

EVALUATION OF ACCELERATED AGING TEST METHODS FOR POLYMERIC MATERIALS IN SOLAR THERMAL APPLICATIONS

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1. Introduction

The long-term thermal stability (LTTS) of polymers is a major criterion for their applicability in solar thermal systems. For example, heat storage applications require a maximum service temperature of about 95°C. To ensure for a proper service, adequate test and evaluation procedures are needed to guard against excessive aging and premature failure. High temperature aging on a specimen level in application relevant environmental conditions is a common approach to evaluate the LTTS of polymeric materials. As shown in previous studies (Kahlen et al., 2010), aging testing on specimen level correlates well with aging results derived from more expensive tests on a component level. However, aging tests on common specimens with application relevant material thickness are usually time-consuming and limited in acceleration by simple enhancement of the testing temperature. Hence, advanced testing concepts are needed for efficient material screening for new applications in solar thermal systems. In the multi-partner cooperative research project *SolPol-1* funded by the Austrian Climate and Energy Fund (KLI:EN) various concepts for accelerated aging testing of polymeric materials in solar thermal applications are currently under development and evaluation.

In the literature, sample thickness and geometry are considered to be two important parameters that strongly influence polymer oxidation, with thinner and cylindrical samples showing higher loss rates of stabilizers as well as higher rates of oxidation than thicker and film-like samples (Schlotter and Furlan, 1992; Billingham and Calvert, 1980). For example, Billingham and Calvert (1980) estimated that the stabilizer loss occurs at least ten times faster in 100 μm thick film than in a 1 mm thick film for the common antioxidant Irganox 1010 in LDPE at room temperature. Hence, within this paper the main focus is to evaluate a testing approach based on micro-sized specimens with thickness dimensions in the μm range well below the nominal component thickness for polyolefin materials used in heat storage tanks.

2. Experimental

A Polyolefin (PO)-based model polymer system with systematic variation of the long-term thermal stabilizer packages (i.e., antioxidants (AO); see Tab. 1) was extruded to 2 mm thick sheets, which are applied by FSAVE (Kassel, GER; wp.fsava.de) for modular heat storage tanks.

Tab. 1: Investigated PO-based material formulations and designations

PO formulation no.	Additional stabilizer	
00	none	
03	AO1	AO3
04	AO1	AO4
08	AO2	AO3
11	AO2	AO4

From the 2 mm thick sheets, on the one hand die-punched specimens with a thickness of 2 mm (type 5a according to ISO 527) were taken (Wallner et al., 2010). On the other, procedures for the preparation of micro-sized specimens with a thickness of about 200 μm were implemented and used. Figure 1 shows the apparatus for the preparation of micro-sized specimens by manual planing which is composed of a planing tool running in a guide.

The aging behavior of the macro-sized specimens was investigated within the master thesis of A. Hagauer (2010), and her results are used for comparison with the data generated as part of the present study (i.e., test conditions were kept identical).



Fig. 1: Manual planing apparatus

Within this study the micro-sized specimens were exposed to hot air at 135°C. Specimens were removed in constant intervals and characterized by mechanical (tensile test) and thermo-analytical methods (Differential Scanning Calorimetry (DSC)). Tensile tests were carried out on the screw-driven tensile test machine Zwick Z2.5 (Zwick GmbH & Co. KG, Ulm, D) at ambient temperature (25°C). The test speed was 50 mm/min. Tensile test data were evaluated with respect to ultimate stress and strain values.

In addition, DSC measurements were carried out on a Perkin Elmer DSC 4000 (Perkin Elmer Instruments GmbH; Überlingen, D) under constant flow of synthetic air of 20 ml/min at a heating/cooling rate of 10 K/min. Samples were first heated from 30°C to 180°C, then cooled to 30°C and heated again until oxidation started.

3. Results

3.1. Specimen quality

The thickness of the planed micro-sized specimens was chosen to be 200 μm which is one tenth of the thickness of the macro-sized ISO 527 specimens. Manual planing of the extruded PO sheets yielded thicknesses between 190 and 210 μm . Figure 1 shows representative stress-strain curves for the 5 materials tested. As the base polymer is identical in all material systems, the differences in yield stress and post-yield behavior are most likely due to slight variation of thickness alongside the specimens due to the manual technique of sample preparation.

Table 2 lists the ultimate mechanical values for unaged macro-sized as well as micro-sized specimens. The stress-at-break σ_B and strain-at-break ε_B values for micro-sized specimens show standard deviations up to 12 %. Although the stress-strain curves as well as the ultimate mechanical properties of unaged micro-sized specimens within a material test series were found to be quite reproducible, further improvements in specimen preparation (i.e., more homogeneous thickness of micro-sized specimens) may help to reduce the data scatter. The different values in yield stress and ultimate properties between the micro-sized specimens and the macro-sized specimens may be attributed to geometry or orientation effects. Further investigations are needed to clarify this influence. The melting enthalpy and oxidation temperature of the materials show no significant differences between macro- and micro-sized specimens (see Tab. 3). Hence, uniform sample preparation can be concluded from tensile test and DSC measurements.

Tab. 2: Ultimate mechanical properties stress at break σ_B and strain at break ε_B for macro- and micro-sized tensile specimens (data for macro-sized specimens taken from Hagauer (2010))

No.	$\sigma_{B,\text{macro-sized}}$ (MPa)	$\varepsilon_{B,\text{macro-sized}}$ (%)	$\sigma_{B,\text{micro-sized}}$ (MPa)	$\varepsilon_{B,\text{micro-sized}}$ (%)
00	40,3	431	$28,8 \pm 0,7$	885 ± 70
03	41,3	468	$28,8 \pm 2,3$	802 ± 93
04	42,1	476	$28,5 \pm 1,1$	778 ± 31
08	42,3	465	$30,9 \pm 1,5$	879 ± 36
11	40,9	466	$27,7 \pm 1,5$	776 ± 41

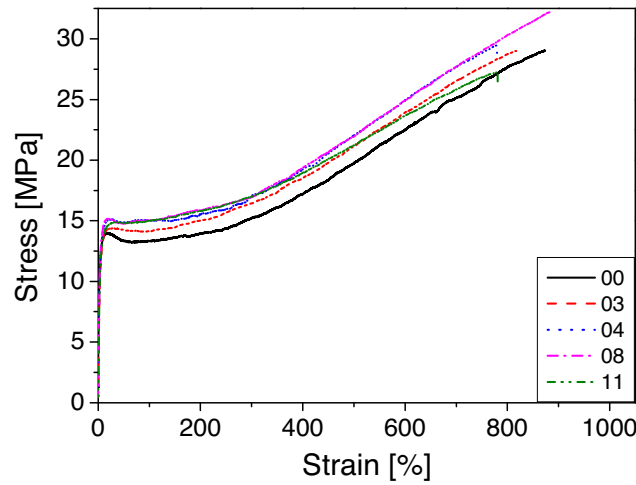


Fig. 2: Representative stress-strain curves of the micro-sized specimens for materials 00, 03, 04, 08, 11

Tab. 3: Melting enthalpy ΔH_M and oxidation temperature T_{OX} of macro- and micro-sized tensile specimen (data for macro-sized specimens taken from Hagauer (2010))

No.	$\Delta H_{M,macro-sized}$ (W/g)	$\Delta H_{M,micro-sized}$ (W/g)	$T_{OX,macro-sized}$ (°C)	$T_{OX,micro-sized}$ (°C)
00	62,5 ± 0,8	70,9 ± 5,4	268 ± 1	269 ± 0
03	69,4 ± 8,2	67,4 ± 5,9	282 ± 1	281 ± 0
04	66,3 ± 4,2	70,9 ± 2,7	283 ± 0	280 ± 0
08	72,2 ± 9,5	66,3 ± 10	277 ± 1	278 ± 0
11	64,4 ± 4,7	68,3 ± 4,7	278 ± 0	276 ± 1

3.2. Aging behavior

For macro- and micro-sized specimens the effect of hot air exposure at 135°C on the oxidation temperature and the strain-at-break values is displayed in figs. 3 and 4. While the oxidation temperatures of the unaged reference materials (00, 03, 04, 08, 11) are in good agreement for micro- and macro-sized specimens, the decrease of oxidation temperature as a function of exposure time appears to be significantly different and depends on the specimen thickness. For the macro-sized specimens a continuous reduction of T_{OX} is observable in fig. 3. After about 100 days of exposure time the materials can be differentiated into two classes with 08 and 11 exhibiting higher oxidation temperatures than 00, 03 and 04. For the micro-sized specimens the oxidation temperature levels off after an initial drop to values of about 254°C to 264°C. Again, higher oxidation temperatures are found for the materials 08 and 11 compared to 00 and 03. The different reduction in oxidation temperature for macro- and micro-sized specimens is presumably an indicator for different aging mechanisms depending on specimen type.

Strain-at-break values ε_B for the unaged macro-sized specimens are between 430 % for material 00 to 476 % for material 04. In contrast, in the reference state, micro-sized specimens exhibit significantly higher strain-at-break values ranging from 776 % for material 11 to 879 % for material 08. The higher initial values of the micro-sized specimens may be attributed to geometry effects or differences in specimen quality. Due to exposure at 135°C, for all materials and independent of the specimen type an initial drop within the first testing interval is observable which can be related to physical aging effects (e.g., postcrystallisation or crystal phase transformation). While for the investigated micro-sized specimens no further drop in strain-at-break values was obtained within exposure times up to 43 d, the macro-sized specimens of some materials (i.e., 00, 03 and 04) exhibit a further significant drop in strain-at-break associated with the embrittlement. As indicated by the oxidation temperature and also by the strain-at-break values after 180 d, the investigated materials can be differentiated into two classes with 00, 03 and 04 showing a more significant degradation than materials 08 and 11. For the micro-sized specimens the exposure times were too short to distinguish the degradation behavior of the various materials. The aging tests for the micro-sized specimens are still ongoing. From the data obtained so far for micro- and macro-sized specimens with a thickness varying by a factor of ten it can be concluded that the acceleration factor is less than four.

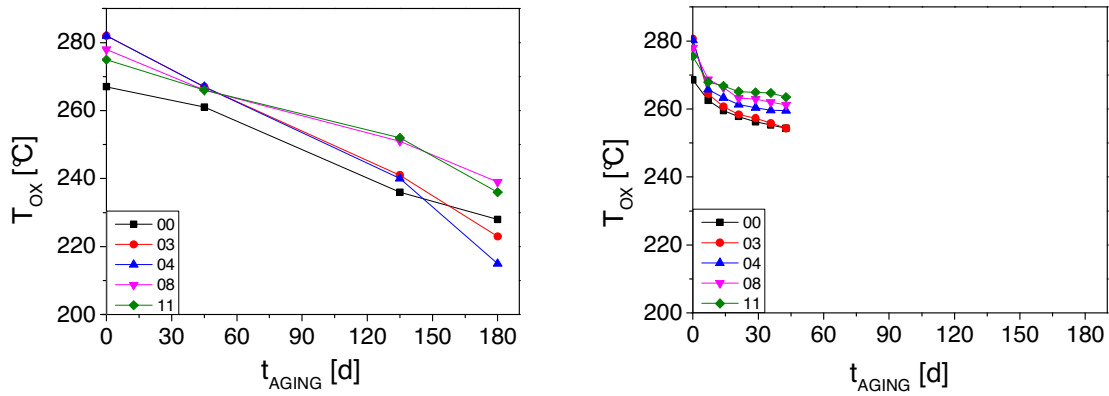


Fig. 3: Oxidation temperature T_{ox} for macro-sized specimens (left; data from Hagauer (2010)) and micro-sized specimens (right) for tested materials

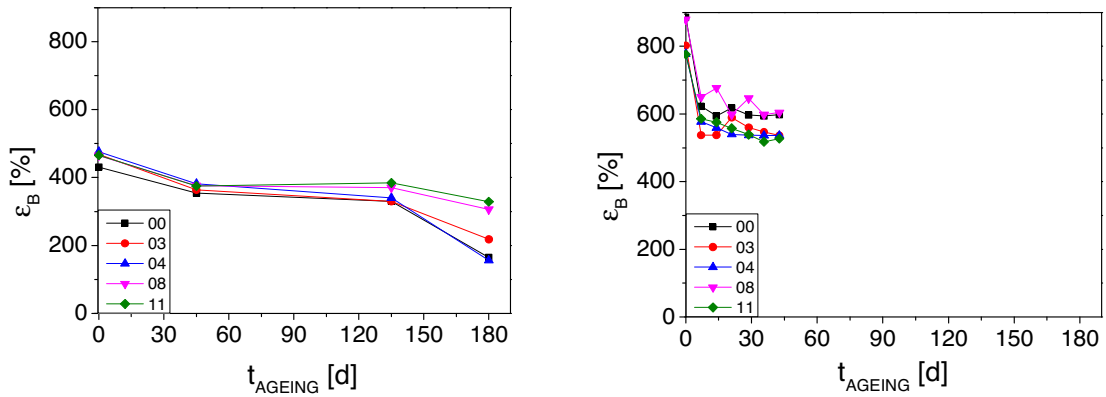


Fig. 4: Strain-at-break values ϵ_B for macro-sized specimens (left; data from Hagauer (2010)) and micro-sized specimens (right) for tested materials

4. Summary and conclusions

In the present study, the aging behaviour of PO model materials (formulations of identical base polymer system with different stabilizer packages) for heat storage applications with maximum service temperatures of about 95°C were investigated. The focus of this paper was on comparing two test methods (DSC and tensile tests) in terms of their applicability to study aging and degradation of such materials by comparing the behavior of preaged macro- and micro-sized specimens.

As revealed by the aging indicators oxidation temperature and strain-at-break, significant physical and chemical aging was detected at an elevated testing temperature of 135°C , which was chosen to accelerated aging effects. For the micro-sized specimens the exposure time of 43 d so far was not long enough to induce significant chemical degradation for the investigated materials. From the aging data derived from macro- and micro-sized specimens it can be concluded that materials 08 and 11 exhibit a better aging behavior in hot air compared to material grades 00, 03 and 04. Interestingly, indications were obtained that the degradation mechanisms might be different and depending on specimen thickness. Due to the fact that the testing times were too short especially for the micro-sized specimens, further aging experiments with longer exposure times will be carried out. Moreover, the obtained indication for specimen thickness dependent degradation mechanisms has to be clarified by a more comprehensive material and stabilizer analysis. The accelerated consumption of stabilizers due to reduced thickness and therefore a higher surface-to-volume ratio could not be clarified as yet. Further investigations are in progress involving automated planing and different specimen thicknesses in order to elucidate the influence of specimen thickness and quality on the degradation behavior of PO-based heat storage materials.

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