GTX after oven ageing at 90 °C and 110 °C respectively. The tests are still running. So far, after test durations of 650 d at 90 °C and 350 d at 110 °C only GTX-W-z showed significant change in maximum tensile force and reached failure criteria $F_{max,res}$ = 50%. In order not to run out of specimens before failure criteria is reached, no tensile tests were performed after 448 d (90 °C) and 224 d (110 °C) on GTX-N-x and GTX-W-y, but visual and manual inspection indicates no significant change in general appearance until 650 d (90 °C) and 350 d (110 °C).

5.2 *High-pressure autoclave tests*

5.2.1 *Sample GTX-N-x*

In Fig. 2 $F_{max,res}$ (square-shaped symbols and dashed fit) and $\varepsilon_{max,res}$ (diamond-shaped symbols and dotted fit) of nonwoven geotextile GTX-N-x are plotted versus exposure time. Furthermore $\Delta n(O_2)/m$ is plotted as continuous graphs with discontinuities at exposure times when the autoclave had to be opened for specimen removal. It is obvious that all three characteristics measured ($F_{max,res}$, $\varepsilon_{max,res}$ and $\Delta n(O_2)/m$) indicate a significant change in material properties after similar exposure times. As expected, the higher the test temperature, the earlier time-till-failure is reached, with the longest test duration of approximately 620 d for test conditions 75 °C and 300 kPa oxygen pressure. Evaluated times-till-failure are listed in section 6, Tab. 3.

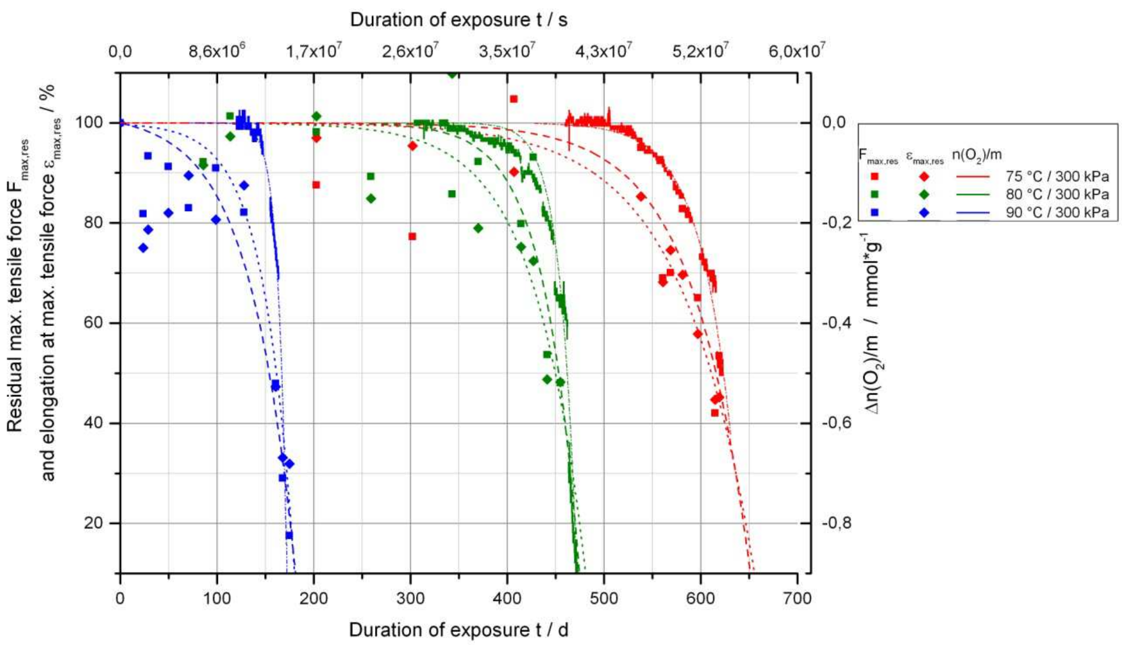

Figure 2. Residual maximum tensile force and residual elongation at maximum tensile force (left) and oxygen consumption per unit mass of specimens (right) versus exposure time in HPAT (75 °C, 80 °C, 90 °C / 300 kPa) – GTX-N-x

5.2.2 *Sample GTX-W-y*

In Fig. 3 test results of GTX-W-y are shown. Compared to GTX-N-x shorter times-till-failure could be determined for HPAT at 80 °C / 300 kPa and 75 °C / 300 kPa but longer times-till-failure for the test at 90 °C / 300 kPa indicating a significantly different dependency of oxidation resistance on temperature. Evaluated times-till-failure are listed in section 6, Tab. 3.

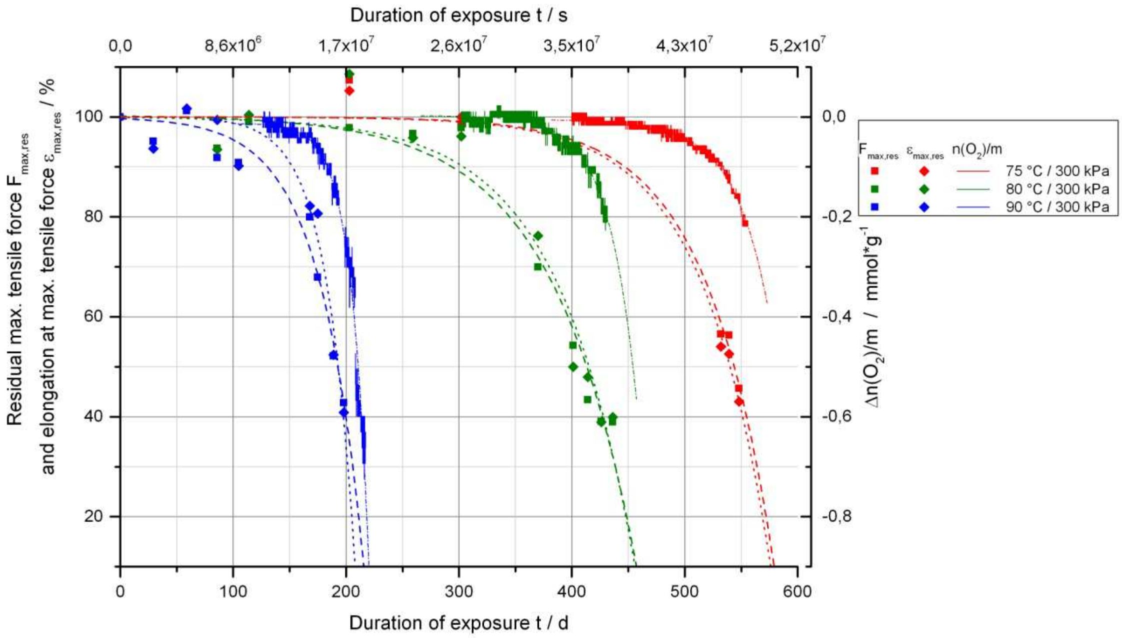

Figure 3. Residual maximum tensile force and residual elongation at maximum tensile force (left) and oxygen consumption per unit mass of specimens (right) versus exposure time in HPAT (75 °C, 80 °C, 90 °C / 300 kPa) – GTX-W-y

5.2.3 *Sample GTX-W-z*

The test results obtained on GTX-W-z are shown in Fig. 4 and 5. In Fig. 4 the graphs for HPAT at the three applied temperatures (75 °C, 80 °C and 90 °C) and 300 kPa oxygen pressure are plotted. Times-till-failure of GTX-W-z are more than three times smaller than for the other two samples. Consequently resistance to oxidation of GTX-W-z is lower than for both other samples.

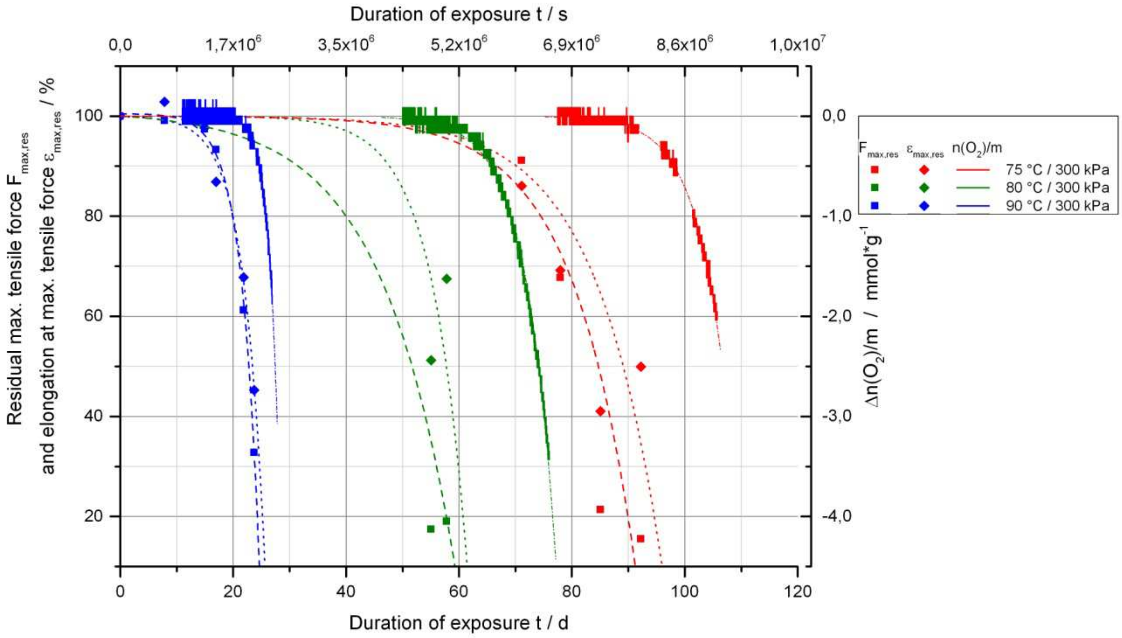

Figure 4. Residual maximum tensile force and residual elongation at maximum tensile force (left) and oxygen consumption per unit mass of specimens (right) versus exposure time in HPAT (75 °C, 80 °C, 90 °C / 300 kPa) – GTX-W-z

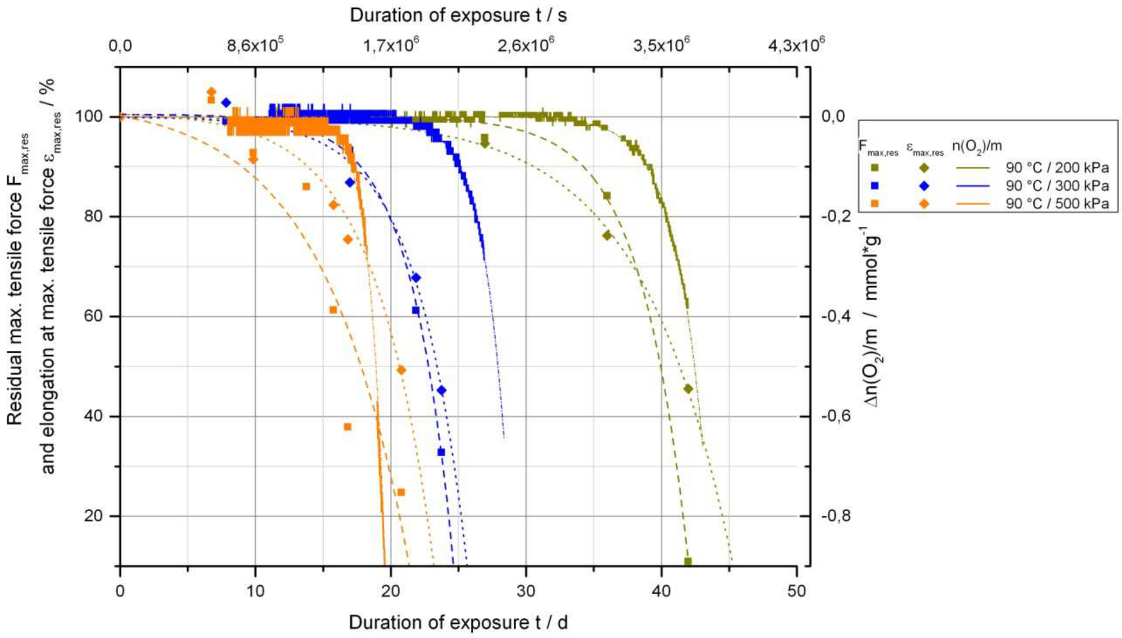

Figure 5. Residual maximum tensile force and residual elongation at maximum tensile force (left) and oxygen consumption per unit mass of specimens (right) versus exposure time in HPAT (90 °C / 200 kPa, 300 kPa, 500 kPa) – GTX-W-z

In Fig. 5 results for pressure variation (200 kPa, 300 kPa and 500 kPa) and 90 °C are shown. As expected, higher oxygen pressures offer more concentrated oxygen levels to react chemically with the polymer, and thus shorten the test duration. All applied pressures are close to oxygen pressure in service (21 kPa partial oxygen pressure) and much lower than the one recommended according to EN ISO 13438 (5100 kPa), resulting in more reliable extrapolations to service conditions (see section 6). Evaluated times-till-failure are listed in section 6, Tab. 3.

6 INTERPRETATIONS AND EXTRAPOLATIONS

In Tab. 3 all times-till-failure evaluated based on the test results given in section 5 are listed. Since after 650 d of oven storage at 90 °C and after 350 d of oven storage at 110 °C GTX-N-x and GTX-W-y show no loss in maximum tensile force, it is obvious that test durations can be reduced significantly by high-pressure autoclave ageing, particularly at elevated oxygen pressures.

In Fig. 6 times-till-failure for all HPATs at 300 kPa are plotted logarithmically versus 1000/T. It is evident that, referring to temperature, an Arrhenius-dependency is given for all three samples, allowing an extrapolation to service temperature and 300 kPa oxygen pressure. Based on the slope of the extrapolation fit, activation energy E_A at 300 kPa can be calculated. $E_A(p(O_2) = 300$ kPa) of sample GTX-W-y (approx. 75 kJ/mol) is much lower than the ones obtained for GTX-N-x (approx. 97 kJ/mol) and GTX-W-z (approx. 95 kJ/mol). For all three samples the three characteristics evaluated ($F_{max,res}$, $\varepsilon_{max,res}$ and $\Delta n(O_2)/m$) lead to similar activation energies. Only $E_A(p(O_2) = 300$ kPa) referring to $\Delta n(O_2)/m$ for GTX-W-z is deviating by slightly more than 5 % from the average value.

The extrapolated time-till-failure for 40 °C and 30 °C respectively and 300 kPa oxygen pressure (blank symbols in Fig. 6) can be interpreted as very conservative service life estimations. In service, due to the low partial oxygen pressure in air, O_2 availability is lower ($p_{par}(O_2) = 21$ kPa) leading to extended service lives.

Table 3. Times-till-failure, determined in high-pressure autoclave and oven testing

Sample name	Test method	Test conditions	Time-till-failure based on ... / d		
			$F_{max,res}$	$\varepsilon_{max,res}$	$\Delta n(O_2)/m$
GTX-N-x	HPAT	75 °C / 300 kPa	616	611	546
		80 °C / 300 kPa	453	450	423
		90 °C / 300 kPa	154	160	146
	Oven	90 °C [1)]	>650[3)]	---	---
		110 °C [2)]	>350[3)]	---	---
GTX-W-y	HPAT	75 °C / 300 kPa	544	540	507
		80 °C / 300 kPa	413	415	397
		90 °C / 300 kPa	193	193	170
	Oven	90 °C [1)]	>650[3)]	---	---
		110 °C [2)]	>350[3)]	---	---
GTX-W-z	HPAT	75 °C / 300 kPa	84.7	89.1	86.2
		80 °C / 300 kPa	51.7	57.8	53.4
		90 °C / 300 kPa	22.9	23.7	20.6
		90 °C / 200 kPa	39.9	41.4	37.4
		90 °C / 500 kPa	17.8	20.6	16.3
	Oven	90 °C [1)]	440	---	---
		110 °C [2)]	336	---	---

[1)] prior to oven testing pre-leaching for 28 d in hot water (80 °C) was carried out according to EN 13257: 2014.
[2)] EN ISO 13438:2004, method A1 (110 ^{0}C) without pre-leaching
[3)] oven test is still running, $F_{max,res} \leq 50\%$ is not yet reached

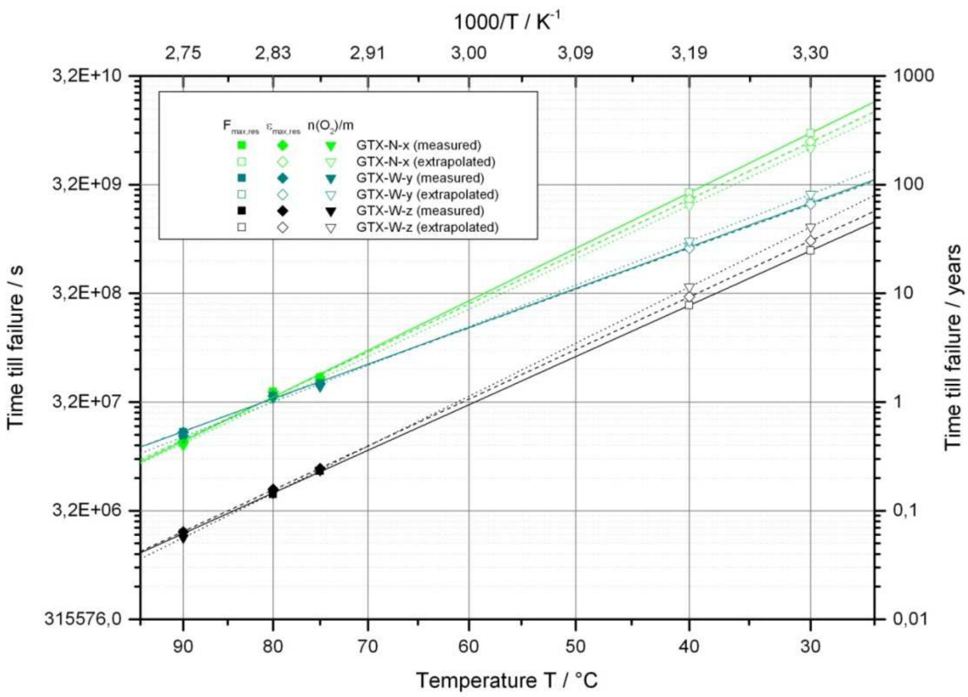

Figure 6. Arrhenius plotting of time-till-failure versus temperature based on HPAT results at 300 kPa – GTX-N-x, GTX-W-y and GTX-W-z

Regarding GTX-W-z HPAT was performed not just at different temperatures but also at different oxygen pressures providing the opportunity to extrapolate to service pressure ($p_{par}(O_2)$ = 21 kPa). Due to the fact that during HPAT testing according to EN ISO 13438, sample material is not directly in contact with gaseous oxygen, but surrounded by an aqueous solution, no extrapolation was carried out using oxygen gas pressure but rather the amount of

dissolved oxygen. Depending on temperature and oxygen pressure in the autoclave above the solution, dissolved oxygen can be calculated based on data provided by Geng and Duan (2010).
In Fig. 7 times-till-failure are plotted double logarithmically against dissolved oxygen. Additionally time-till-failure as determined in oven ageing at 90 °C is included. The extrapolation time-till-failure based on HPAT results is much lower than the one determined in oven testing (difference of factor 3). The main reason for this observation surely is the fact that in HPAT the sample is surrounded by an aqueous solution, whereas in oven testing the sample is in contact with air. Thus the test conditions are different which naturally leads to different test results. Due to the fact that, beside oxidation, leaching by the aqueous solution is given as a second ageing process in HPAT, ageing in high-pressure surely is the more severe test and consequently leads to shorter times-till-failure. By testing at more than three different oxygen pressures uncertainty of the extrapolation will reduce and the difference in the extrapolated time-till-failure based on HPAT test results and measured oven test result might be lower. Depending on the application in service, the GTX can be in contact with wet, humid or dry soil or other substances.
For determination of service life at service conditions simultaneous extrapolation of temperature as well as oxygen availability is necessary. Most commonly used for this kind of extrapolation is an exponential fit (Eq. 4) stated by Schröder et al. (2008). This fit was developed based on data resulting from HPAT at very high oxygen pressure (≥ 1.1 MPa). Since $\ln(t_{failure})$ is rather a function of $\ln(c(O_2))$ than $c(O_2)$ at low oxygen availabilities, close to ambient pressure Schröder's fit was adjusted and Eq. 5 was applied for extrapolation regarding temperature and oxygen availability.

$$t_{\text{failure}} = A_1 \cdot \exp\left(\frac{-(B_1 + D_1 \cdot c_{O2})}{R \cdot T}\right) \qquad (4)$$

$$t_{\text{failure}} = A_2 \cdot \exp\left(\frac{-(B_2 + D_2 \cdot \ln(c_{O2}))}{R \cdot T}\right) \qquad (5)$$

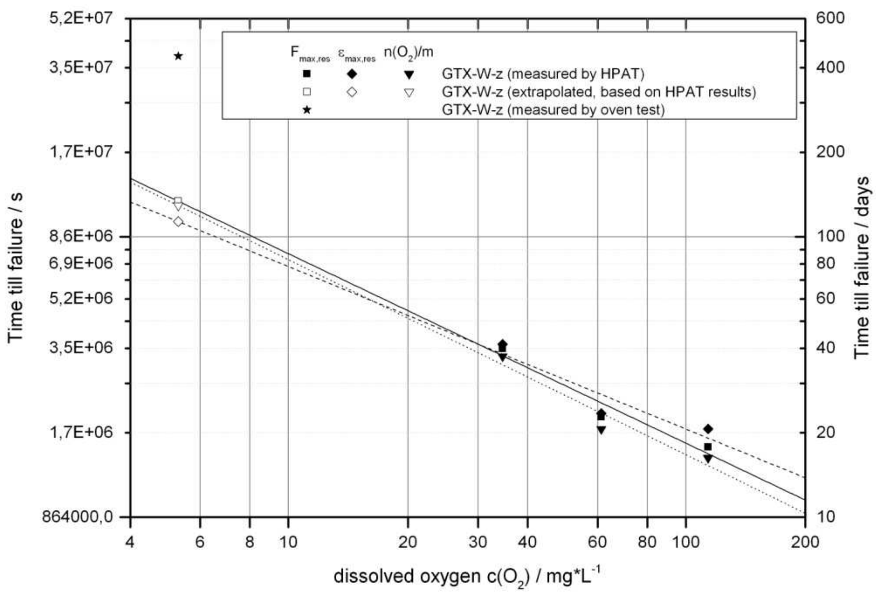

Figure 7: Double logarithmic plotting of time-till-failure versus amount of dissolved oxygen based on HPAT results – GTX-W-z

In Fig. 8 simultaneous extrapolation of times-till-failure based on $F_{max,res}$ test results of GTX-W-z to service temperature and oxygen availability at service is shown graphically.

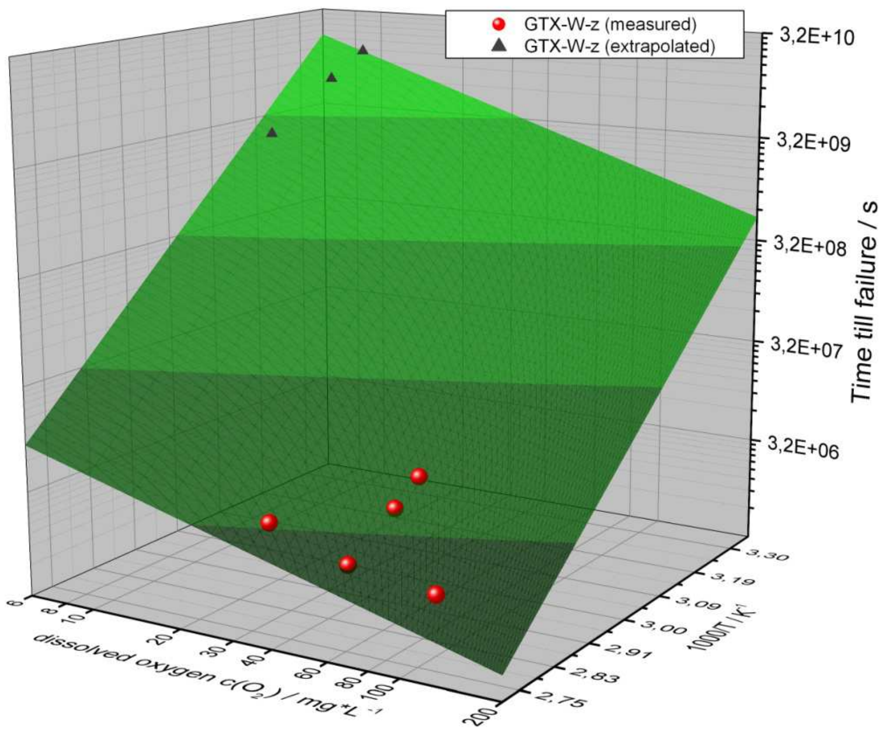

Figure 8: Time-till-failure versus temperature and dissolved oxygen based on $F_{max,res}$-HPAT results – GTX-W-z

In Tab. 4 extrapolated service lives at possible service conditions (25 °C, 30 °C and 40 °C / 21 kPa) are listed. Due to the fact that time-till-failure is almost always a function of exp(1/T) it is inevitable that slightly different test results lead to strongly deviating extrapolated values, particularly at low temperatures. Therefore it is not surprising that extrapolations based on $F_{max,res}$, $\varepsilon_{max,res}$ and $\Delta n(O_2)/m$ result in significantly different service lives. Nevertheless all obtained values are considered realistic and in the same order of magnitude. As apparent by Fig. 8 extrapolation is based on a plane surface and therefore activation energy results from the tilted position of this plane surface and consequently is pressure dependent. Activation energy E_A of GTX-W-z at atmospheric pressure was determined ranging between 84 and 93 kJ/mol, depending on the characteristic ($F_{max,res}$, $\varepsilon_{max,res}$ or $\Delta n(O_2)/m$) used for extrapolation.

Table 4. Times-till-failure at service conditions (T ≤ 40 °C, $p_{par}(O_2)$ = 21 kPa), extrapolated based on HPAT results

Sample name	Service temperature / °C	Service life based on ... / years		
		$F_{max,res}$	$\varepsilon_{max,res}$	$\Delta n(O_2)/m$
GTX-W-z	25	378	242	569
	30	213	139	308
	40	70.0	47.4	93.3

7 CONCLUSIONS

Based on HPAT at 300 kPa oxygen pressure and different temperatures on GTX-N-x and GTX-W-y service life referring to oxidation could be estimated for both GTXs at service temperature and 300 kPa. Since at service conditions (service temperature and atmospheric pressure) oxygen availability is much lower (21 kPa) the estimated times-till-failure at 40 °C/

300 kPa (≥ 65 years for GTX-N-x and ≥ 25 years for GTX-W-y) can be interpreted as very conservative service life estimations. Oven test results on GTX-N-x and GTX-W-y at 90 °C and 110 °C are to be determined in order to verify HPAT test results.
GTX-W-z was tested even more extensively in order to perform an extrapolation to both, service temperature and available amount of oxygen in service. In consideration of the times-till-failure determined it is obvious that GTX-W-z is not stabilized as high as both other GTXs. Nonetheless extrapolations based on HPAT results lead to a service life referring to oxidation of ≥ 45 years at 40 °C. Activation energy E_A amounts to 84 to 93 kJ/mol and is therefore consistent with E_A for oxidation of PP found in literature. When considering oven test result and HPAT result referring to the same test condition (90 °C) it becomes apparent that oven test leads to longer times-till-failure, most probably due to lack of leaching which is an additional ageing process present during HPAT. Therefore high-pressure autoclave ageing leads to more conservative results compared with oven ageing.
In order to verify the extrapolation fit regarding oxygen availability for GTX-W-z an additional test at even lower oxygen pressure (≤ 200 kPa) will be performed. In view of the extrapolations regarding GTX-W-z service lives at service conditions for GTX-N-x and GTX-W-y can be expected to be much higher than the estimated times-till-failure at service temperature and 300 kPa. In order to confirm this expectation additional HPATs at 90 °C and two further test pressures are required.
Furthermore with this study it can be proven, that recording and evaluating of oxygen pressure during HPAT in order to determine oxygen consumption due to chemical reaction with the polymer is a very elegant new tool. Evaluation of oxygen consumption leads to similar results as tensile properties but is much more accurate in terms of time-till-failure determination. Moreover no specimens have to be removed from the high-pressure autoclave and no subsequent (tensile) tests are required.

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