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Effect of thickness and temperature on the global aging behavior of polypropylene random copolymers for seasonal thermal energy storages

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ABSTRACT

This paper deals with the global aging behaviour of a polypropylene random copolymer liner material for seasonal thermal energy storages. Hot air aging experiments at elevated temperatures of 95 °C, 115 °C and 135 °C were carried out using micro-sized specimens with thicknesses ranging from 50 to 2000 µm. The aging indicator strain-at-break was monitored for an exposure of up to 1500 days. Potential and Arrhenius equations were used to fit the experimental hot air aging data referring to thickness and temperature dependency. A semi-empirical model was established and used to assess the lifetimes of polypropylene based thermal energy storage liners. The high quality of the thickness/temperature-model was approved by low divergence of the lifetime values between experimental and modelled failure data. Depending on the temperature loading profile of the seasonal thermal energy storage lifetime values ranging from 20 to 47 years were deduced for a PP liner with a thickness of 2 mm.

1. Introduction

In the most recent solar thermal district heating plant projects in Denmark, polymeric materials are used as liners for thermal energy storages (Köhl et al., 2012). In contrast to stainless steel, polymeric liner materials exhibit a better competitiveness especially for big storage volumes greater than 20,000 m^3 (Heller, 2000). While polyethylene grades (PE-RT) are well established, special PP grades (PP-R; polypropylene random copolymer) with unique crystalline structures resulting in improved impact toughness or long term creep resistance are under development (Grabmayer, 2014; Povacz et al., 2016). The long-term stability against thermo-oxidation is essential to ensure functionality and durability of hot water storages at service temperatures up to 95 °C for at least 15–20 years (Köhl et al., 2012; Ochs, 2008; Paranovska and Pedersen, 2016). While polyethylene materials exhibit a more critical degradation behaviour in hot water environment than in hot air, interestingly a reverse phenomenon and an overall better global aging performance was reported for special polypropylene grades (Grabmayer, 2014).

The long-term thermo-oxidative behaviour of polymeric materials is commonly investigated by using oven aging test at elevated temperatures (Gijsman, 1994; Kahlen et al., 2010a; Olivares et al., 2010; Celina, 2013). Diffusion limited oxidation is an important factor of polymer aging and strongly influenced by the thickness of the specimen (Audouin et al., 1994; Grabmayer et al., 2015). As pointed out by Gugumus (1996) under accelerated aging conditions the surface regions are significantly more affected by aging processes than the bulk material. Hence, the reduction of the specimen thickness is an interesting alternative for accelerated, lab-scale material degradation testing (Faulkner, 1986; Fayolle et al., 2000; Povacz, 2014). Gijsman (1994) carried out a comprehensive study on the effect of specimen thickness on the aging behaviour and ascertained a pronounced effect for polypropylene grades depending on the stabilizer package. Other options for acceleration of thermo-oxidative degradation are to enhance the temperature or the oxygen pressure (e.g., (Grabmayer et al., 2014). So far, no comprehensive studies on the effect of both, temperature and thickness, on the long-term aging behaviour of polypropylene liner materials were published. Hence, it is the main objective of this paper to evaluate the effect of thickness and temperature on the global aging behaviour of polypropylene liner materials with special crystalline morphology. Using ultimate failure data a thickness/temperature model should be established and used to assess the lifetime under service-relevant loading conditions. This is of utmost importance for reliable market introduction of PP liner materials for large solar-thermal district heating systems with seasonal storages. Most recent projects in Denmark or Germany used polyethylene as liner material with a

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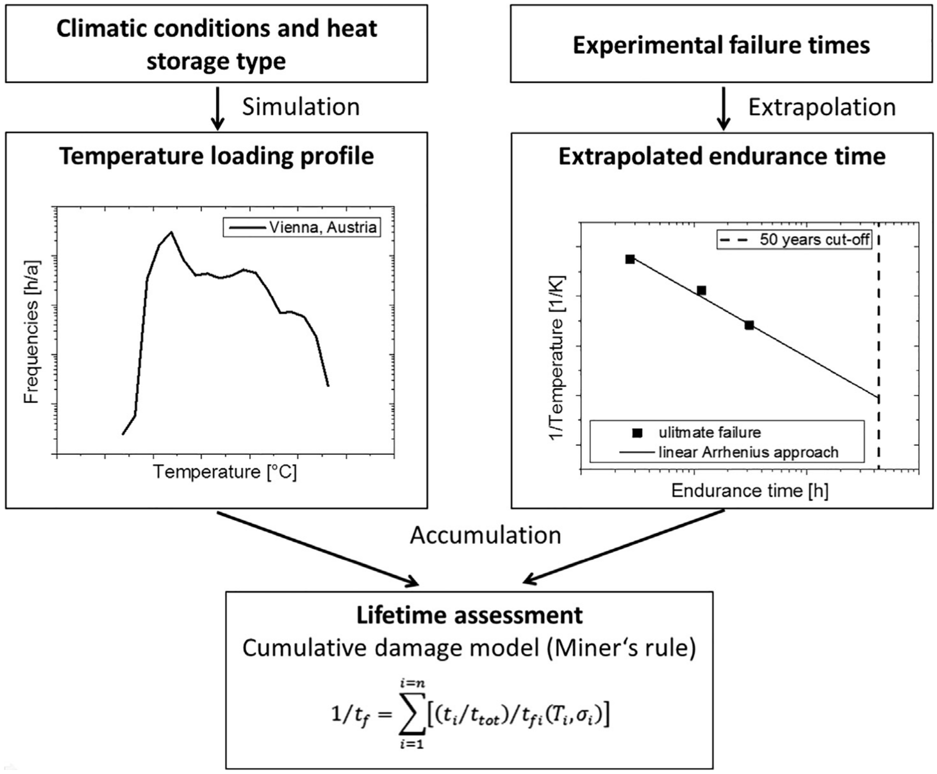

Fig. 1. Lifetime assessment approach based on the simulation of loading profiles, the extrapolation of experimental aging data and the accumulation of damages (EN ISO 13760).

maximum storage temperature of 90 °C. So far, only limited experience on the long-term performance of polymeric liner materials was gained within an actual operation period of about 10 years.

2. Methodological approach

2.1. Material, aging conditions and characterization

A commercial PP random copolymer (PP-R) with base stabilization commonly used in piping applications was used. Details as to the molecular structure, morphology and the stabilizers are given in Grabmayer (2014) and Beißmann et al. (2013). The PP-R grade was extruded to a 2 mm thick sheet. Using an automated planning technique (Grabmayer et al., 2015) micro-sized specimens with a length of at least 150 mm and thickness values of 50 µm, 200 µm and 500 µm were manufactured. ISO 5A specimens with a thickness of 2000 µm were prepared by die-punching.

Due to the more critical aging behaviour in hot air than water, primarily hot air exposure was performed. Therefore, specimens were exposed in a Binder FED53 (Tuttlingen, Germany) heating chamber with forced circulation at temperatures of 95 °C, 115 °C and 135 °C. Four specimens were examined per aging interval.

To evaluate the aging behaviour, tensile tests were carried out at room temperature using a screw-driven universal testing machine at a deformation rate of 10 mm/min. As aging indicator, strain-at-break was monitored over the aging period (e.g., (Wallner et al., 2004; Kahlen et al., 2010d). Ultimate failure was classified when strain-at-break values dropped below strain-at-yield value ($\varepsilon_b < \varepsilon_y$), which was 17% for the unaged specimens.

2.2. Modelling the thickness/temperature dependency

To develop a semi-empirical model describing the effect of specimen thickness and temperature on global aging behaviour, experimental failure data were determined for specimen of differing thickness (50 µm, 200 µm, 500 µm and 2000 µm) and at temperatures of 95 °C, 115 °C and 135 °C. The thickness and temperature dependency on global aging behaviour was considered separately and merged. A similar approach was implemented by Hülsmann and Wallner (2017) to describe the temperature and thickness dependent permeation in photovoltaic encapsulation materials.

The thickness dependency of the measured failure data was fitted by a potential function (Eq. (1)). To describe the temperature effect the well-established Arrhenius model was considered (Eq. (2)). In Eqs. (1) and (2) the endurance time ($t_{endurance}$) as a function of thickness (d) or temperature (T) is modelled considering material specific constants (A, B, C), the activation energy (E_A) and the gas constant (R).

$$t_{endurance} = B \cdot d^C \tag{1}$$

$$\ln t_{endurance} = \ln A + 1/T \cdot E_A/R \tag{2}$$

The thickness and temperature dependency of global aging behaviour were merged assuming a two dimensional model (Eq. (3)) to describe the endurance time. Here, variables with index "0" are experimental values whereby C and E_A are calculated material specific constants from Eqs. (1) and 2.

$$t_{endurance} = \frac{t_0}{d_0^C} \cdot e^{\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \cdot d^C \tag{3}$$

2.3. Lifetime assessment

For lifetime estimation a cumulative damage approach was used implemented 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 (see Fig. 1). Based on climatic conditions