Lifetime assessment of pit thermal energy storages based on various polyolefinic liner materials

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Abstract

This paper deals with the lifetime assessment of polyolefinic liner materials for pit thermal energy storages (PTES). Micro-specimen of a novel high temperature resistant polypropylene (PP-HTR) grade were examined at elevated temperatures ranging from 85 to 135°C. As ageing indicators, oxidation onset temperature and strain-at-break values were determined by thermal analysis and tensile testing, respectively. The endurance data of the PP-HTR model material was compared to commercial polypropylene random copolymer (PP-R) and high density polyethylene (PE-RT) grades designed for hot water pipe applications. Extrapolation of ageing data was performed from elevated to service-relevant temperatures and from micro-specimen to 2 mm thick liners. The temperature dependency was described by an Arrhenius law, whereas the thickness effect was modelled with a potential equations. Lifetime values of 2 mm thick liners were deduced for various implemented and concepted PTES projects in Europe. Therefore, a cumulative damage model was assumed. The novel PP-HTR liner exhibited a superior long-term durability, outperforming PP-R and PE-RT materials by a factor of 4 and 6, respectively.

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1. Introduction and objectives

Heating and cooling accounts for half of the European Union's (EU-27) overall energy demand. More than 60% of this demand is currently generated by fossil fuels, while only 13% is derived from renewable energy sources [1]. District heating is essential for efficient thermal energy supply, presently contributing to about 12% of the final energy use [2,3]. A significant increase in thermal energy demand is expected within the next decades [2]. While solar energy supply is gaining importance, a persistent challenge lies in the mismatch between demand and generation, limiting the achievable solar fraction of a district heating system. To overcome this problem, large thermal energy storages (LTES) have been developed. According to Sveinbjörnsson et al. [4], the disparity between heat demand and production constraints the solar thermal fraction of district heating systems to 20%. However, the integration of seasonal thermal energy storages has demonstrated the capability to elevate solar thermal fractions to more than 40%, presenting a promising outlook for enhanced sustainability and reduced reliance on fossil fuels in the heating and cooling sector. The higher the volume of the thermal energy storage the lower are the specific capital costs (€/m³) [5,6]. In principle pit thermal energy storages (PTES) are not limited by their volume. Moreover, they are easy to scale-up [5,7–9]. Hence, PTES are the dominating large storage system in the market. While PTES have mainly been installed in Danish districts such as Vojens (203,000 m³), Marstal (75,000 m³), Høje-Taastrup (75,000 m³) or Dronninglund (60,000 m³), there are plans for the realization of PTES Germany, France and Austria.

A PTES is a large excavated basin filled with water as a heat carrier fluid. The excavated soil is used to increase the embankment height and the storage volume. As a water barrier, polymeric liners made from polyethylene high density (PE-RT) are well-established. The geomembrane is extruded to a thickness of up to 3 mm and a width of several meters and directly welded on site. Correct welding parameters are crucial to ensure water tightness and durability [10,11]. PE liners are mainly used for lower-temperature seasonal PTES such as in Vojens and Dronninglund with operating temperatures up to 85°C. For higher-temperature storages with a constant temperature of 90°C, novel PP-R liner materials have been developed and commercialized. For a buffer storage in the city of Høje-Taastrup, a so-called high temperature resistant polypropylene (PP-HTR) liner based on PP random copolymers (PP-R) modified with an unique stabilizer package was used.

During service, ageing of polyolefinic materials leads to time-dependent physical and chemical changes, affecting their multifunctional property profile. Elevated temperatures induce re- and post-crystallization effects, associated with morphological changes on a micro-scale, such as crystal lamellae thickness or spherulite density. Densification within spherulites imposes internal mechanical stresses within the interphases, resulting in local ageing and a loss in ductility [12]. According to Maringer et al. [13], stabilizers are accumulating at the boundaries of spherulites, protecting the interspherulitic tie molecules which are essential for the ductile mechanical behaviour. Re- and post-crystallization mechanisms are also enforcing migration effects, associated with a loss in stabilizer content, especially in the early ageing stage.

Thermooxidation takes already place at ambient conditions and is significantly enhanced at elevated temperatures [14,15]. Abstraction of hydrogen from the polymer chain results in the formation of polymer radicals. Subsequent reactions lead to the generation of hydroperoxides, promoting chain scission, cross-linking and the formation of low-molecular mass products, depending on the chemical structure of the polyolefin [14,16]. As thermooxidation progresses, polyolefins experience a reduction in key properties such as elongation at break, tensile strength and impact resistance. Chain scission and cross-linking contribute to a change in molecular mass often associated with a reduction in tie macromolecule density and embrittlement of the polymeric material [12]. To enhance the processability and durability of polyolefins, various antioxidants and stabilizers can be added [17]. The optimization of polyolefin material formulation is still a main research topic [18–20].

Characterization of the ageing behaviour of polyolefinic liners is commonly based on exposure in hot air or water at elevated temperatures [17,21–25]. Adequate global ageing approaches are taking diffusion limited oxidation (DLO) effects into account [24–27]. The heterogeneous degradation mechanism was first described by Cunliffe & Davis [28] for photo-oxidative processes and later generalized by Gillen & Clough [29] and Audouin et al. [30]. Lifetime assessment approaches are based on extrapolation of ageing data from elevated temperatures to service relevant conditions [23–25]. Temperature dependency of polymers is often described by the Arrhenius equation [15,31,32]. In contrast, thickness dependency is following a potential equation [24,25]. While lifetime data of polyolefin liners have been established for PE materials, there is still a lack of data for novel PP compounds.

Hence, the main objective of this paper was to investigate the long-term behaviour of a novel PP-HTR liner material. Endurance times were determined at elevated temperatures, extrapolated to service relevant conditions and used for lifetime assessment assuming cumulative damages. A specific aim of this study was to compare state-of-the-art and novel liner materials as to their effect on the lifetime of already implemented and concepted PTES.

2. Experimental

In the following the methodological approach is described. Ageing data for state-of-the-art polyethylene high density (PE-RT) liner materials [24] and a commercially available polypropylene random copolymer (PP-R) [12,25] were taken from relevant literature. While polyethylene exhibits a more pronounced degradation behaviour in hot water, polypropylene grades are more prone to degradation in hot air [33]. For the novel high temperature resistant polypropylene (PP-HTR) with an unique stabilizer package, ageing experiments were carried out in hot air. The effect of specimen thickness on the durability of PE-RT and PP-R is well described in literature [24,25]. As to the specimen thickness, similar effects were assumed for PP-R and PP-HTR. Hence, in this study ageing experiments were only performed for PP-HTR micro-specimen with a thickness of 100 µm.

2.1. Materials, specimen and ageing conditions

A random polypropylene copolymer (PP-R), base stabilized with the phenolic antioxidant Irganox 1330 was used [12,34]. A novel formulation with an unique stabilizer package was compounded on a Leistritz ZSE 18 MAXX (Nürnberg, Germany) twin screw extruder. The compound was injection moulded to 20 x 20 cm² sheets with a thickness of 2 mm on a SmartPower 120 machine (Wittmann-Battenfeld, Kottingbrunn, Austria). Slicing of the 100 µm thick micro-specimen was carried out on an EMCO E600 (Hallein, Austria) CNC-milling machine. Therefore, a home-made cutting tool and a process, ensuring a thickness accuracy of ± 1 µm, was utilized [17,21]. Hot air ageing was performed in Binder FED 53 (Tuttlingen, Germany) heating chambers with forced air convection. The exposure temperatures were ranging from 85 to 135°C with temperature intervals of 10°C. At defined time intervals, specimen were removed and assessed as to relevant ageing indicators.

2.2. Characterization and evaluation methods

To assess stabilizer and polymer deterioration, Differential Scanning Calorimetry (DSC) was performed. Thermograms were recorded on a DSC 4000 (Perkin Elmer, Waltham, USA). Samples of approximately 1 mg were taken from the cross-section of the micro-specimen and placed into perforated 3 µL aluminum pans. Thermal analysis was carried out from ambient to 300°C at a heating rate of 10°C/min. The DSC cell was purged with synthetic air at a constant flow of 20 mL/min. For evaluation of the oxidation onset temperature (OOT) the tangent method was employed.

The end of the endurance time, associated with full embrittlement of the 100 µm thick specimen was determined by tensile testing using a Z2.5 universal testing machine (Zwick Roel, Ulm, Germany). The clamping length was 50 mm, the testing rate 50 mm/min. Ultimate mechanical failure was classified, when strain-at-break values dropped below strain-at-yield ($\varepsilon b < \varepsilon y$). At the yield point of semi-crystalline polymers, the initiation of interspherulitic damage and voiding occurs. In the post-yield regime, failure of the spherulites and rearrangement of crystal lamellae takes place [35]. Hence, the selected failure criterion of strain-at-break dropping below strain-at-yield indicates ultimate mechanical failure resulting from a reduction of interspherulitic tie macromolecule density [34]. For the investigated PP-HTR grade yielding was initiated at an applied strain of 20%.

2.3. Lifetime assessment

For lifetime estimation, a cumulative damage approach was utilized. This approach was implemented for black pigmented PP solar absorber materials in [36] and further developed in [24,25]. Lifetime assessment is based on the extrapolation of ageing data from elevated to service-relevant temperatures (see **Eq. 1**) and from 100 µm specimen to 2 mm thick liners (see **Eq. 2**) [25]. While the temperature dependency is following an Arrhenius law, the thickness effect is described by a potential equation [24,37]. The endurance time ($\mathbf{t_{endurance}}$) is dependent on the thickness **d** and the temperature **T**, whereas **A**, **B** and **C** are material constants. $\mathbf{E_A}$ is the activation energy and **R** the gas constant. As already applied by Leijström & Ifwarson [38], a cut off and then a constant value was assumed at an endurance time of 50 years.

$$\ln t_{endurance} = \ln A + \frac{1000}{T} * \frac{E_A}{R} \qquad \textbf{Eq. 1}$$

$$t_{endurance} = B \cdot d^C \qquad \textbf{Eq. 2}$$

Temperature dependent damages were accumulated. Hence, the ultimate lifetime was estimated by weighting the extrapolated endurance times with the frequency distribution of the annual temperature profile of a PTES. A more detailed explanation is given in [24,25]. While in previous studies lifetime estimates were deduced considering simplified, theoretical profiles, experimental and simulated temperature load profiles for already implemented and concepted PTES were used. The most critical temperature is at the top liner of a PTES. Hence, lifetime estimates were deduced for the top liner.

3. Results and discussion

3.1. Long-term ageing behaviour of PP-R and PP-HTR

In the following, the long-term hot air ageing behaviour of the investigated PP-HTR liner material is described and discussed at exposure temperatures of 85 to 135°C. The obtained data are systematically compared to previously published ageing data for PP-R [34]. Oxidation onset temperature (OOT) and strain-at-break are illustrated in **Fig. 1** to **Fig. 3** as a function of exposure time and temperature. While closed symbols represent intact micro-specimen, open symbols indicate full embrittlement with strain-at-break values dropping below strain-at-yield.

Oxidation onset temperatures (OOT), for PP-HTR at different hot air exposure temperatures ranging from 85 to 135°C are displayed in **Fig. 1**. Phenolic antioxidants and thiosynergists exhibit their maximum protection efficiency at temperatures of 110°C or higher [12,39]. In contrast, hindered amine light stabilizer (HALS) are typically added to improve the durability at temperatures of 100°C and below [39]. It is well described in literature, that HALS do not have a strong effect on the oxidation onset temperature or induction time [40].

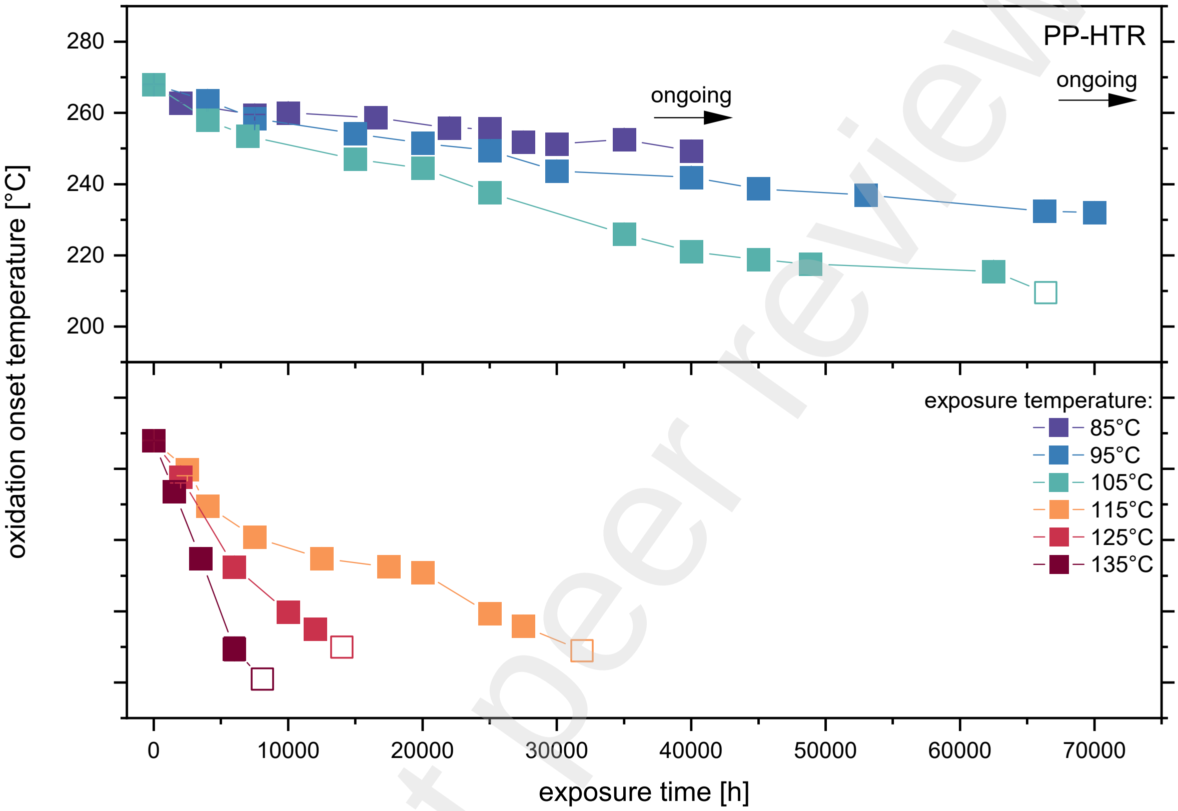

Fig. 1: Oxidation onset temperature of PP-HTR micro-specimen exposed to hot air at temperatures ranging from 85 to 135°C.

In the reference state, an initial OOT value of 268°C was deduced for the unaged PP-HTR. Interestingly, a similar value of 267°C was determined for the PP-R grade stabilized just with phenolic antioxidants [34]. Hence, the additional stabilizer package did not affect the onset of oxidation of the unaged reference material. Exposure under dry heat and elevated temperatures led to an initial drop in OOT by about 15°C. Previous studies have confirmed that an excess in stabilizer content is associated with migration and evaporation of stabilizers from the material. This effect was especially noticeable during the initial hours of exposure at elevated temperatures [34,38]. Nevertheless, the drop in OOT values was slightly lower compared to ageing data of PP-R [18], probably resulting from synergistic effects of phenolic and non-phenolic antioxidants.

After the initial drop, a linear decrease in oxidation temperature was observed, exhibiting a more pronounced slope at higher exposure temperatures. As illustrated in **Fig. 2** for selected exposure temperatures of 95, 115 and 135°C, the OOT values of PP-HTR were comparable to PP-R up to an exposure time limit. Exceeding this limit, the drop in oxidation onset temperature was more pronounced for PP-R. The limits or transitions were detected at 15,000, 10,000 and 2,500 hours for temperatures of 95, 115 and 135°C, respectively. According to FTIR measurements and the evaluation of the phenol index, describing the amount of active phenolic groups, the limit or transition in PP-R is linked to a loss of about 50% of phenolic antioxidants [12]. In associated studies [12,41] it was shown that single-oxidized degradation products of Irganox 1330 reach a content plateau of 15 to 20% prior to full embrittlement. These degradation products are primarily splitting-off derivatives which do not have a stabilizing effect. Hence, the transition point is presumably related to a critical concentration of stabilizing functional groups, or a critical molar mass degradation of the PP-R base material. The addition of the triple stabilizer package to the PP-HTR grade did not reveal this limit or transition in the OOT curve. Critical oxidation onset temperature values associated with full embrittlement of the micro-specimen were ranging from 200 to 210°C. The exposure time to achieve this critical OOT value was significantly higher for the PP-HTR material.

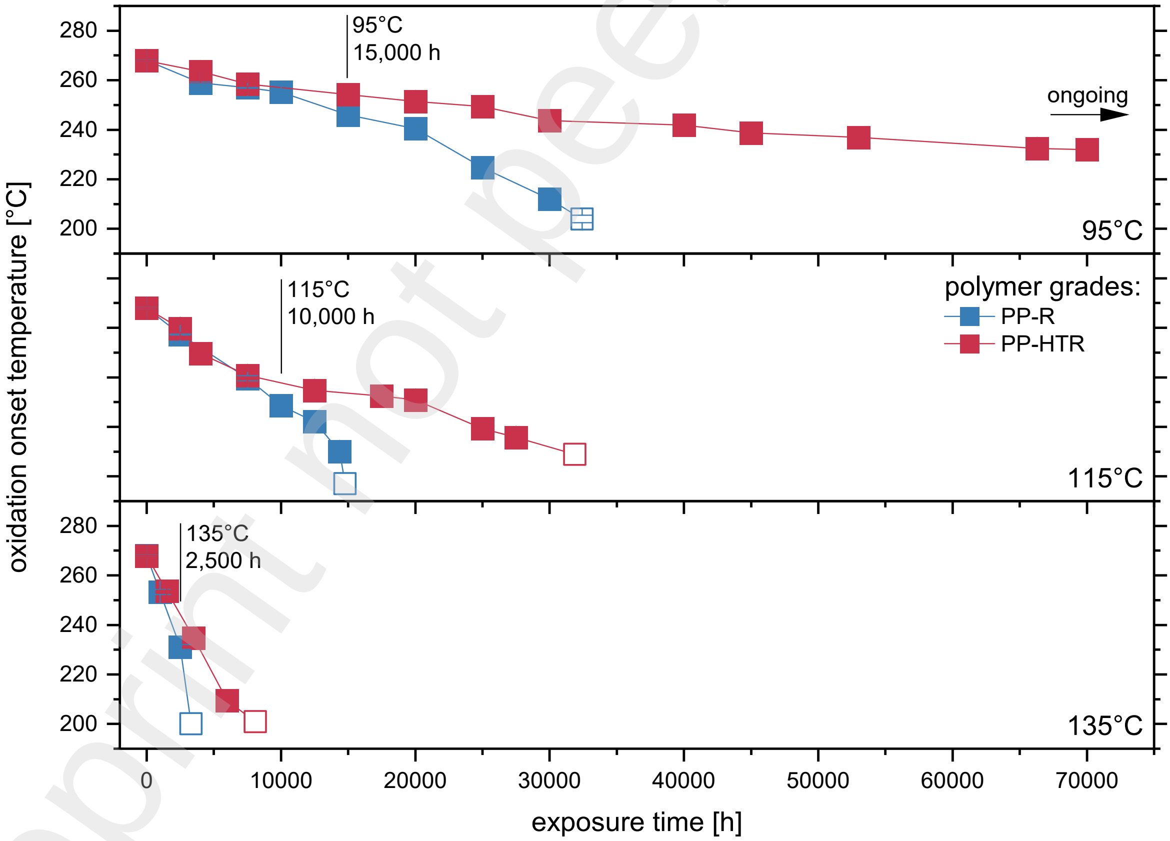

Fig. 2: Oxidation onset temperature values of PP-R and PP-HTR micro-specimen exposed to dry heat at temperatures of 95, 115 and 135°C.

Strain-at-break values of PP-HTR micro-specimen are illustrated in **Fig. 3** as a function of exposure time at temperatures ranging from 85 to 135°C. In the reference state, strain-at-break and strain-at-yield values amounted to 530 and 20%, respectively. Hot air exposure resulted in a significant decrease in strain-at-break within the early ageing stage. The initial reduction in strain-at-break is presumably related to re- and post-crystallization effects. Densification within spherulites results in the accumulation of internal mechanical stresses within the interphase or the boundary zone of the spherulites [12,35]. A similar behaviour was observed for PP-R [12,34]. Hence, the addition of the stabilizer package had no effect on the initial reduction in strain-at-break. Afterwards, a plateau of strain-at-break was discernible at 40 to 90% prior to full embrittlement indicated by open symbols.

Within the induction time prior to full embrittlement stabilizers are deteriorated. Moreover, the average molar mass of PP macromolecules is reduced associated with a decrease in tie molecule density [42]. The initial mean molar mass of the PP-R base grade was 775 kg/mol. A critical molar mass value of 300 kg/mol associated with full embrittlement was deduced by Grabmann et al. [34]. The end of the induction time and full embrittlement were achieved for PP-HTR after 8,100; 14,000; 32,000 and 65,000 hours at 135, 125, 115 and 105°C, respectively. As indicated by the arrows, ageing experiments are still ongoing for micro-specimen hot air aged at 95 and 85°C.

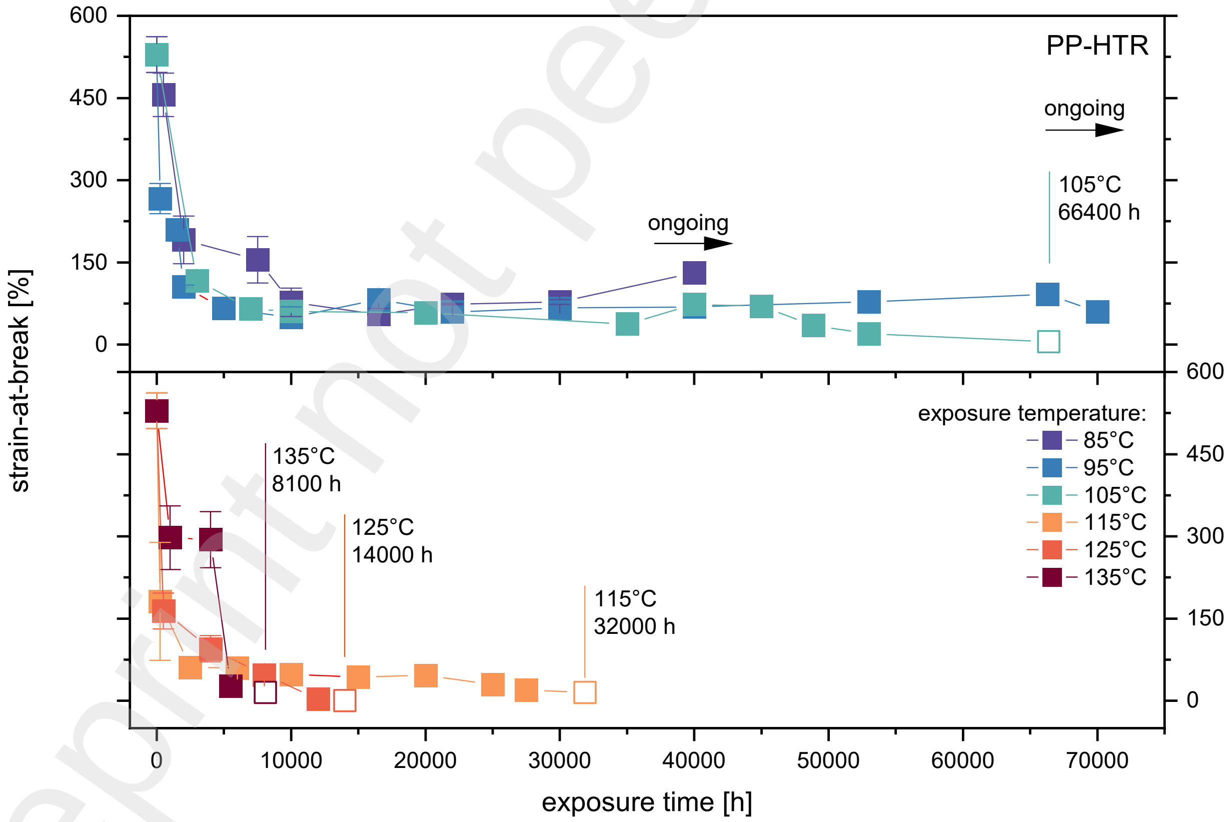

Fig. 3: Strain-at-break of PP-HTR micro-specimen exposed to hot air at temperatures ranging from 85 to 135°C.

3.2. Extrapolation of time-to-embrittlement data

Endurance times based on critical strain-at-break values of 100 µm thick specimen are plotted in **Fig. 4** as a function of reciprocal temperature. The long-term behaviour of the PP-HTR model material is compared to the commercial PE-RT [24] and PP-R [12,34] grades. For PE-RT, endurance times of 2,200; 3,900 and 5,900 hours were obtained at exposure temperatures of 115, 105 and 95°C, respectively. For the base stabilized PP-R, endurance times of 3,500; 6,000; 14,000 and 22,000 hours were reported for exposure temperatures of 135, 125, 115 and 105°C, respectively. In this study, a further endurance time data point of 32,000 hours was deduced for PP-R at an exposure temperature of 95°C (light grey circle), corroborating the Arrhenius extrapolation model. For PP-HTR, a factor of 17 or 3 longer endurance times were achieved compared to PE-RT or PP-R micro-specimen, respectively.

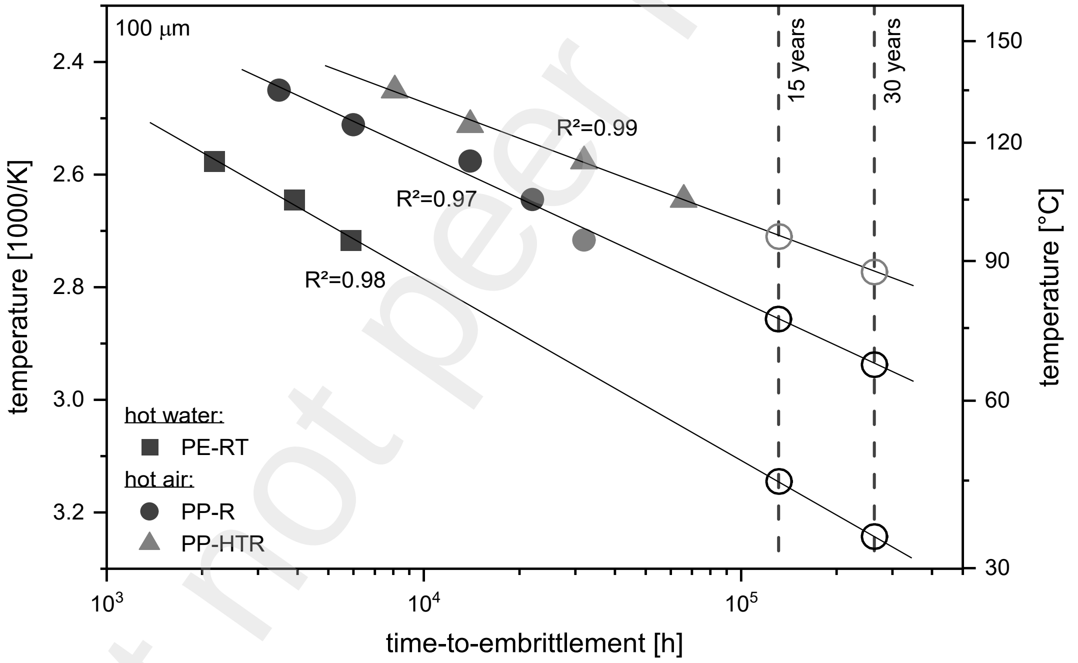

Fig. 4: Experimental endurance times and Arrhenius fits of 100 µm thick micro-specimen based on PE-RT [24], PP-R [25,34] and PP-HTR.

For PP-R micro-specimen, a stepwise Arrhenius-like behaviour with a transition temperature at 110°C and a reduced activation energy at lower exposure temperatures was reported [12]. However, the stabilizer content and not strain-at-break was monitored and extrapolated to estimate the endurance time. It was hypothesized, that the transition temperature was at the end of the inner mobility transition within crystal lamellae and at the onset of the melting peak, resulting in a difference in phenolic antioxidant compatibility [43,44]. Another explanation for the transition could be the protection efficiency of phenolic antioxidants being more effective at 110°C and higher temperatures [39].

The additional stabilizer package in PP-HTR including also non-phenolic antioxidants presumably allows to avoid the stepwise Arrhenius-like behaviour. Some non-phenolic antioxidants are characterized by a better protection efficiency at temperatures of 100°C and below [39]. Non-published ageing experiments show a significantly higher content of stabilizing groups at exposure temperatures of 95°C and below [45].

Based on linear Arrhenius fits, activation energy values $\mathbf{E_A}$ of 68.5, 75.0 and 91.5 kJ/mol with coefficients of determination $\mathbf{R^2}$ of 0.98, 0.97 and 0.99 were determined for PE-RT, PP-R and PP-HTR, respectively. A slightly lower activation energy of 52.4 kJ/mol was reported for a phenolic antioxidants stabilized PE-RT liner for landfill applications [46]. As ageing indicator the oxidation induction time (OIT) was monitored. A more service-relevant ageing study with hot water on one side and hot air on the other was carried out for a PTES PE-RT liner. The reported activation energy value of 58 kJ/mol is slightly below the value obtained in this work [47].

Buffer storages are commonly operated with a constant temperature at the top of the storage. Therefore, the maximum constant temperature allowing for an lifetime of 15 and 30 years of the micro-specimen was deduced from the Arrhenius fit. While for 100 µm thick PE-RT, a constant temperature limit of 45 and 35°C was deduced, for PP-R, 77 and 67°C and for PP-HTR 96 and 88°C were obtained.

Based on experimental ageing data, thickness extrapolation factors were reported for PE-RT [24] and PP-R [25]. An increase from 100 µm to 2 mm of thickness, resulted in a factor of up to 5 and 1.75 longer endurance times of PE-RT and PP-R respectively. The lower thickness effect of PP-R compared to PE-RT is presumably related to the lower degree of crystallinity and a higher oxygen permeability in PP-R [48]. For the investigated PP-HTR, the PP-R thickness factor of 1.75 was assumed and used for lifetime assessment.

Endurance times at a fixed temperature were estimated for 2 mm thick liners made from PE-RT, PP-R and PP-HTR grades at temperatures ranging from 60 to 90°C (see **Fig. 5**). A cut-off time of 50 years was considered. Up to a service temperature of 50, 60 and 80°C, no drop of the maximum endurance time below 50 years was deduced for PE-RT, PP-R and PP-HTR, respectively. Higher service temperatures led to a reduction in lifetime below the assumed cut-off. At 90°C, the novel PP-HTR liner material exhibited longer endurance times by a factor of 6.7 and 4.2 in comparison to the PE-RT and PP-R grades.

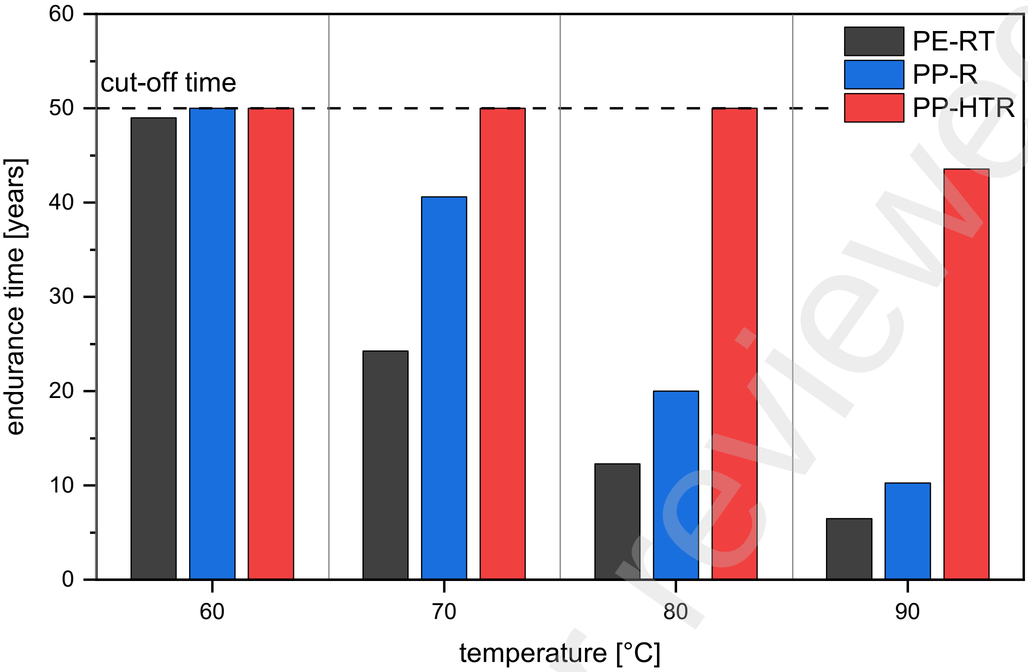

Fig. 5: Calculated endurance times for 2 mm thick liners based on PE-RT, PP-R and PP-HTR at constant temperature levels of 60, 70, 80 and 90°C.

4. PTES storages and estimated liner lifetime

In the following, temperature loading profiles are depicted (see **Fig. 6**), described and discussed for various implemented and concepted PTES. The already implemented 70,000 m³ PTES in Høje Taastrup is operating as a buffer storage with a capacity of 3,300 MWh and is linked to a transmission line that connects various heat generators (4 combined heat and power (CHP) plants, 3 waste incineration plants, reserve and peak load power plants) in the greater area of Copenhagen [9]. With up to 25 energy utilization cycles per year and a permanent temperature of 90°C at the top of the PTES [49], it is designed to optimize the electricity and heat generation of the connected power plants. The storage brings significant value by improved efficiency of CHP and waste incineration plants, reduced peak loads and bypass operation [9]. About 14,000 m² of PP-HTR liner were installed.

The seasonal thermal storage in Dronninglund is operating at a temperature range of 30 – 85°C. The 60,000 m³ pit is charged by a 37,500 m² solar collector field, bio oil boiler driven heat pump and a natural gas boiler. The storage is making a significant contribution to the cities district heating network suppling thermal energy to approximately 1,350 households [49]. For insulation around 12,000 m² of liners were needed for the pit and the lid structure.

The city of Dresden (Germany) is planing a PTES to improve the heat supply to around 120,000 households and 5,700 commercial building via the 560 km long district heating network. Four different versions with storage volumes ranging from 100,000 to 500,000 m³ are under consideration. The storage should be connected to a 70,000 m² solar collector plant. Furthermore, four gas boilers should cover the peak loads. Based on simulations, the PTES is primarily operating at 95°C (see **Fig. 6**) [50]. Dependent on the volume, polymer liners of up to 120,000 m² for the pit and the floating lid structure are required.

The PTES in Aachen-Walheim is designed as a hybrid storage, combining a buffer and a seasonal storage, with a pronounced discharge cycle in the winter month. Throughout the remaining periods, the 65,000 m³ storage should operate at a constant water temperature of 70 to 75°C at the top of the PTES (see **Fig. 6**). The facility will be powered by a solar thermal energy plant. Approximately 10,000 m² of liners are required only for the pit. For the lid structure an alternative solution is planned.

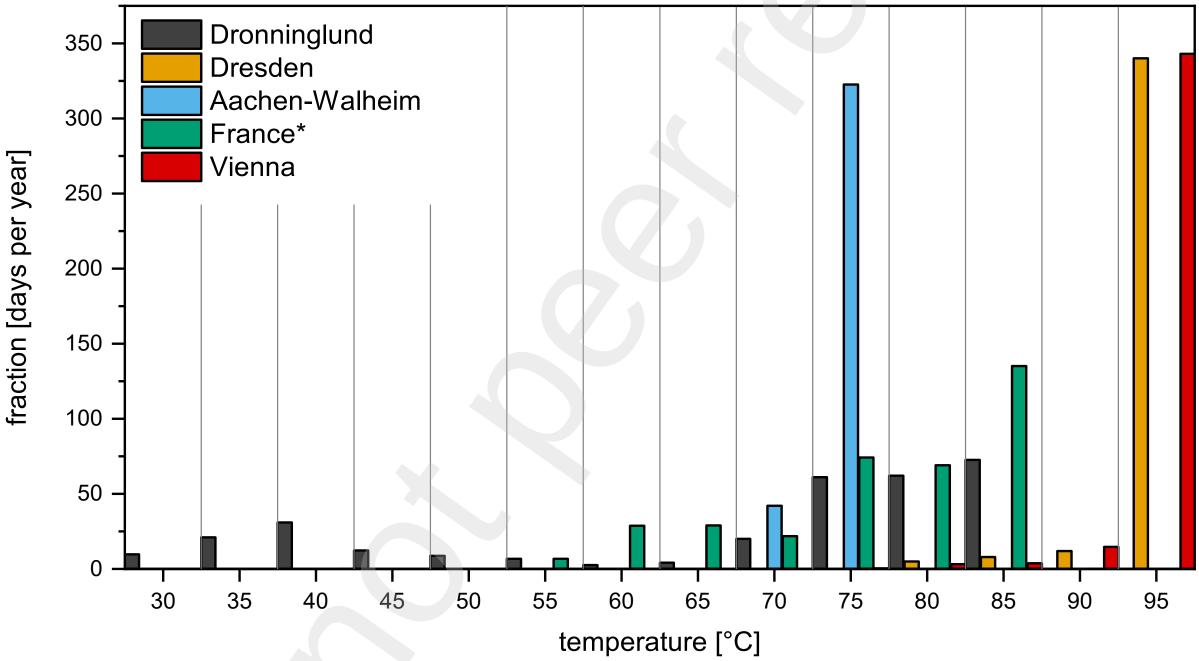

Fig. 6: Temperature loading histograms of the TES in Denmark (Dronninglund), Germany (Dresden, Aachen-Walheim), France (*not defined yet) and Austria (Vienna).

Based on a case study a 100,000 m³ PTES is under development by the company NewHeat in France. However, the specific location is not fixed yet. This PTES should store energy from a solar thermal plant and industrial waste heat. For the installation of the storage around 25,000 m² of liners are needed for the pit and the lid structure. The PTES will be operated as a seasonal storage at a temperature ranging from 55 to 85°C with a higher fraction at elevated water temperatures (see **Fig. 6**).

The project in Vienna (Austria) is designed as a tank thermal energy storage (TTES) with an overall volume of 40,000 m³. It is considered to be a buffer storage with several utilization cycles per year, operating primarily at 95°C at the top of the TTES (see **Fig. 6**). Vertical lining of the tank, using conventional polymeric liners is not possible. The high water temperature and the creep behaviour of polyolefinic materials would result in time dependent thickness reduction of the liner. Hence, concrete protection liners are preferred which allow for anchoring of the liner into the concrete wall [52].

The above mentioned storages were considered for lifetime assessment assuming cumulative damages and a liner thickness of 2 mm. Therefore, the according thickness dependency values were applied. While the PTES in Aachen-Walheim exhibited the longest lifetime, the high water temperature of up to 95°C in Dresden and Vienna resulted in the lowest values (see **Tab. 1**). The novel PP-HTR liner achieved enhanced long-term material behaviour with longer estimated lifetimes by a factor of up to 6 and 3.9 in comparison to PE-RT and PP-R, respectively. The lifetime data clearly reveal, that the well-established PE-RT grade is already at the durability limit (20 years) in less challenging storages such as Aachen-Walheim. For such storages, at least the PP-R grade is highly recommended. In case of constant service temperatures around 90°C or higher, only PP-HTR is applicable. Even a double-liner solution from PE-RT, as considered in the storage in Meldorf, or the use of PP-R liners does not allow to achieve lifetime values of at least 20 years.

Tab. 1: Lifetime estimates in years for three different liner materials based on temperature loading profiles of TES in Denmark (Dronninglund), Germany (Dresden, Aachen-Walheim), France (*location not defined yet) and Austria (Vienna).

[years]	Høje Taastrup	Dronning-lund	Dresden	Aachen-Walheim	France*	Vienna
PE-RT	6.5	17	5.0	17.8	13.2	4.9
PP-R	10.3	25.7	7.8	29.4	21.0	7.6
PP-HTR	43.6	50.0	29.9	50.0	50.0	29.5

5. Summary and conclusions

To assess the lifetime of a high temperature resistant polypropylene random copolymer (PP-HTR) liner material for pit thermal energy storages (PTES), the long-term behaviour of 100 µm thick micro-specimen was examined. Ageing experiments were conducted in dry heat at temperatures ranging from 85 to 135°C. Exposed micro-specimen were characterized by differential scanning calorimetry (DSC) and monotonic tensile testing. Ageing indicators such as the oxidation onset temperature (OOT) and strain-at-break values were deduced. Ultimate mechanical failure was defined, when the strain-at-break value dropped below strain-at-yield. So far, a maximum exposure time of 70,000 hours was achieved. The long-term material behaviour of the novel PP-HTR liner material, was compared to ageing data of a commercial polyethylene high density (PE-RT) and a phenolic base-stabilized polypropylene random copolymer (PP-R).

Exposure of PP-HTR in hot air led to an initial decrease in OOT values within the early ageing stage. This drop was primarily attributed to migration and evaporation of stabilizers. Further exposure revealed a continuous reduction in oxidation temperature. Critical oxidation onset temperature values, associated with full embrittlement of micro-specimen, were ranging from 200 to 210°C. Interestingly, the OOT values of PP-HTR were comparable to PP-R up to an exposure time limit. Exceeding this transition, the drop in oxidation onset temperature was more pronounced for PP-R. This effect was attributed to a drop in phenolic antioxidants below a critical value. Presumably, the phenolic antioxidants were protected by the additional non-phenolic stabilizers in PP-HTR.

The strain-at-break values exhibited also an initial drop, which was presumably related to re- and post-crystallization effects. Densification within spherulites could induce inter-spherulitic mechanical stresses. Subsequent to the initial drop, a plateau in strain-at-break values of around 90% was detected. Full embrittlement was reached at 135, 125, 115 and 105°C after 8,100; 14,000; 32,000 and 66,400 hours, respectively. PP-HTR exhibited up to a factor of 17 and 3 longer endurance times in comparison to PE-RT and PP-R micro-specimen, respectively.

The ageing data were extrapolated to service-relevant temperatures. Moreover, the positive effect of liner thickness was considered adequately. Assuming cumulative damages, lifetime estimates were deduced for 2 thick liners to be used for various thermal energy storages with different temperature loading profiles. Lifetime estimates were calculated for the already existing storages in Høje Taastrup and Dronninglund and for conceptualized facilities in Germany, France and Austria. Depending on the storage type and liner material, lifetime values ranging from 4.9 to 50 years were estimated. PE-RT and PP-R revealed acceptable lifetime values of about 20 years just for less critical temperature loading profiles ranging from 30 to 80°C. In contrast, a much better durability and lifetime expectancy was deduced for the PP-HTR liner, especially for more challenging temperature loading profiles and continuous storage temperatures of around 90°C or higher.

6. Acknowledgement

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