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Long-term behaviour of welded polypropylene liners for pit thermal energy storages

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ABSTRACT

This paper deals with the global ageing behaviour of a polypropylene random copolymer (PP-R) liner material with tailor-made primary structure, morphology and stabilization package. Specific focus was given to the long-term behaviour of the liner material in the welding zones. Conventional weld line testing was not feasible due to plastic deformation of the peel arms. Hence, a novel testing approach based on micro-sized specimen was implemented and used. The PP-R liner was welded varying the hot wedge temperatures ranging from 320 to 410 °C. For accelerated ageing, welded micro-specimens with a thickness of 100 µm were manufactured and exposed to hot air at 95, 115 and 135 °C. The investigated ageing indicators included phenol index and oxidation temperature which are highly sensitive to stabilizer degradation. Moreover, the carbonyl index and strain-atbreak values were monitored reflecting primarily polymer degradation. To evaluate potential effects of welding, welded and unwelded micro-specimens were compared. By assessment of phenol index and oxidation temperature a critical temperature dependent consumption of stabilizer was ascertained. Nevertheless, the rate of stabilizer degradation was comparable for unwelded and welded PP-R. The investigated hot wedge temperatures had no significant impact on further stabilizer depletion or polymer degradation. So far, failure of the PP-R material was obtained for an exposure temperature of 135 °C after 3750 h. The long-term behaviour and the embrittlement time of the polymer material was not affected by welding.

1. Introduction and objectives

For giga-scale thermal energy storages, polymeric liner materials are well established as water barrier layers. Commonly, extruded geomembranes based on polyethylene grades are used. Liners with a width of up to 7 m are welded together using a semi-automatic hot wedge apparatus on construction site. The hot wedge temperature amounts up to 400 °C, which is well above the melting range of the liner materials. As described in literature [1–4], the polymeric liner materials are prone to severe material degradation at elevated temperatures around the melting range. Usually the maximum service temperature of liner materials is at least 20 °C below the melting peak temperature, which is about 130 °C for polyethylene (PE) and 140 °C for random polypropylene copolymer (PP-R) based liners.

Characterization of welded liners is usually done by T-peel and creep rupture tests [5]. These methods give basic information on the failure mode (failure of peel arm or welding spot) and the quality of the welding seam. In case of welded liners, failure of the peel arm is quite common. Furthermore, macroscopic peel specimen with rather undefined access of environmental media are used. The applicability of peel testing for assessment of the long-term behaviour of welded liners is limited. Moreover, it does not allow for accelerated ageing testing on lab-scale.

To assess the long-term behaviour, oven ageing at elevated temperatures is well established [4,6–9]. The degradation and ageing performance are dependent on multiple factors. While acceleration by high temperature, usually following Arrhenius relationships, is well accepted, novel concepts are based on diffusion limited oxidation (DLO) approaches [10]. Hence, the overall lifetime is also significantly affected by the geometry of the component. To allow for accelerated long-term testing, a global ageing approach based on micro-sized specimen with well-defined thickness in the range from 50 to 500 μ m has been developed, implemented and applied successfully for unwelded PE and PP-R

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liner materials [2,3]. Comparing 2 mm and 50 µm thick specimens, acceleration factors of about 10 and 2 were deduced for PE and PP-R liner materials, respectively. The significant differences in acceleration factor were attributed to a lower degree of crystallinity of PP-R associated with higher oxygen diffusion rates [11].

The main objective of this paper was to further develop the accelerated ageing test approach based on micro-sized specimens, to allow for long-term characterization of welded liners. So far, this processing step was not taken into account in long-term performance analysis and lifetime assessment of liners for giga-scale thermal energy storages. Adequate specimen preparation techniques were implemented and used for welding seams joined at different hot wedge temperatures. The ageing behaviour of welded PP-R specimen was investigated and compared to extruded, unwelded liners.

2. Methodological approach

Well-established peel or creep rupture testing of welded liners [5] does not allow for accelerated assessment of the long-term behaviour due to failure of the peel arm, unrealistic stress concentrations at the edges of the welding zones and the macroscopic geometry. While creep is a physical failure phenomenon induced by mechanical stresses and enhanced by temperature, the service life of liners in seasonal storages is dominated by chemical degradation processes not reflected by a creep test. Hence, a novel methodological approach based on welded, microsized specimen and allowing for assessment of chemical degradation processes within the welding zone was implemented. From hot wedge welded liners strips with a width of 20 mm were cut and embedded in epoxy resin (see Fig. 1a). The welding seam was oriented perpendicular to strip direction. By CNC milling micro-sized specimen with the welding seam located in the middle section were prepared. These specimens were put into a sample holder and exposed to hot air in a convection oven (see Fig. 1b). After defined exposure intervals, specimens were removed and characterized by IR spectroscopy, thermal analysis and tensile testing. Sensitive ageing indicators were deduced and compared for both, welded and unwelded liner specimens (see Fig. 1c).

3. Experimental

3.1. Materials, specimens, and ageing conditions

PP-R model liners with a thickness of 2 mm were manufactured on an Extruder EN45-25D (Extrudex Kunststoffmaschinen, Mühlacker, Germany) by AGRU Kunststofftechnik (Bad Hall, Austria). The investigated PP-R grade contained 0.55 m% of phenolic antioxidants based on a 2:5 mixture of Irganox 1010 and Irganox 1330 [9]. The liner was welded using a Geostar G7 from Leister Technologies AG (Kaegiswil,

Switzerland) at hot wedge temperatures of 320, 360, 390 and 410 $^{\circ}$ C. Overlapping double welding seams as shown in Fig. 2 were manufactured. Such welding seams allow for detection of leakages by introducing pressurized air.

For accelerated ageing in hot air environment, which is for PP-R more critical than hot water [2], micro-sized specimen with a thickness of 100 μ m were prepared. The slices were taken by CNC-milling using an EMCO E600 (Hallein, Austria). As depicted in Fig. 3, the welding seam was embedded in epoxy resin, clamped in a workpiece holder and sliced, using a home-built tool with a razor knife [8]. The thickness accuracy of the micro-specimens was 100 \pm 1 μ m [13].

Accelerated ageing was carried out in hot air at 95, 115 and 135 °C. Therefore, FED 53 heating chambers (Binder, Tuttlingen, Germany) with forced air circulation were used. For positioning of specimen in the convection oven, a home-built sample holder was employed (see Fig. 4). After defined intervals, specimens were removed and characterized. So far, a maximum exposure time of 12,500 h has been achieved for the welded liners. While the specimens at 135 °C hot air are already fully degraded, ageing experiments at 115 and 95° are carried on.

Regarding the application of the PP-R material as a liner in giga-scale thermal energy storages, it is emphasized, that in this study, micro-sized specimens (factor of 20 lower thickness) with a non-optimized stabilizer package, based only on phenolic antioxidants, have been investigated. An even better long-term behaviour was ascertained for 2 mm thick unwelded liners based on an optimized PP-R grade [14].

3.2. Material characterization and ageing indicators

For material characterization analytical and technological methods were used. To assess stabilizer and polymer degradation, infrared (IR) spectroscopy and differential scanning calorimetry (DSC) were performed. Furthermore, ultimate failure of welded and unwelded PP-R specimens were characterized by monotonic tensile testing. As ageing indicators, phenol index, oxidation onset temperature, carbonyl index and strain-at-break were evaluated.

For determination of phenol and carbonyl index, IR spectroscopy was performed using a Perkin Elmer Spectrum 100 (Waltham, USA). Spectra were recorded in a wavenumber range from 650 to 4000 cm⁻¹ at a spectral resolution of 4 cm⁻¹. Four spectra were measured and



Fig. 2. Schematic drawing of a double-welded overlapping liner [12]



specimen by CNC milling sized specimen in hot air

Characterisation by IR spectroscopy, thermal analysis and tensile testing

Fig. 1. Methodological approach for accelerated ageing testing of welded liners.



(a) Welded liner sample embedded partly in epoxy resin



(b) Component clamped in a work piece holder, slicing tool and curled specimen



(c) Double welded, micro-sized specimen with a thickness of 100 µm

Fig. 3. Slicing of micro-specimens on a CNC-milling machine.

averaged. While the transmission mode was used to assess the weakly absorbing phenol peak of the antioxidants over the entire thickness, carbonyl index was deduced from spectra in attenuated total reflection (ATR) mode probing primarily the surface of the specimen [15].

Thermal analysis was carried out on a DSC 4000 (Perkin Elmer, Waltham, USA). Samples of about 2 mg were taken from the cross section of the micro-specimen. The sample was placed in a perforated 3 μL aluminium pan. DSC runs were performed from ambient to 300 °C at 10 °C min^{-1}. The cell was purged with synthetic air at a constant flow of 20 mL min^{-1}. From the dynamic DSC thermogram the oxidation onset temperature was deduced. As shown in [8], the oxidation onset temperature of phenolic antioxidants modified polyolefins is correlating with the remaining content of stabilizer.

To characterize the end of the induction period associated with full embrittlement and carbonyl build-up, tensile tests on a Z2.5 universal testing machine (Zwick Roel, Ulm, Germany) were conducted at ambient conditions (23 °C, 50%rh). The clamping length of the 100 μ m thick micro-specimen was 60 mm including both welding zones in the middle. The testing rate was 50 mm min⁻¹.

To describe the long-term behaviour phenol index, oxidation onset temperature, carbonyl index and strain-at-break were evaluated. The integral of the phenol absorption peak at 3646 cm⁻¹ was divided by the integral of the neighbouring absorption peak at 3765 cm⁻¹, which can be attributed to the co-catalyst Al_2O_3 [16]. As shown in [9], a phenol index (PI) of 2.0 indicates full deterioration of phenolic antioxidant as assessed by HPLC-UV. The amount of non-oxidized phenolic antioxidants was below the detection limit of 0.01 m%. For evaluation of the oxidation temperature from dynamic DSC plots, the tangent method was used. For the investigated PP-R grade an oxidation onset temperature of 230 °C is a measure for full deterioration of phenolic antioxidants. It is in agreement with a PI value of 2.0 [9].

Carbonyl index (CI) is a well-established indicator for the end of

induction period due to rapid increase of degradation products from the polyolefinic macromolecular structure. Initial carbonyl build-up rate is of an order of 10E-8 s⁻¹ at 30 °C [17] and increases especially in the final stage of ageing, which is characterized by significant embrittlement [18]. Carbonyl index was quantified by normalisation of the C=O stretching absorption peak at 1715 cm⁻¹ by the absorption value at 974 cm⁻¹. The latter peak is related to the resonant state of CH₃ rocking of isotactic polypropylene [19]. As evidenced in previous studies, a carbonyl index of 0.5 was defined as critical value indicating severe polymer degradation along with molar mass reduction and associated embrittlement [9]. Ultimate mechanical failure was classified, when strain-at-break dropped below strain-at-yield values ($\varepsilon_b < \varepsilon_v$). At yield point of semi-crystalline polymeric materials, such as PP, often interspherulitic voiding is initiated. In the post-yield regime, failure of the spherulites and rearrangement of crystal lamellae associated with fibrillation takes place [20]. The considered ultimate failure criteria strain-at-break below strain-at-yield indicates interspherulitic failure due to excessive degradation of interspherulitic tie molecules [9]. For the investigated, welded PP-R specimen initiation of yielding was obtained at a crosshead displacement of 4.2 mm, which gives an engineering strain value of 7%. To allow for comparison with unwelded specimens, relative strain values normalized by the initial value in the reference state were deduced. Strain-at-yield of the unwelded microsized liner specimen was at 17%.

4. Results and discussion

4.1. Phenol index and oxidation onset temperature

The initial phenol index (PI) value of the unwelded liner was 6.1. A good agreement with previous investigations on the unwelded liner was obtained [9]. Liners welded at a hot wedge temperature of 410 $^{\circ}$ C



Fig. 4. Home-built workpiece holder for micro-sized specimen.

showed PI values which were comparable to the unwelded material. With decreasing hot wedge temperature, slightly lower phenol indices were discernible in the reference state. Interestingly, a linear correlation with a degree of determination R^2 of 0.995 of phenol index in the reference state and hot wedge temperature was deduced (s. Fig. 5). The differences of phenol index in reference state were higher than the scatter band and thus significantly dependent on hot wedge temperature. Most likely, higher hot wedge temperatures lead to a better and more homogenous interdiffusion of PP-R macromolecules and



Fig. 5. Phenol index of unaged, 100 μm thick specimens as a function of hot wedge temperature.

stabilizers during the welding process. However, the hot wedge dependent differences in phenol index are not unambiguous. Hence, the obtained linear relationship should be corroborated by more accurate quantification of phenolic antioxidants by high pressure liquid chromatography with UV-detection. Adequate methodologies were developed and implemented by Beißmann et al. [21] for PP-R. In this study, focus was given to the evaluation of effect of ageing on relative content of phenolic functional groups.

As shown in Fig. 6, the reduction rate of phenol index was significantly dependent on hot air ageing temperature. The higher the temperature, the more pronounced was the decay of phenol index. The closed symbols in Fig. 6 represent specimen without ultimate failure. In contrast, open symbols indicate embrittled micro-specimen. For the unwelded liners embrittlement occurred at a critical phenol index of 1.0 independent on hot air temperature. This result is in contradiction to Grabmann et al. [9] who defined a critical phenol index value of 2.0 based on exceeding the HPLC detection limit of non-oxidized phenol antioxidants amounting to 0.01 m%. While HPLC does not consider partly degraded antioxidants [21], the phenol index value reflects phenol entities available also in partly oxidized stabilizers. Hence, the criterion for full stabilizer deterioration was changed to a phenol index of 1.0.

In addition to oxidation, diffusion and evaporation also lead to decrease in active stabilizer content [22]. This effect is especially noticeable in the early ageing state, especially at the lower exposure temperature of 95 $^{\circ}$ C. Most likely,

post-crystallisation mechanisms at 95 °C lead to a higher degree of crystallinity associated with loss of phenolic antioxidants. In contrast, 115 and 135 °C is closer to the melting region of the investigated PP-R grade enhancing the amorphous phase fraction and the compatibility with phenolic antioxidants. Neglecting the first drop in phenol index at 95 °C, a linear fit was applied to the experimental phenol index data. Values, higher than the critical value of 1.0 were considered. Gradients of -1.2E-4, -3.7E-4 and -15.0E-4 h⁻¹ were deduced for the unwelded micro- specimens for ageing temperatures of 95, 115 and 135 °C, respectively. Critical exposure times of 28,000, 14,000 and 3350 h were obtained. These values are in good agreement with the endurance times of 30,000, 14,500 and 3300 h measured and predicted for unwelded liners [9]. An Arrhenius fit of the critical exposure times at 95, 115 and 135 °C resulted in an activation energy of 65.7 kJ mol⁻¹. The degree of determination R² was 0.95. The obtained activation energy value is lower compared to data published by Achimsky et al. [23] and Celina et al. [24] ranging from 102 to 107 kJ mol⁻¹. However, the literature values are characteristic for PP homopolymers, while in this study a special random copolymer with ethylene comonomer was investigated.

As clearly discernible in Fig. 6, welding at a hot wedge temperature of 320 and 410 °C had no significant impact on the decay of phenol index compared to unwelded, micro-sized PP-R specimens. Presumably, the residual phosphitic processing stabilizer was sufficient to protect the phenolic long-term antioxidants. Although slight differences in phenol index were obtained in the unaged reference state, the overall decay of phenol index was independent on welding and hot wedge temperature. Based on this result, a comparable endurance time could be expected for unwelded and welded micro-sized specimens.

In Fig. 7 the oxidation onset temperatures (T_{OX}) of unwelded liner and specimen welded at hot wedge temperatures of 320 and 410 °C are depicted for different hot air temperatures and ageing times. Moreover, the oxidation onset temperatures of unwelded samples are correlated at different ageing temperatures to the phenol index. Initial T_{OX} values were ranging from 267 to 268 °C. These values were comparable to data provided by Kahlen et al. [25] for polypropylene random copolymer grades. The initial effect of welding and hot wedge temperature on oxidation onset temperature was negligible. Although this is in contrast to the slight impact of welding and hot wedge temperature on phenol index, the oxidation onset temperature indicates that phenolic antioxidants are not deteriorated by welding. The deviations in phenol index of



Fig. 6. Phenol index of 100 µm thick PP-R specimens, unwelded and welded at 320 and 410 °C exposed to hot air at 95, 115 and 135 °C.



Fig. 7. Oxidation temperature of 100 µm thick PP-R specimens, unwelded and welded at 320 and 410 °C exposed to hot air at 95, 115 and 135 °C.

welded and unwelded specimen in the reference state are most likely related to differences in stabilizer content due to recrystallisation effects. Polymer additives are primarily discernible at the interfaces of spherulites or crystal lamellae [26].

An initial drop of oxidation onset temperature was ascertained, which was slightly dependent on hot air temperature. This drop is most likely related to evaporation of phenolic antioxidants enhanced and induced by re- and post-crystallisation. Similar to the phenol index, a temperature dependent decrease of oxidation temperature was observed, which was linear after the initial drop and going through a second transition at higher ageing times. The second transition was more pronounced for lower exposure temperatures of 95 and 115 °C, leading to a more S-shaped degradation curve. The oxidation onset temperature values at 135 °C within the first 500 h were in good agreement with data reported for PP-R grades aged at 140 °C in hot air [25]. So far, no distinct difference of the oxidation onset temperature of unwelded and welded micro-specimens was discernible confirming the conclusions deduced from phenol index.

In Fig. 8 the oxidation onset temperature is correlated with the phenol index of unwelded micro-specimens exposed at 95, 115 and 135 °C. The data of the initial drop of oxidation onset temperature and phenol index were neglected. At the highest exposure temperature of 135 °C a linear relationship with a degree of determination of 0.98 was deduced. Interestingly, the degree of determination of the linear regression was lower at 115 °C ($R^2 = 0.85$) and at 95 °C ($R^2 = 0.79$). Presumably, the decay of oxidation onset temperature is related to both, deterioration of phenolic antioxidants and the PP random copolymer. A slight molar mass degradation was discernible for the investigated PP-R grade already within the induction period [27]. Kahlen et al. [25] reported a relative decrease of weight average molar mass of 20% for PP random copolymer grades aged in hot air at 140 °C. While weight average molar mass values of 800 to 1200 kg mol⁻¹ were stated in literature [25,27], the critical average molar mass associated with full embrittlement of about 300 kg mol⁻¹ was deduced for the investigated random PP copolymer [9]. This critical molar mass value is slightly higher than data of 150 to 230 kg mol⁻¹ reported for an isotactic PP homopolymer [28].

4.2. Carbonyl index and strain-at-break

To analyse the polymer degradation in the geomembrane over time IR spectroscopy and tensile tests were performed. In Fig. 9 carbonyl index values are shown as a function of ageing time in hot air at 95, 115 and 135 °C for unwelded micro-specimen and specimen welded at 320 and 410 °C of hot wedge temperature. At higher carbonyl index values of 0.35 to 0.50 secondary carbonyls such as linear and cyclic esters (1740 to 1790 cm^{-1}), aldehydes (1730 to 1735 cm^{-1}) and saturated and unsaturated ketones (1690 to 1725 cm⁻¹) were found in direct transmission spectra [29,30]. Due to total absorption in the transmission spectra of the investigated PP-R micro-specimen, the carbonyl index was evaluated from more surface-sensitive attenuated total reflection (ATR) spectra. The initial carbonyl index values of the unaged, welded and unwelded micro-sized specimens were in the range from 0.1 to 0.2. Interestingly, a slight increase of carbonyl index was discernible especially at lower hot air ageing temperatures of 95 and 115 °C in the entire exposure time range. In agreement with a critical phenol index of 1.0,

the carbonyl index of the unwelded micro-specimen exceeded a critical value of 0.5. While at 135 °C a quite common relationship for the carbonyl index with a slight increase within the induction period and a pronounced increase at the end of induction period was obtained, at 115 and 95 °C a continuous linear rise in carbonyl index until ultimate failure was detected. For the linear fit a degree of determination R^2 of 0.81 and 0.95 was deduced for 115 and 95 °C, respectively. This is an indication, that presumably slightly different ageing and degradation mechanisms are dominant at 95, 115 and 135 °C.

In Fig. 10 strain-at-break values normalized by the initial value are depicted as a function of ageing time at 95, 115 and 135 °C. The strainat-break values in the reference state amounted to about 30% for the welded specimens, whereas it was 550% for the unwelded slices. A possible reason for these distinct differences are small air inclusions detected in the middle of the welding spot. Moreover, a lower cooling rate after welding allowed for differences in semi-crystalline morphology. Nevertheless, an initial drop of strain-at-break was discernible for both, unwelded and welded specimens. Hence, the reand post-crystallisation effects [31] due to exposure at elevated temperatures took also place in the welded specimen. Interestingly, the initial drop of strain-at-break was more pronounced for unwelded specimen aged at 95 and 115 °C, but less pronounced for 135 °C. Most likely, internal stresses at grain boundaries are less pronounced at 135 °C, which is already within the melting peak of the investigated PP-R material. The higher amount of amorphous phase fraction associated with an enhanced inner mobility at 135 °C would allow for better stress relaxation in the amorphous interphase between crystalline domains. Full embrittlement at 135 °C was independent on welding. While the unwelded micro-specimen, exhibited an embrittlement time of 3300 h [9], the welded specimens embrittled after 3750 h at 135 °C. Similar to the other ageing indicators, welding had no impact on mechanical embrittlement of the investigated PP-R liner material.

5. Summary and conclusions

To assess the effect of welding on the ageing behaviour of a novel PP-R material for lining of large thermal energy storages, a test methodology based on micro-specimens with thickness of 100 μ m was



Fig. 8. Correlation of phenol index and oxidation temperature of unwelded specimens exposed to hot air at 95, 115 and 135 °C.



Fig. 9. Carbonyl index of 100 µm thick PP-R specimens, unwelded and welded at 320 and 410 °C exposed to hot air at 95, 115 and 135 °C.



Fig. 10. Normalized strain-at-break of 100 µm thick PP-R specimens, unwelded and welded at 320 and 410 °C exposed to hot air at 95, 115 and 135 °C.

implemented and used. The results clearly showed that this methodology allows for accelerated description of chemical degradation within the welding zone. In contrast, the established peel test [5] on welded macroscopic and exposed specimen cannot be used for long-term ageing studies due to preferred failure of the embrittled peel arm, which is more prone to diffusion limited oxidation than the thicker welding line. Furthermore, the deficiencies of creep rupture testing which is primarily related to non-service relevant, physical failure mechanisms could be overcome by the novel ageing testing methodology for welded liners. behaviour was ascertained which was comparable to unwelded liners. Hot wedge welding along with the process temperature had no significant impact on the hot air degradation behaviour. Hence, the main conclusion of this study is that welding in a well-defined processing temperature range does not compromise the expected lifetime of the investigated novel PP-R liner material.

The detailed analysis of the ageing indicators phenol index and oxidation onset temperature revealed that the phenolic antioxidants were not significantly deteriorated in the welding process, even at the highest investigated hot wedge temperature of 410 °C. For both,

For micro-specimen taken from double welded liners an ageing

unwelded and welded micro-specimen a quite comparable decay of phenol index and oxidation onset temperature over ageing time was ascertained. The temperature dependent gradients of the fit to the phenol index could be described by an Arrhenius relationship yielding an activation energy of 67.1 kg mol⁻¹. In comparison to literature data for polypropylene homopolymer grades, the activation energy of the investigated PP-R grade was about 35% lower. So far, critical phenol index and oxidation onset temperatures have been achieved just at 135 °C after 3750 h of hot air exposure.

The ageing indicators carbonyl index and strain-at-break, which are more sensitive to polymer degradation revealed an induction period-like behaviour, especially for high exposure temperatures. In agreement with a critical phenol index of 1.0 or a critical oxidation onset temperature of 230 °C, full embrittlement of the investigated micro-specimen was obtained at a carbonyl index of 0.5. The results of the unwelded micro-specimen were in good agreement with literature data [9,25].

The ageing investigations of the PP-R model grade at lower temperatures of 95 and 115 °C are continued. Furthermore, optimized PP-R grades with more complex and advanced stabilizer formulations considering also non-phenolic antioxidants will be included in future welding and ageing studies. Preliminary results for the optimized grade indicate, that the time-to-embrittlement can be improved significantly by a factor of 2. Due to diffusion limited oxidation effects, ultimate degradation of the investigated PP-R grade is about 2 times faster for micro-sized specimen with a thickness of 100 μ m compared to 2 mm thick macroscopic liners [8]. For the welding seam with a thickness of commonly 3.5 mm an even better endurance time is to be expected.

CRediT authorship contribution statement

Lukas Peham: Conceptualization, Methodology, Writing - Original draft preparation.

Gernot M. Wallner: Project administration, Supervision, Writing - Original draft preparation.

Michael Grabmann: Testing of unwelded liners.

David Nitsche: Extrusion and welding of PP-liner.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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