

Aging and Lifetime Assessment of Polyethylene Liners for Heat Storages – Effect of Liner Thickness

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Abstract

This paper deals with the global aging behavior and lifetime assessment of polyethylene liner materials for seasonal heat storages. Hot water aging experiments at elevated temperatures of 95, 105 and 115°C were carried out using specimens with various thicknesses of 100, 500 and 2000 µm. The aging indicator strain-at-break was monitored for up to 1500 days. The experimental hot water data were fitted by potential and Arrhenius equations referring to thickness and temperature dependency. By merging both equations a semi-empirical model was established and used for lifetime estimation of polyethylene liner materials. The low divergence of the lifetime values between experimental and calculated failure data indicates the high accuracy of the thickness/temperature-model. A lifetime value of 18 years was derived for 3 mm thick polyethylene based liner materials for solar district heating systems.

Keywords: Polyethylene liner material, Seasonal heat storage, Thickness/temperature depending model, Lifetime.

1. Introduction

The share of polymeric materials for hot water seasonal heat storages increased steadily due to lower material costs and installation costs compared to stainless steel (Köhl et al., 2012). A better competitiveness especially for big storage volumes greater than 20.000 m³ is given by replacing steel with polymeric liner materials (Heller, 2000). Regarding the material grades, the most common polymeric liner materials are based on special polyethylene grades (PE-RT) or polypropylene random copolymers (PP-R) (Grabmayer, 2014). Improved long-term stability against thermo-oxidation given by stabilization packages is essential to ensure functionality and durability at service temperatures of up to 95°C for more than 20 years (Schramm and Jeruzal, 2006; Paranoska and Pedersen, 2016). While polypropylene materials exhibit a more critical degradation behavior in hot air environment than in hot water, interestingly a reverse phenomenon was reported for polyethylene liner grades (Grabmayer, 2014).

Oven aging tests at elevated temperatures are commonly performed to evaluate the long-term thermo-oxidation behavior of polymeric materials (Gijnsman, 1994; Kahlen et al., 2010a; Olivares et al., 2010; Celina, 2013). Enhanced temperatures result in accelerated aging processes with reduced experimental time (Kahlen et al., 2010c, 2010d; Olivares et al., 2010) (Kahlen et al., 2010a; Olivares et al., 2010). Polymer aging is strongly influenced by diffusion limited oxidation (Audouin et al., 1994). Hence, a reduction of the specimen thickness leads to accelerated aging processes (Gugumus, 1996; Grabmayer et al., 2015).

So far, no comprehensive studies on temperature and thickness depending global aging behavior of polyethylene liner materials were published. Hence, it is the main objective of this paper to establish a thickness/temperature model using ultimate failure data. Lifetime assessment under service-relevant loading conditions should be executed for typical liner thicknesses of 2 and 3 mm. This is of utmost importance to clarify the durability of polymeric liner materials and to compare polyolefin liner materials for large solar-thermal district heating systems with seasonal heat storages.

2. Methodological approach

2.1 Materials, aging conditions and characterization methods

A commercial polyethylene high density grade was used. Details as to the molecular structure, morphology and the stabilizers are given in Grabmayer (2014) and Beißmann et al. (2013). The PE grade was extruded to a 2 mm thick sheet by AGRU Kunststofftechnik GmbH. Specimen with various thicknesses of 100 and 500 μm and a length of at least 150 mm were manufactured by using an automated planning technique (Grabmayer et al., 2015). Additionally, ISO 5A specimens with a thickness of 2000 μm were prepared by die-punching.

Due to the more critical aging behavior in water than in air, primarily hot water exposure was performed. The specimens were aged in closed stainless steel vessels with integrated specimen holder at temperatures of 95, 105 and 115°C using a Binder FED53 (Tuttlingen, Germany) heating chamber with forced circulation. Whenever specimens were removed from the vessels, the deionized water was changed. Four specimens were examined per aging interval.

To assess the aging behavior, tensile tests were carried out at ambient conditions using a screw-driven universal testing machine at a deformation rate of 50 mm/min. For various polymeric materials used in solar energy engineering the ultimate mechanical properties strain-at-break or tensile strength are highly sensitive indicators to monitor both, physical and chemical aging phenomena (Wallner et al., 2004; Povacz et al., 2014; Povacz et al., 2016). As aging indicator, strain-at-break was evaluated over the aging period. Ultimate failure was defined when strain-at-break values dropped below the strain-at-yield value ($\epsilon_b < \epsilon_y$). The limit value for ϵ_y was 20% for all investigated specimen thicknesses.

2.2 Modelling the thickness/temperature dependency

A semi-empirical model describing the effect of specimen thickness and exposure temperature on global aging behavior was evolved. Therefore, experimental failure data for specimens of various thicknesses (100, 500 and 2000 μm) at aging temperatures of 95, 105 and 115°C were applied. The thickness and temperature dependency was considered separately and merged. Hülsmann and Wallner (2017) used a similar approach to describe the temperature and thickness dependent water vapor permeation in photovoltaic encapsulation materials.

By using a potential function (eq. 1) the thickness dependency of the failure data was fitted. The effect of temperature on global aging behavior was considered by the well-established Arrhenius model (eq. 2). Both equations give the endurance time ($t_{\text{endurance}}$) as a function of thickness (d) or temperature (T) considering material specific constants (A, B, C), the activation energy (E_A) and the gas constant (R).

$$t_{\text{endurance}} = B * d^C \quad (\text{eq. 1})$$

$$\ln t_{\text{endurance}} = \ln A + \frac{1}{T} * \frac{E_A}{R} \quad (\text{eq. 2})$$

The thickness and temperature dependent endurance time is calculated by a two dimensional model (eq. 3). Here, variables with index “0” are experimental values whereby C and E_A are calculated material specific constants from eq. 1 and 2.

$$t_{\text{endurance}} = \frac{t_0}{d_0^C} * e^{\frac{E_A}{R} * (\frac{1}{T} - \frac{1}{T_0})} * d^C \quad (\text{eq. 3})$$

2.3 Lifetime assessment

For lifetime estimation a cumulative damage approach was used, established by Wallner et al. (2016) for black-pigmented PP solar absorber materials. The lifetime assessment approach is based on the simulation of temperature loading profiles for liner materials, the extrapolation of experimental aging data from elevated temperatures to service relevant temperatures and the accumulation of damages at different temperature levels. Temperature loading profiles for seasonal heat storages are dependent on the plant type. As minimum temperature level 50°C was considered for the storage temperature in winter months. Temperature of the storage system increases during warm-weather months and reaches maximum temperature level of 85°C in summer (see Fig. 1). Comparable loading profiles were assumed by Ochs (2008) and deduced for seasonal pit storages in Denmark (Paranovska and Pedersen, 2016).

Experimental aging data obtained at 115, 105 and 95°C were extrapolated to service relevant temperatures (50

to 85°C) using the linear Arrhenius fit approach. Various aging processes and temperature degradation mechanisms as described by Gugumus (1999), Celina et al. (2005), Hoàng and Lowe (2008) and Kahlen et al. (2010c, 2010d) were neglected. According to ISO 13760 a cumulative damage model was used to calculate lifetime values. The theoretical temperature loading profile was transformed to frequency distributions. The lifetime was derived by weighting the frequency distributions with extrapolated endurance times.

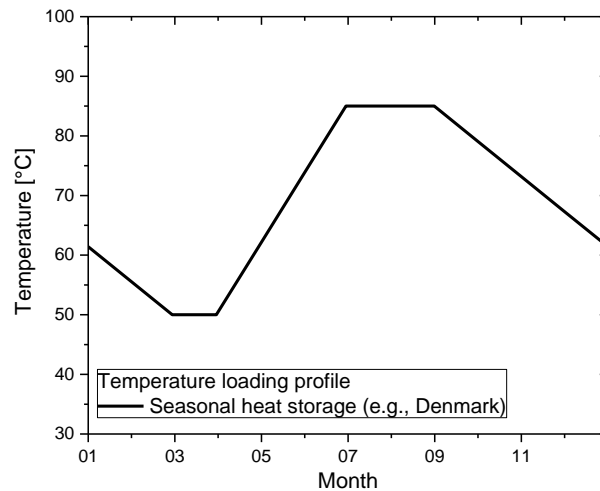


Fig. 1: Assumed temperature loading profile for a seasonal heat storage in Northern hemisphere.

3. Results and discussion

3.1. Hot water aging behavior of the PE liner material

Aging data for up to 900 days in hot air and hot water for micro- and macro-sized specimens are based on previous investigations of Grabmayer et al. (2014). The main result of this study was that the investigated polyethylene liner material revealed a more critical aging behavior in hot water than hot air. Based on these results it was decided to focus on hot water aging. While all specimens were embrittled at 115°C within up to 443 days, no failure for 2000 µm specimens at 95°C were obtained within 1500 days of exposure. These aging experiments are still ongoing.

Figure 2 depicts strain-at-break values of the investigated 100 and 500 µm thick PE liner grade as a function of aging time in hot water at elevated temperatures. Ultimate failure with strain-at-break values below yield point (20%) is indicated with open symbols in the chart. The unaged 100 and 500 µm specimens revealed high ductility with strain-at-break values up to 1400%. Due to different specimen thickness, the unaged 500 µm specimens exhibited slightly lower strain-at-break values. A significant drop in strain-at-break values appeared after initial aging within the first few days. This drop was more pronounced for the 100 µm specimens at all investigated exposure temperatures. This reduction in ultimate strain is presumably related to crystallization effects and higher interspherulitic, internal stresses. In course of aging, strain-at-break values leveled off at about 750 and 1250% for 100 and 500 µm thick specimens, respectively. These plateaus are more pronounced for thicker specimens and lower exposure temperatures. Subsequently, a drop of strain-at-break values was observed resulting in ultimate failure for 115 and 105°C exposure. Interestingly, for 95°C aging experiments a second plateau with strain-at-break values of 25 to 150% was obtained before embrittlement occurred. Ultimate failure first appeared at 115°C after 91 days for 100 µm specimens. Increasing specimen thickness resulted in longer aging times up to 278 and 443 days for 500 and 2000 µm specimens, respectively. Hence, diffusion limited oxidation processes as postulated by Audouin et al. (1994) or Celina (2013) were also ascertained for the investigated PE grade. An less pronounced effect of specimen thickness on endurance times was also described by Grabmayer et al. (2015) for different polypropylene grades. The experimental failure times of the investigated PE liner material of different thicknesses are summarized in Table 1. Up to 1500 days no embrittlement occurred at an exposure temperature of 95°C for 2000 µm specimens. In 115°C hot water a reduction of thickness from 2000 to 100 µm (factor 20) and 500 to 100 µm (factor 5) resulted in a 4.9 and 3.1

times accelerated aging, respectively. Acceleration factors of 5.5 and 2.7 were deduced by exposing to hot water at 105°C. For aging in 95°C hot water an acceleration factor of 3.1 was derived for a thickness reduction from 500 to 100 µm. Compared to data provided by Grabmayer et al. (2015) or Povacz (2014) for polypropylene, for the investigated PE liner material a more pronounced specimen thickness dependency on global aging behavior for similar thickness reduction and exposure temperature was obtained. The acceleration factors are below 2 for PP specimen with comparable thickness. Based on these results, it was unambiguously confirmed that localized aging effects play a significant role in polyethylene oxidation as pointed out by Audouin et al. (1994) or Celina (2013).

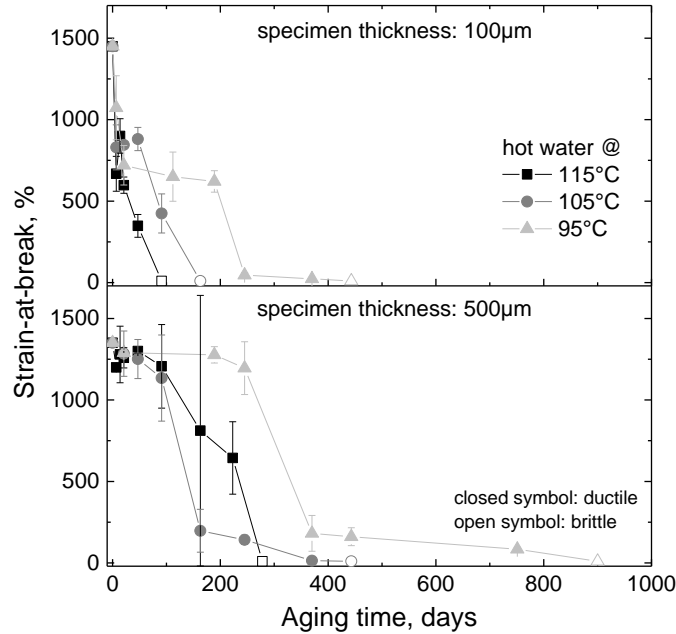


Fig. 2: Strain-at-break of micro-sized PE specimens with a thickness of 100 and 500 µm as a function of aging time exposed in hot water at 115, 105 and 95°C.

Tab. 1: Embrittlement times of PE liner specimens with varying thickness in hot water at 115, 105 and 95°C.

Specimen thickness, µm	Failure time in days in hot water at		
	115°C	105°C	95°C
100	91	163	245
500	278	443	751
2000	443	900	> 1500

3.2. Theoretical model for thickness and temperature dependency

The experimental aging data in hot water at different temperatures and for various PE specimen thicknesses were used to evolve a semi-empirical model. Therefore, the factors specimen thickness and exposure temperature were considered separately and finally merged to a two-dimensional model. Figure 3 depicts the dependency of failure time as a function of specimen thickness in hot water at 115, 105 and 95°C. The fits of the experimental data with potential functions resulted in high coefficients of determination. No embrittlement was observed for 2000 µm specimens in 95°C hot water within 1500 days, so fit parameters gathered from 115 and 105°C aging data were used to implement the model. A significant temperature dependent difference was deduced for the fit parameter B. The material specific constant C was calculated and determined with 0.5522 for the semi-empirical model. For C a temperature induced deviation of <5% was ascertained. Hence, an arithmetic value was deduced and used for the two-dimensional model. The validity and reliability of this parameter will be further improved by continuation of the aging experiments at 95°C.

Experimental aging data and related Arrhenius fittings as a function of temperature are plotted in Fig. 4. Slightly thickness dependent E_A/R -ratios ranging from 7.1 to 10.4 x10³ K were derived. The E_A/R -ratios were lower for the thinner specimen, which already failed at all investigated temperatures. Due to non-failure of 2000 µm thick

specimens at 95°C within 1500 days, extrapolation was done by only two aging data points resulting in a higher E_A/R value. By using Arrhenius fit parameters gathered from 100 and 500 μm thick specimens an average value of $7.1 \times 10^3 \text{ K}$ was used for the two-dimensional model. A specimen thickness dependent E_A/R -ratio can be implemented in the semi-empirical model finishing aging experiments at 95°C. The obtained activation energies are in the range from 59 to 86 kJ/mol. These values are comparable to data given for polyolefins (Kahlen et al., 2010b), but slightly lower than data for specific polyethylene grades (Anderson and Freeman, 1961; Peterson et al., 2001; Gao et al., 2003; Mueller and Jakob, 2003).

As zero or reference values the endurance time at a thickness of 500 μm and a temperature of 105°C were selected. These reference values resulted in best reproduction of experimental values and lowest deviations between theoretical and experimental endurance times. The comparison of the experimental and theoretical values of thick specimens at low temperatures (2000 μm at 105°C and 500 μm at 95°C) revealed a deviation of about 10%, reflecting the uncertainty of the model. Improved accuracy will be achieved by continuation of the experiments at 95°C until ultimate failure of 2000 μm specimens. Figure 5 depicts the calculated endurance times depending on various specimen thicknesses and a wide range of hot water temperature based on equation 3. It can be clearly seen for the plotted range, that the specimen thickness has also a significant impact on the failure times. At 95°C the expected endurance time is compared to 100 μm specimens a factor of 5 and 7 higher for 2 and 3 mm liners, respectively.

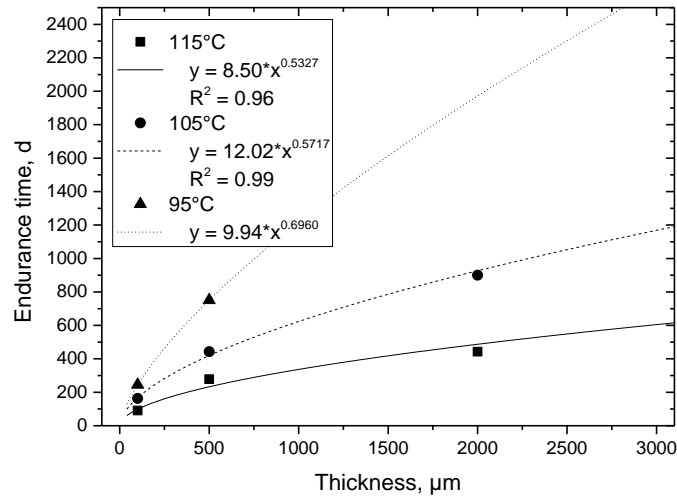


Fig. 3: Experimental endurance time dots and potential fit for aging of PE specimens with varying thickness in hot water at 115, 105 and 95°C.

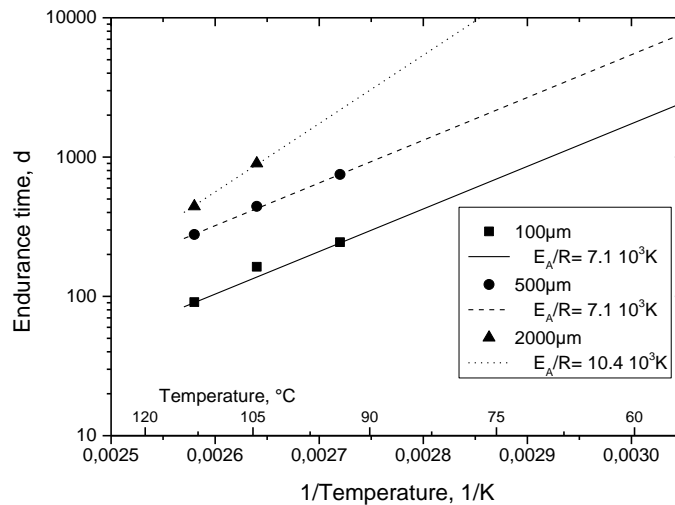


Fig. 4: Experimental endurance time dots and Arrhenius fit for 100, 500 and 2000 μm thick specimens at different temperatures.

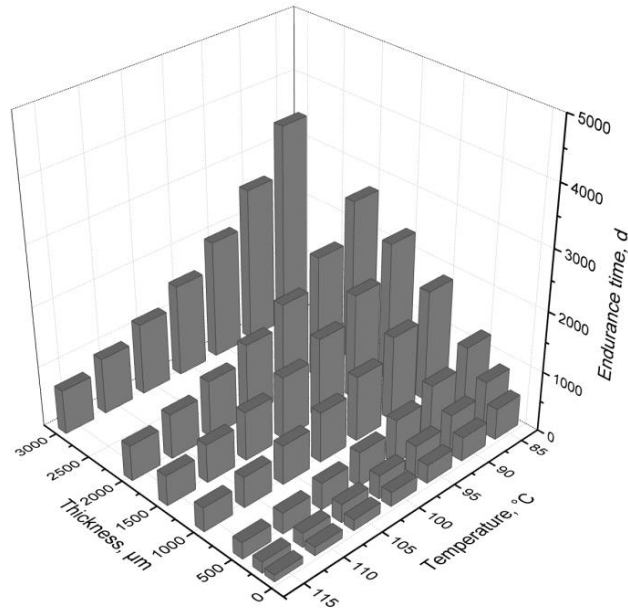


Fig. 5: Calculated endurance times of the investigated polyethylene liner material depending on specimen thickness (100 to 3000 μm) and hot water temperature (85 to 115°C).

3.3 Estimated lifetimes for PE liners

To deduce the lifetime of polyethylene liner materials experimental and theoretical, temperature dependent endurance times were considered. In Fig. 6 the experimental (filled symbols) and theoretical (open symbols) endurance times are displayed for a commercially relevant liner thickness of 2 mm and the reference thickness 500 μm. Additionally, theoretical embrittlement times for a 3 mm thick PE liner are plotted. The closed grey symbol indicates the current maximum exposure time of the non-failed 2000 μm specimens in hot water at 95°C. A good agreement of experimental and theoretical endurance times was obtained with slightly (~10%) overestimated theoretical embrittlement times for the 2 mm thick specimen. By weighting the temperature dependent endurance times with the frequency distribution of the seasonal heat storage lifetime values of 7, 15 and 18 years were obtained for liner thickness of 500, 2000 and 3000 μm. The lifetime values of this study are slightly lower than lifetime estimates published by Paranovska and Pedersen (2016) for polyethylene liners in seasonal storages of Danish solar district heating systems. The deviation of <20% is attributable to different aging and evaluation procedures and other polyethylene material formulations. However, the results of our and the Danish study are in a comparable lifetime range.

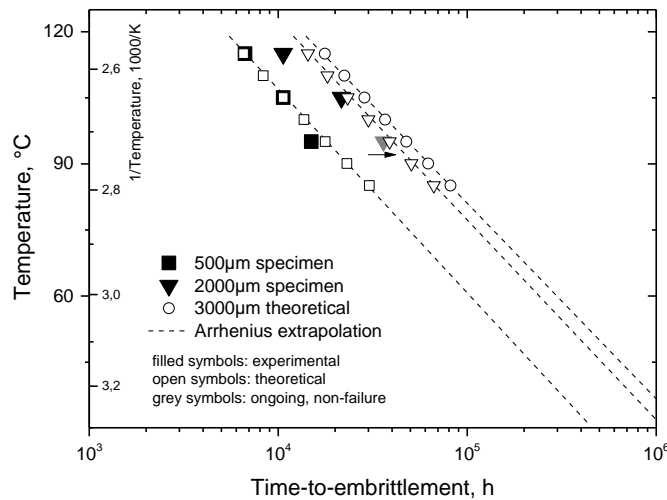


Fig. 6: Experimental and calculated failure times for 500 and 2000 μm thick PE liners.

4. Summary and conclusion

To assess the lifetime of a polyethylene liner material grade, experimental failure data of 100, 500 and 2000 μm thick specimens were gathered at elevated temperatures in hot water. The experimental aging data were used to implement a semi-empirical thickness/temperature-model using a potential and an Arrhenius fit. As a result endurance times for polyethylene liner specimens in a wide range of thickness and temperature (100 to 3000 μm , 85 to 115°C) were derived. Lifetime values were deduced by weighting the endurance times with a temperature loading profile of seasonal heat storages in Danish solar district heating systems.

The polyethylene specimens were exposed to the more critical environment hot water at 95, 105 and 115°C. The strain-at-break values dropped within the first aging interval which was mainly attributed to physical recrystallization mechanisms. After the initial drop a plateau was obtained which was more pronounced at lower exposure temperatures and for thicker specimens. Ultimate failure characterized by full embrittlement was significantly thickness and temperature dependent. A factor of 5 and 3 shorter embrittlement times were discerned by reducing specimen thickness by a factor of 20 and 5 (2000 to 100 μm , 500 to 100 μm), respectively. Similar acceleration factors were obtained for the exposure temperatures of 95 and 105°C. This thickness dependency was fitted with potential functions with a slightly temperature dependent exponent. The effect of temperature was described by an Arrhenius fit. Minor differences in activation energy for hot water exposure at 115 and 105°C were calculated. The implemented two-dimensional model for thickness and temperature dependency was corroborated.

Lifetime values of 15 and 18 years were deduced for PE liners with a thickness of 2 and 3 mm, respectively. Compared to published values for currently used polyethylene liner materials a slightly lower performance was obtained for the investigated polyethylene grade mainly related to differences of the material grade, aging conditions and the failure criterion. Hence, it is concluded that current PE grades reveal sufficient performance for pit storages. However, for insulated tank storages with higher operating temperatures a new class of polymeric liner materials has to be developed. As described in an associated study (Grabmann et al., 2017) polypropylene copolymers are a potential alternative.

5. Acknowledgment

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