Comparative study: Oven tests and high-pressure autoclave tests (HPAT) on one commercially available PE-HD material

Anja Martin & Helmut Zanzinger

SKZ – German Plastics Center, Germany

ABSTRACT: A polyethylene high density (PE-HD) product has been subjected to a very extensive test program to compare the oven method with the high pressure autoclave test (HPAT) method regarding life time estimation and energy/time demand. Oven tests have been carried out at four temperatures between 85 °C and 100 °C for more than three years and they are still running. After three years, oxidation induction time (OIT) has decreased significantly, but mechanical properties remain unchanged so far. Alongside high-pressure autoclave tests (HPAT) have been performed at various test temperatures between 60 °C and 90 °C and oxygen pressures between 165 kPa and 5,100 kPa in a considerably shorter period of time. The estimation of end-of-life at a service temperature of 40 °C and atmospheric pressure are lying in the range of 220 years to 330 years with calculated activation energies between 90 kJ/mol and 94 kJ/mol. By comparing the energy demand the savings potential of using HPAT method instead of oven ageing is enormous. The HPAT method with approx. 4,600 kWh and 1,100 d test duration in total was much more electrical energy and time saving than the oven method with more than 28,600 kWh and more than 4,500 d test duration. With regard to a reduced test program (already fewer measurements are sufficient) HPAT method with 2,400 kWh (630 d test duration) has an energy saving of about 90% compared with the oven method with more than 22,500 kWh (3,500 d test duration).

Keywords: oxidation, ageing, high-pressure autoclave test (HPAT), oven, life time estimation, end-of-life, PE-HD

1 INTRODUCTION

There is no doubt that the end-of-life of geosynthetics is defined - among other things - by their resistance to ageing. For polyolefin-based products, oxidation is the critical ageing process. In order to estimate the end-of-life of a plastic product there are in principle three test methods available pertaining the topic of accelerated oxidative ageing in the laboratory: conventional oven ageing in air taking advantage of acceleration due to elevated temperature, conventional oven ageing in an aqueous solution at elevated temperatures considering ageing due to leaching and HPAT providing acceleration due to elevated temperature, leaching and an elevated availability of oxygen. The first two methods are well established, but they are time consuming and tests require a lot of energy.

The aim of this study is a comparison between oven ageing and HPAT method regarding lifetime estimation, energy requirement and test time demand. Therefore, one PE-HD sample was subjected to ageing by using these two ageing methods.

2 MATERIAL AND TEST METHODS

2.1 *Sample*

This study focuses on one commercially available PE-HD plastic pipe (outside diameter: 110 mm, wall thickness: 10 mm) containing a typical phenolic stabilization package ($OIT_{200\,°C}$: 124 min).

2.2 *Oven test method*

During oven ageing according to ISO 2578, specimens (type 2 according to EN ISO 6259-3) were stored in an oven at various elevated temperatures (85 °C, 90 °C, 95 °C and 100 °C). After certain time intervals, OIT-measurements and tensile tests were performed. The oven ageing tests have been running for more than three years.

2.3 *High-pressure autoclave test (HPAT) method*

HPAT is used to simulate accelerated ageing. The tests have been carried out in acc. with ISO 13438 (method C) with the test conditions (O_2-pressure and temperature) as shown in Tab. 1. In HPAT, tensile specimens (type 2 according to EN ISO 6259-3) have been subjected to elevated temperatures and oxygen pressures in a pressure vessel filled partly with aqueous medium. Test specimens have been withdrawn from the high-pressure autoclaves with progress of immersion time and tensile tests have been performed on the withdrawn specimens. Oxygen pressure in the autoclave has been recorded continuously. A decrease in pressure can be related to chemical reaction of oxygen with the polymer and therefore a change in molecular morphology. As 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 Eq. 1.

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

where 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,
T : absolute Temperature R: ideal gas constant

Due to removal of specimens during exposure, the quantity of specimens in the autoclave reduces with progressing duration of exposure which must be taken into account. Therefore $\Delta n(O_2)/m$ (m = mass of specimens in the autoclave) not $\Delta n(O_2)$, is the suitable characteristic referring to the amount of consumed oxygen.

Table 1. Test conditions (O_2-pressure and temperature) for HPAT.

Temperature [°C]	O_2-pressure [MPa]							
	0.165	0.2	0.3	0.6	1.1	2.1	3.6	5.1
60								X
70								X
80								X
90	X	X	X	X	X	X	X	X

While the specimens are exposed to an elevated temperature in the dry state (in air) during oven ageing, the test specimens in the high-pressure autoclave test are surrounded by an aqueous solution of an elevated temperature with a high proportion of dissolved oxygen. As a result, HPAT specimens are in direct contact with liquid, and there is a possibility that additives such as stabilizers will be washed out, unlike oven ageing. This leaching is also observed in the application (Vogt 2010) and may result in addition to the oxidation of the stabilizer, in addition to a decrease in the stabilizer content and thus a shorter service life. Furthermore, it is assumed that the steady high oxygen pressure in the container prevents oxygen sinks, which can become the limiting factor in the reaction during oven ageing (Zweifel 1997). The high-pressure autoclave test is thereby the "more demanding" test method.

2.4 *Characterization tests during oven ageing and HPAT*

OIT is often used as a measure of the thermo-oxidative stability, even if only the consumption of the anti-oxidants is tested by this experiment. OIT describes the duration of time for which the polymer is still protected from oxidative degradation by the antioxidants at the measuring temperature. If the OIT value approaches zero after a certain storage time due to ageing, the stabilizer is completely exhausted. OIT tests were carried out acc. to ISO 11357-6 at measurement temperatures of 180 °C (on specimens subject-ed to HPAT) and 200 °C (on specimens subjected to oven ageing). The OIT specimens have been taken from the complete cross section of the aged sample.

The mechanical properties were determined by performing tensile tests according to ISO 6259-3. The tests were carried out with a universal tensile testing machine (Zwick 1445) with specimen type 2, clamping length of 80 mm and a test speed of 25 mm/min. The elongation was measured by means of an optical extensometer.

2.5 *Electrical energy measurements*

The demand for energy in 115 L ovens type "Binder FED115" was determined with a power meter model "Reichelt KD-302" during heat-up phase and after reaching the testing temperature. The energy consumption of the container heating elements and all other energy-requiring components of the autoclave (magnetic stirrer, control cabinet, data logging) in the heating phase (from room temperature up to 90 °C) and the electrical energy requirement per operating day after reaching the test temperatures (from 60 °C to 90 °C) were determined by using a voltage quality analyzer "Janitza UMG 605".

3 TEST RESULTS

3.1 *Oven test results*

As it is shown in Fig. 1, even after more than 3 years exposure at 95 °C and 85 °C (or rather nearly 3 years exposure at 100 °C and 90 °C) in the ovens, the tensile properties (yield stress and elongation at break) of the exposed specimens are still on the same level as the unaged specimens. During ageing process the $OIT_{200\,°C}$ drops down and reached a value of 150 s after 820 d at100 °C oven ageing temperature. At lower temperatures, the decrease of OIT value is slower.

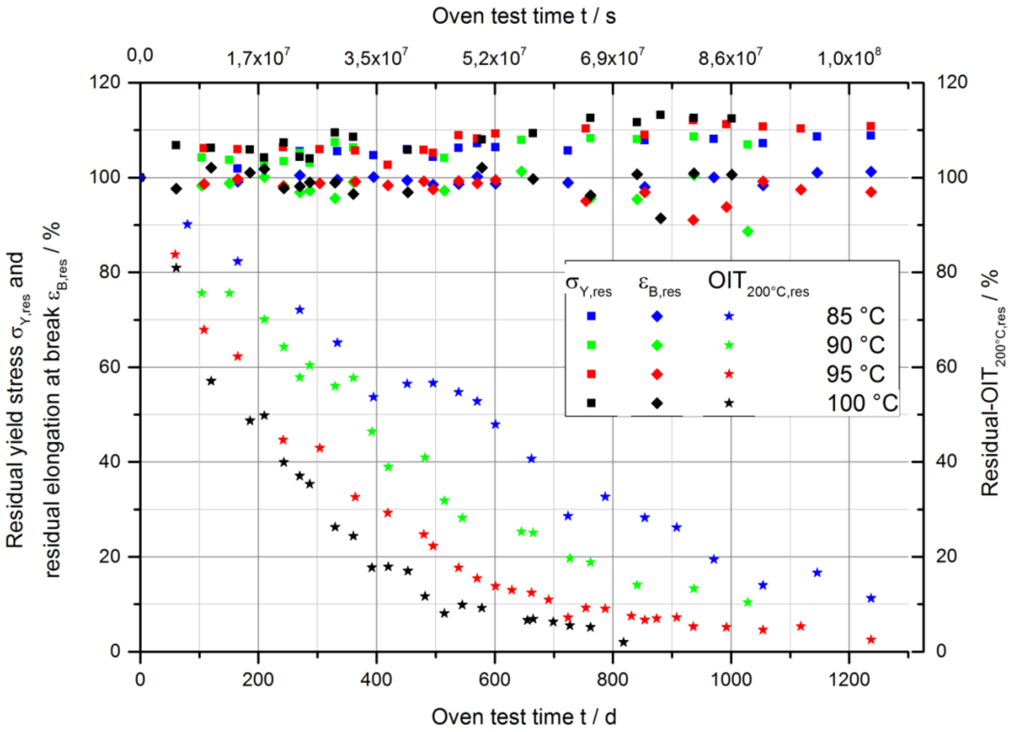

Figure 1. Residual mechanical properties and residual OIT during oven ageing.

In the oxidative ageing process of phenolic-stabilized materials, the stabilizer is first consumed before the polymer molecules were attacked. It is known (Mueller 2007) that the oxidation degradation starts when the OIT value has dropped to very low values. According to the three-stage-oxidation-model published by

Hsuan and Koerner (1998) and Hsuan and Li (2005), a decrease of mechanical properties will be detected after the induction stage (second stage). This means, that even after this long testing time of approx. 3 years, the failure time is not reached yet.

3.2 *HPAT results*

HPAT tests were performed at different temperatures and different O_2-pressures. In Fig. 2, the tensile properties and the consumed O_2 amount per gram of specimen are shown for different O_2-pressures at 90 °C.

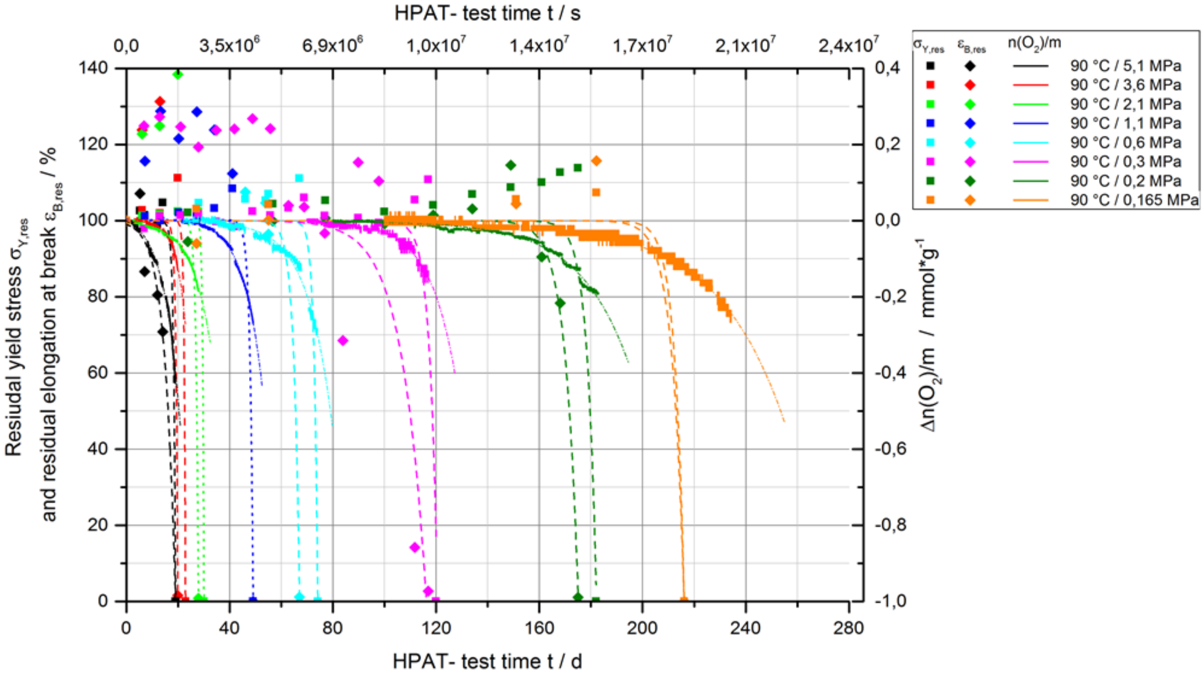

Figure 2. Residual mechanical properties and the consumed O2 per gram of specimen material for HPAT at different O2-pressures and at 90 °C.

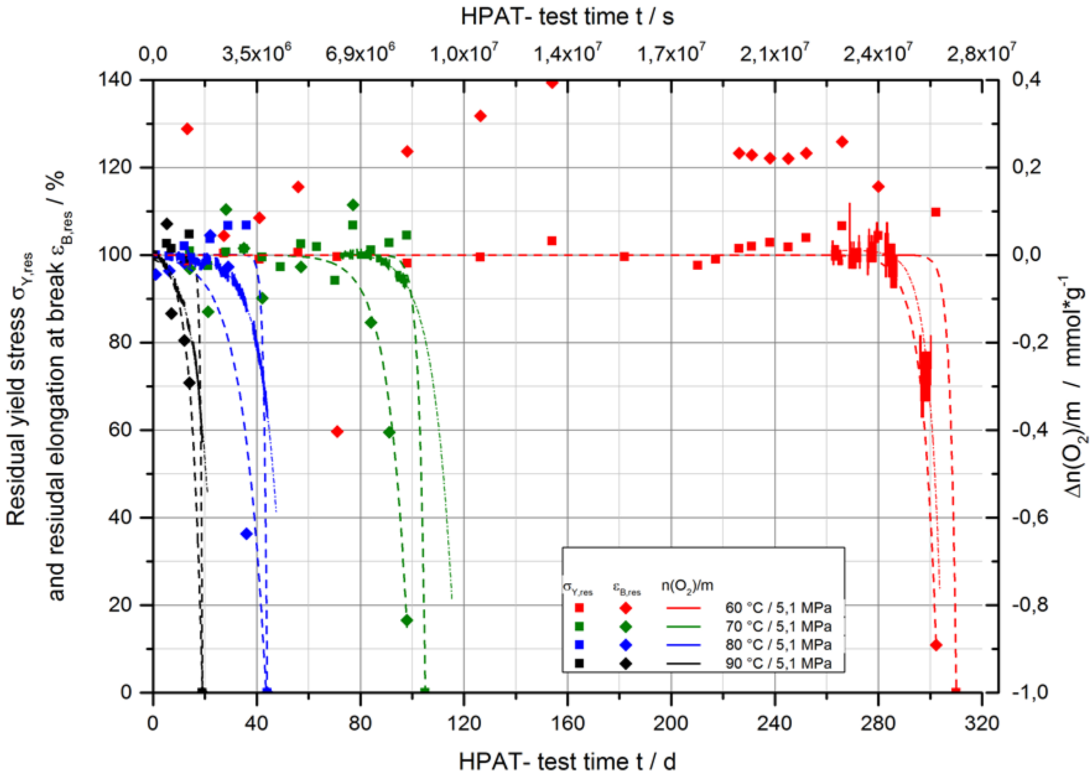

Figure 3. Residual mechanical properties and the consumed O2 amount per gram of specimen material for HPAT at different temperatures and at 5.1 MPa O2-pressure.

In addition, as shown in Fig. 3, the temperatures (each at 5.1 MPa oxygen pressure) were changed for each test. Both in terms of pressure and temperature variation, it can be seen that the mechanical loss of stability is associated with O_2 consumption in the autoclave. Therefore time until failure was defined as residual elongation at break and residual yield stress decreased to 50%. Additionally, time-until-failure was set as the amount of consumed O_2 reaching 0.2 mmol/g. The testing times (times-until-failure) at each test condition are shown in Tab. 2. The higher the test temperatures and the higher the O_2-pressure, the shorter the times-until-failure are.

Table 2. Failure times in HPAT for three different assessment criteria.

O_2-pressure [MPa]	Dissolved oxygen amount [mg/L]	Temperature [°C]	Test time [d] until $\varepsilon_{b,res}$ = 50%	Test time [d] until $\sigma_{Y,res}$ = 50%	Test time [d] until $n(O_2)/m$ = -0.2 mmol/g
0.165	25	90	208	207	229
0.2	35	90	172	181	182
0.3	61	90	110	120	120
0.6	140	90	66	74	70
1.1	264	90	49	49	47
2.1	498	90	27	30	29
3.6	850	90	20	23	22
5.1	1262	90	16	19	15
5.1	1302	80	38	44	40
5.1	1363	70	94	105	105
5.1	1449	60	301	302	298

The above-mentioned three assessment criteria were used for end-of-life estimations shown in Fig. 4 and in Fig. 5. The failure times were plotted vs. the oxygen pressure-dependent concentration of dissolved oxygen in the medium and the inverse absolute temperature. The linear extrapolations in Fig. 4 give, with a coefficient of determination of R^2 = 0.993 to 0.999, for each failure criterion the failure times at 90 °C and oxygen partial pressure of the atmosphere (21 kPa corresponds to the dissolved oxygen amount of 5.3 mg/L at 90 °C (Ming Geng & Zhenhao Duan 2010)). Failure times at application temperature (e.g. 40 °C) and oxygen pressure of 5.1 MPa are obtained by linear extrapolation (R^2 = 0.996 to 0.999) as shown in Fig. 5. For the determination of the service life at service temperature (e.g. 40 °C) and application pressure (oxygen partial pressure of 21 kPa), Eq. 2 was used. The results could be shown on a 3D-plot (Fig. 6).

$$z = z_0 + a\,x + b\,y \tag{2}$$

where z_o, a and b = constants, x = inverse temperature [K^{-1}], y = ln (concentration of dissolved oxygen), z = ln (failure time)

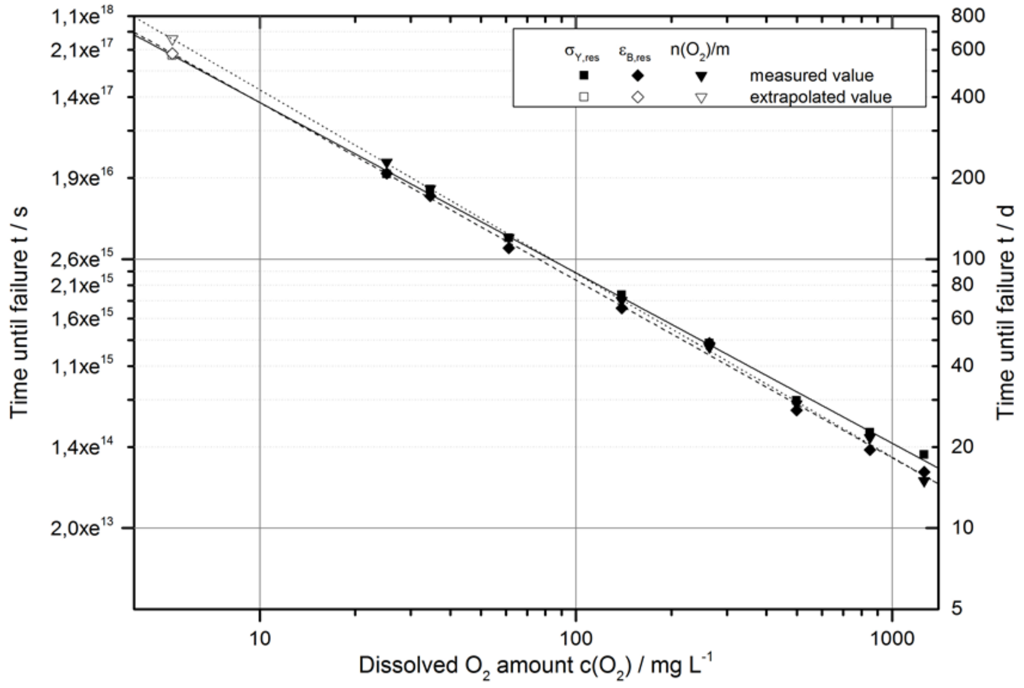

Figure 4. Double logarithmic plot of the measured and extrapolated failure times as a function of the amount of oxygen dissolved in the medium at 90 °C in HPAT.

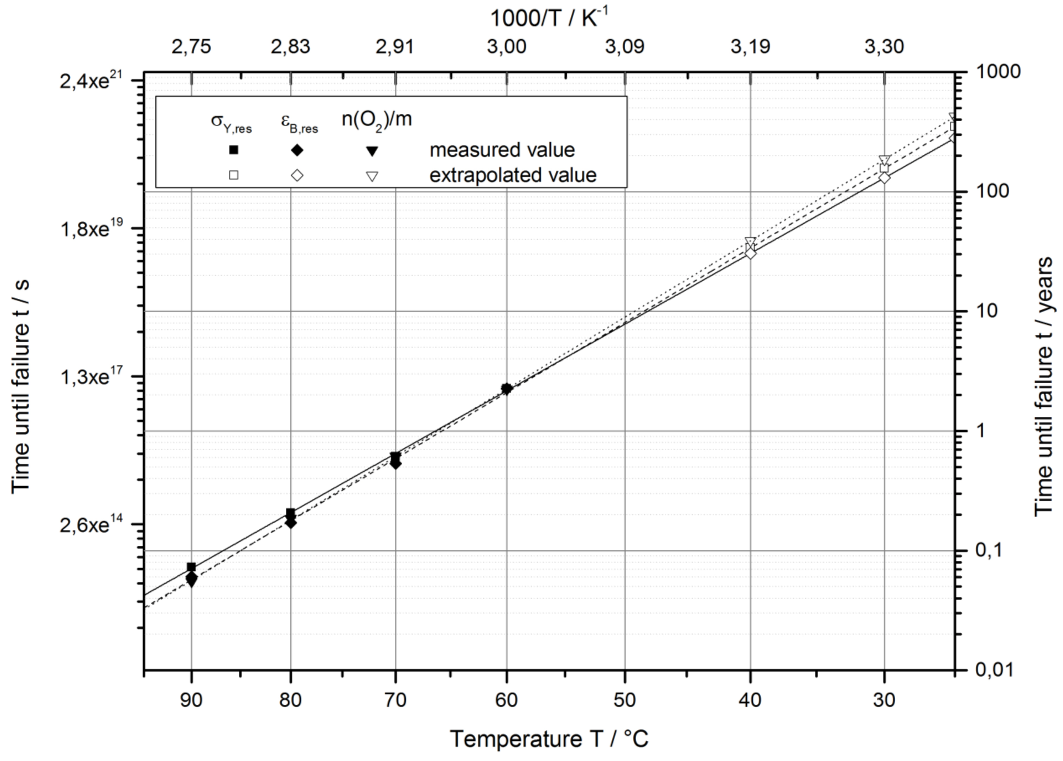

Figure 5. Logarithmic plot of measured and extrapolated failure times as a function of inverse absolute temperature in the HPAT at 5.1 MPa.

Fig. g shows the logarithmized concentration of dissolved oxygen, the inverse absolute temperature and the logarithmized failure times based for example on $\varepsilon_{b,res}$ = 50% were plotted as a 3D-extrapolation. Tab. 3 shows the estimated service lives in years obtained at a service temperature of 40 °C taking into account all failure criteria (dissolved oxygen amount is 6.9 mg/L at 40 °C and at atmospheric pressure, here 21 kPa). The activation energies resulting from the extrapolation fits were between 90 kJ/mol and 94 kJ/mol. The literature value of the activation energy for PE is given as E_a= 90 kJ/mol (Vogt 2010).

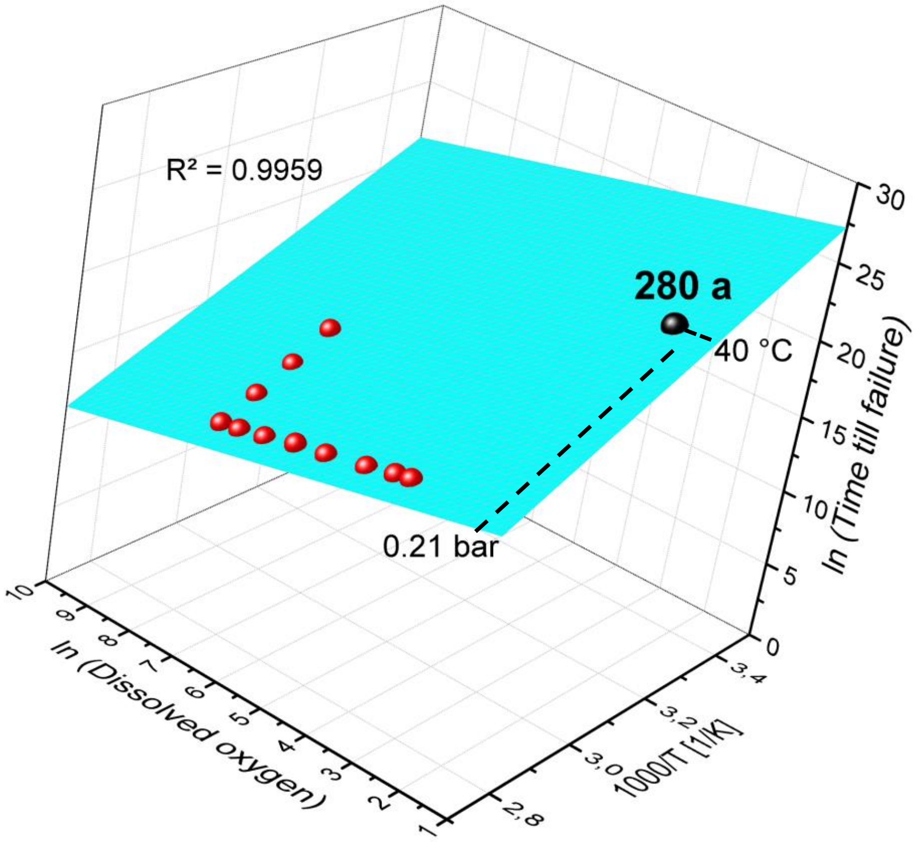

Figure 6. 3D-extrapolation to application conditions based on residual elongation at break (εb,res = 50 %).

Table 3. End-of-service-life estimations at service temperature (40 °C) and the oxygen partial pressure of the atmosphere (21 kPa) based on the 3D-extrapolation, taking into account various failure criteria.

Temperature [°C]	End-of-life [year] based on		
	$\varepsilon_{b,res}$ = 50%	$\sigma_{Y,res}$ = 50%	$n(O_2)/m$ = -0.2 mmol/g
40	280	220	330

4 ASSESSMENT OF OVEN METHOD AND HPAT METHOD

4.1 *Lifetime estimation*

Even after three years of oven ageing at borderline high test temperatures the mechanical properties are still on a high level. A lifetime estimation based on a reduction of mechanical properties is not possible in this status. This means for modern PE materials, oven ageing at reasonable temperatures is already reaching its limits, as the performance of PE materials is often so high that no results can be achieved in acceptable testing times.
On the other hand, the HPAT method provided plausible end-of-life estimations (Table 3) with activation energies meeting the literature values.

4.2 *Electrical energy and testing time demand*

4.2.1 *Full test program with ovens in this study*

During the heat up phase to operating temperature of 90 °C in oven ageing 0.24 kWh was consumed. At operating temperature 6.0 kWh per day at 90 °C, or 6.7 kWh per day at 100 °C was needed. The heating process thus plays only a minor role even with short testing times. The current demand for energy until this status of oven ageing has been 28,600 kWh for over 4,500 d (over 12 years) testing time in total.

4.2.2 *Reduced test program with ovens for routine testing:*

Arrhenius extrapolation requires at least three data points, which are recorded at ambient conditions. Thus under ideal conditions one of the four test temperatures could be neglected. For example, the following temperatures 85 °C, 95 °C and 100 °C could be chosen for routine test. The energy requirement for the oven method (for the tests running until now) resulting from this test volume amounts to more than 22,500 kWh with a cumulative test duration of more than 3,500 d.

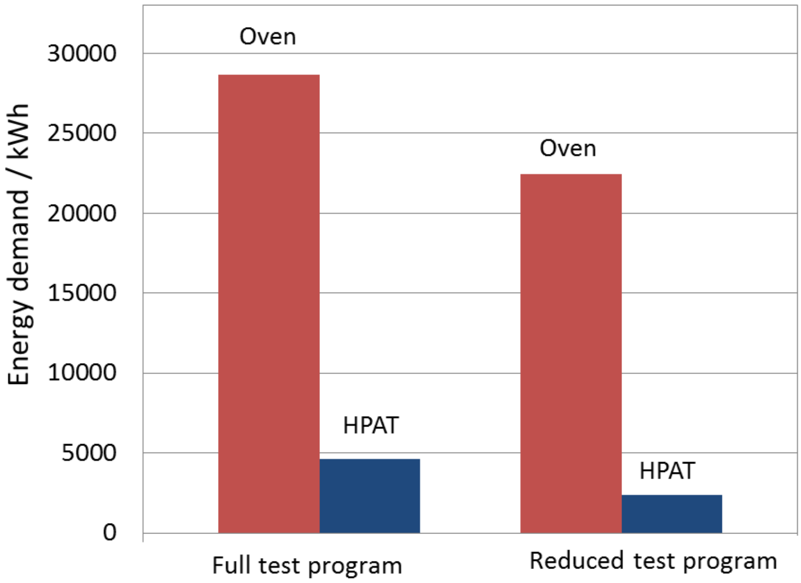

Figure 7. Comparison of energy demand of oven method and HPAT method (full and reduced test program).

4.2.3 *Full test program with HPAT in this study*

Electrical energy of 1.4 kWh was required to heat up a autoclave with a volume of 9 L from room temperature to 90 °C. Approx. 5.2 kwh was needed per day for the test temperature of 90 °C. The total energy consumption for all eleven HPATs used for this study was approximately 4,600 kWh with a total testing time of 1,100 d.

4.2.4 *Reduced test program with HPAT for routine testing*

The HPAT method requires at least five data points for 3D-extrapolation. This means the number of tests for routine testing can be reduced, but tests at the lowest temperature and lowest pressure should be preferred to get appropriate results. The HPAT energy demand would have been 2,400 kWh with a test duration of 630 d (taking into account the tests with conditions 165 kPa / 90 °C, 600 kPa / 90 °C, 5.1 MPa / 90 °C and 5.1 MPa / 80 °C and 5.1 MPa / 60 °C).

4.2.5 *Comparison of electrical energy and testing time demand*

In Fig. 7, the energy demands of HPATs (full study and reduced test program) as well as the energy demands of oven tests (full study and reduced test program) are compared. It shows that conventional oven ageing tests consume by far more energy than HPATs and even more relevant is that oven tests last much longer than HPATs.

5 CONCLUSION

The experimental results of this study show that by using the HPAT method (based on various failure criteria), an oxidative service life of $\geq$220 years at 40 °C service temperature can be predicted. The calculated activation energies meet the expected activation energy of PE in the literature. Thus, the HPAT method proves to be suitable for lifetime estimations regarding resistance to oxidation.

For modern PE materials, the oven ageing is already reaching its limits for practicability, as the performance of PE materials is often so high that no results can be achieved in acceptable times. Even after three years testing time, no reduction in mechanical properties have been detected in this study.

The energy requirement of the two test methods depends very much on the test duration and the scope of the test program. Within the scope of this research project, four test temperatures for the lifetime estimation were covered by the oven method and a complete test matrix with eight different oxygen pressures and four temperatures were used in the HPAT method. With about 4,600 kWh and a total testing time of 1,100 d the HPAT method was much more energy and time saving than the oven method with more than 28,600 kWh (4,500 d). Because already fewer measurements are sufficient to gain estimations for the end-of-life, the energy demands of “reduced test programs” were calculated in addition. With regard to these reduced test programs the HPAT method with 2,400 kWh (630 d test duration) is also about 90 % more energy saving than the reduced test program of the oven method with more than 22,500 kWh (3,500 d test duration).

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