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Sustainable insulation for sustainable DHC

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Abstract

The piping network is the essence of DHC. Its insulation is fundamental for its correct and efficient functioning. State of the art DHC networks are insulated with polyurethane (PU) foam, which presents outstanding mechanical and insulating properties. However, the high toxicity of the diisocyanates (European Chemical Agency, 2008) required for its production and the recently approved European Restriction on their Use (European Commission, 2020) highlight the need for sustainable alternatives.

Polyethylene terephthalate (PET) foam has been previously identified as a promising candidate for DHC given its mechanical properties (Ramnäs, 2008) and high insulation capacity retention, due to slow gas diffusion (Mangs, 2005) . However, its behavior upon ageing remains unexplored. Without this knowledge, the material cannot be reliably introduced in the market. The objective of this work is to experimentally investigate PET foam's ageing behavior, with a focus on the effects of thermal cycling, thermally induced crystallinity and hygrothermal degradation on its mechanical properties.

Different ageing trials were conducted in an environmental chamber. The effects on the mechanical properties and crystalline structure were evaluated. No degradation was found in the scenarios covered by this study. Service temperature over 100 °C is found possible thanks to thermally induced crystallization.

1. Introduction

District Heating (DH) networks are called to bring sustainability through the decarbonization of the heating sector. But as we curve towards a circular economy, the term sustainable expands from carbon neutral to additionally recyclable and non-toxic.

The energy efficiency of state-of the art DH pipelines is warrantied with polyurethane foam (PU), which presents outstanding thermal conductivity values as well as the necessary load bearing capacity to support the acting stresses on buried pipelines. However, the recently approved restriction on diisocyanates [1], required for the PU manufacturing, highlights its toxicity [2] and the urge to look for more sustainable materials. The lower operating

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Nomenclature

DSC	Differential Scanning Calorimetry
$\sigma_{c,10}$	compression strength at 10% strain
$\sigma_{f,max}$	maximal flexural strength
ε_f	strain at break
r.H	relative humidity
ΔH_f	enthalpy of fusion, measured at the melting point
ΔH_f^0	enthalpy of fusion of the 100% crystalline polymer, measured at the equilibrium melting point
T_g	glass transition temperature
U	toughness
X_c	weight degree of crystallinity

temperature of the 4th generation DH [3] opens up the possibility, not only to include renewable and waste heat sources in the system, but to use alternative polymeric foams.

A promising candidate is polyethylene terephthalate (PET) foam. PET is non-toxic and recyclable, and its current wide use across sectors and established recycling processes allows for a cascading-use of the material, as well as a competitive price. PET foam has been previously explored for DH applications [4,5]. Results showed excellent thermal resistance ageing behavior due to very low gas diffusion rates, which would allow long-term energy efficiency of the system. In terms of mechanical properties, PET foam showed outstanding creep behavior, as well as possessing a compression strength over 0,3 MPa required by EN 253, under temperatures up to 80 °C, after which a reduction of the strength occurs due to the transition from the glassy to the rubbery state [5].

However, for successful commercial implementation, knowledge on its ageing behavior is needed to confirm the attainment of the required service life. In this paper we summarize our efforts to close this knowledge gap.

Previous research has shown that thermal and thermoxidative degradation of PET occurs at or above the melting temperature of PET ($\sim$250 °C) and the reaction rate at lower temperatures is very low [6,7] and hence not an issue for DH applications. The temperature fluctuations of the system however expose the pipeline's materials to mechanical and thermal cyclic loading. We have found that this causes degradation of the mechanical properties of PU pre-insulated pipes [8] and could also be the case for PET. The vicinity of the operation temperature with the materials T_g and hence fluctuation around it could also lead to changes in crystallinity, impacting on the mechanical properties. Therefore, the effects of thermal cycling were evaluated.

Another source of degradation could be moisture. Buried DH pipelines can be located below the groundwater level and damage due to moisture is reported to be frequently encountered in the field [9]. Though the HDPE casing protects the insulation from water ingress, it has been recently reported that moisture penetrates the casing [10]. While an aluminum layer is an efficient diffusion barrier [11], moisture can still penetrate through the pipe ends and joints [9,11]. Moisture can degrade the mechanical properties of polymeric foams due to plasticization and swelling [12]. Further degradation risk involves hydrolysis, which has been widely reported for PET, above T_g [i.e. 13,14]. Therefore, hygrothermal ageing was the second degradation pathway investigated.

2. Materials and methods

2.1. Materials

Commercial closed cell cyclopentane-blown PET foam boards (Gurit Kerdyn Green) of two densities were examined: 80 and 100 kg/m^3.

2.2. Thermal cycling ageing trials and evaluation

Specimens of approx. 50 × 50 × 50 mm were subjected to thermal cycling inside an environmental chamber (Weiss WK1 340, Reiskirchen, Germany). Three trials were conducted according to the following profiles:

• Thermal Cycling A.

Temperature was varied between 25 °C and 100 °C. The upper temperature was chosen above PET's T_g to examine the potential changes in the crystalline structure. The duration of the temperature ramps was 30 min, and the set points were held for 75 mins. This was kept equal for all trials. The number of cycles was set to 250, which is the number of cycles established for fatigue check for secondary effects for distribution lines according to [15].

• Thermal Cycling B.

Temperature was varied between 25 °C and 75 °C, as to assess the effects of cycling below PETs T_g. The number of cycles was set at 125, which is half of the number of cycles established for fatigue check for secondary effects for distribution lines according to [15].

• Thermal Cycling C.

Temperature was varied between 25 °C and 75 °C, and the number of cycles was set at 250 for the same reason as in A.

Evaluation:

Reference (unaged) and aged samples were tested under compression at room temperature in a universal testing machine following standard [16] as far as possible. The samples were tested in the direction perpendicular to the extrusion, which would correspond to the radial direction of the pipes.

Five specimens were tested per condition, under a displacement-controlled rate of 2 mm/s. The force was measured with a 20 kN load cell, accuracy class 0.5 (HBM, Darmstadt, Germany). The strain was measured by 3D digital image correlation (DIC) [17] using an ARAMIS 5M adjustable stereo camera system (GOM mbh, Braunschweig, Germany). The images were acquired at frequency of 1 Hz. Samples where individually accurately measured using calliper and weighed prior testing.

Engineering stress–strain curves where derived from the obtained data. The E modulus is obtained for each case from the slope of the initial linear segment of the curves. The compressive stress at 10% strain ($\sigma_{c,10}$) was obtained, and both parameters were used to assess the changes in mechanical properties.

Crystallinity of the 80 kg/m^3 foam unaged and after A ageing was assessed through DSC following [18] standard with a heating rate of 10 k/min. This analysis was conducted in duplicate. The degree of crystallinity is calculated as:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \tag{1}$$

were ΔH_f^0 is taken as 140 J/g [19].

2.3. Behavior under temperature

Additional compression tests of unaged specimens were conducted under temperature. For this, an environmental chamber (Weiss WK3-180/70/5-UKA, Reiskirchen, Germany) was placed around the universal testing machine. Samples were tested at 70 °C and 100 °C after ∼2 h of temperature stabilization. Additional samples were temperature soaked overnight at 100 °C and then tested at 100, 70 or 85 °C. Ca. 2 h of temperature stabilization at the testing T was applied prior the test.

2.4. Hygrothermal ageing trials and evaluation

Samples were aged at 40 °C and 80% r.H inside an environmental chamber (Memmert ICH-C, Schwabach, Germany) for up to six months. The selected temperature corresponds to an accelerated ageing from the ground moisture temperature (around 10 °C), but with a comfortable ΔT of 20 °C from T_g, considering the depression in T_g caused by the moisture [20] . Ageing above T_g would alter the degradation mechanisms. The selected relative humidity is the maximal allowed by the chamber.

Specimens of approx. 200 × 25 × 25 mm before and after ageing were subjected to a 3-point bending test under a displacement-controlled rate of 1.5 mm/min. The force was measured with a 2 kN load cell, accuracy class 0.5 (HBM, Darmstadt, Germany) and the strain with DIC as described in the previous section.

Engineering stress–strain curves where derived from the obtained data. The maximum flexural stress ($\sigma_{f,max}$) and strain at break (ε_f) were obtained from the curves. The E modulus is derived for each case from the slope of

the initial linear segment of the curves. The toughness was calculated as the integral under the stress–strain curve, according to (2):

$$U = \int_0^{\varepsilon_f} \sigma_{f,max} \cdot d\varepsilon \tag{2}$$

Degradation was assessed in terms of the changes in mechanical properties.

3. Results

3.1. Thermal cycling ageing

Fig. 1 presents the engineering stress–strain curves for the samples tested under compression, in unaged condition and after thermal cycling trials A, B and C for the foam 80 kg/m^3 (a) and 100 kg/m^3 (b). The E modulus and σ_{10} obtained from the curves are summarized in Table 1.
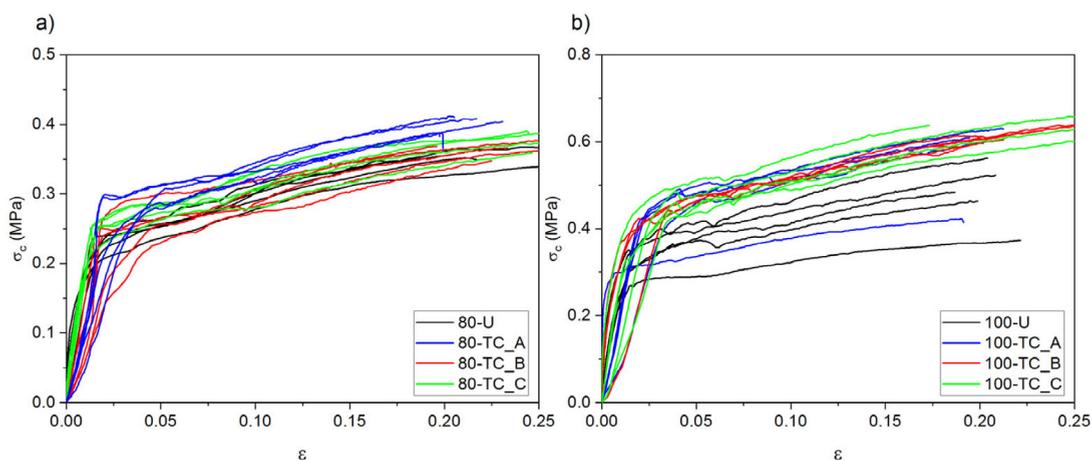
Fig. 1. Compression stress–strain curves for foam 80 (a) and 100 (b) unaged (U) and after thermal cycling ageing A, B and C trials.

Table 1. Mechanical Properties derived from compression tests, unaged and after thermal cyclic ageing.

	E modulus (MPa)				σ_{10} (MPa)			
	Unaged	TC-A	TC-B	TC-C	Unaged	TC-A	TC-B	TC-C
80	15.83 ± 2.15	12.5 ± 4.71	10.83 ± 3.99	15.3 ± 2.57	0.30 ± 0.01	0.33 ± 0.01	0.29 ± 0.02	0.31 ± 0.02
100	24.02 ± 1.84	20.09 ± 3.39	27.08 ± 8.77	23.16 ± 7.71	0.41 ± 0.05	0.49 ± 0.07	0.51 ± 0.02	0.52 ± 0.03

As can be seen in Fig. 1(a) and (b) and Table 1, the applied thermal cycles did not produce a significant change in the mechanical properties. An increase in the strength for foam 100 after trials B and C can be noted. Given the variability between samples, this increase should be taken with care.

No significant change in weight or dimensions was detected after the ageing trials.

A representative DSC curve for foam 80 unaged and after trial TC-A is presented in Fig. 2. The presented curves correspond to the second heating ramp. From the curves and Eq. (1) a weight % crystallinity of 33.8% for unaged and 31.3% for aged foam 80 can be derived.

3.2. Behavior under temperature

Fig. 3 presents the engineering stress–strain curves from compression tests conducted at different temperatures. The left column presents the results of tests conducted after a short stabilization time of approx. 2 h, for foam 100 (a) and foam 80 (c). As can be seen, the strength is progressively reduced as the temperature is increased. The
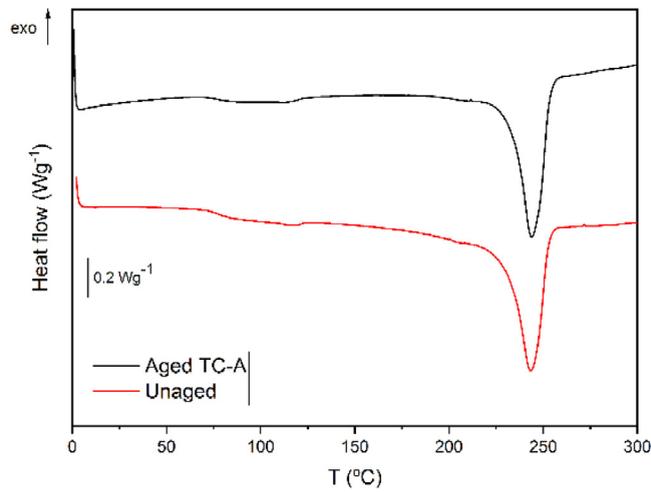
Fig. 2. DSC curves for unaged and TC-A aged 80 kg/m³ PET foam.
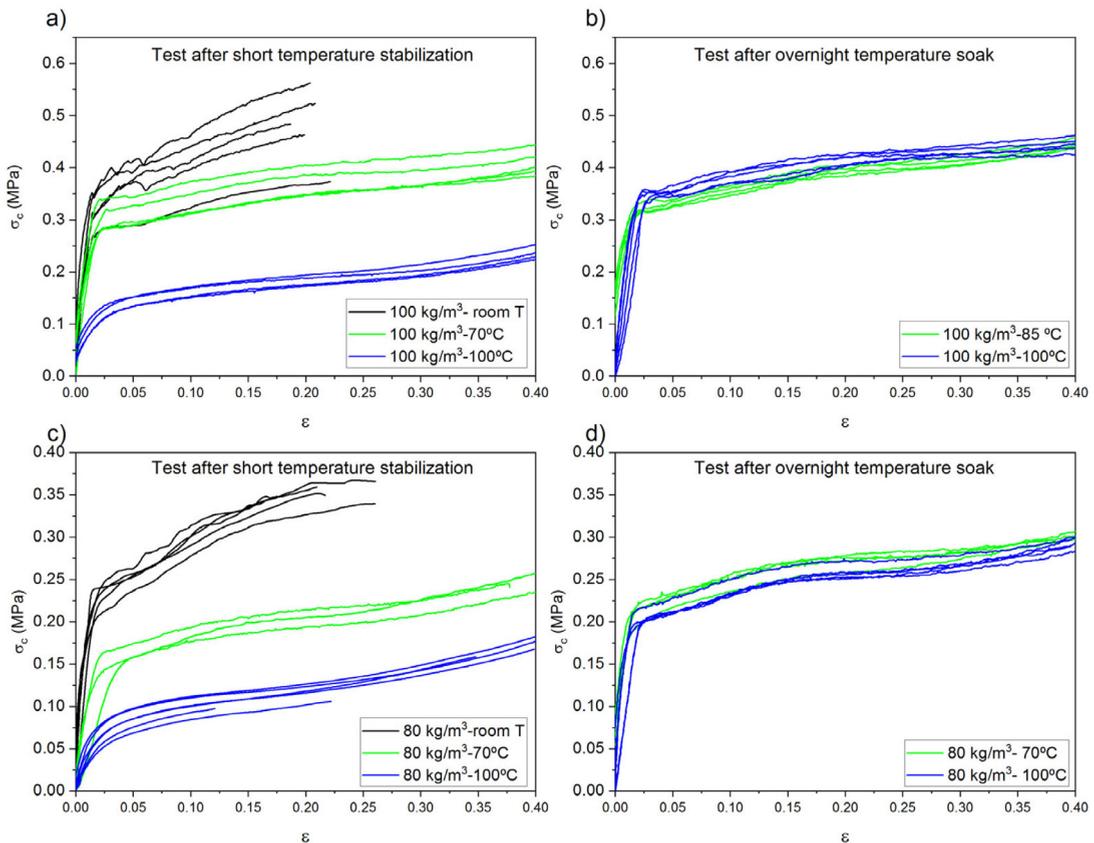
Fig. 3. Stress–Strain curves for samples tested under temperature for foam 100 (a) and 80 (c). Samples tested under temperature after an overnight 100 °C temperate soak are presented in (b) (foam 100) and (d) (foam 80).

graphs on the right column present the foams tested at the same temperatures, but after an overnight temperature soak at 100 °C. The strength is significantly increased, from 0.1 ± 0.01 MPa to $0.23\% \pm 0.009$ MPa for the 80 foam and from 0.16 ± 0.01 MPa to 0.38 ± 0.01 MPa for the 100 PET foam when testing at 100 °C after overnight

soak, meaning a 130% strength increase. This significantly reduces the gap with the behavior at room temperature. The implication on this regarding the selection of the design values at the network operation point and possible service temperatures will be discussed in Section 4.

3.3. Hygrothermal ageing

Fig. 4 presents the bending stress–strain curves for foam 80 (a) and 100 (b). Foam 80 was tested in both the extrusion (E) and parallel (P) directions, unaged (FU) and aged (FA) after 6 months. Foam 100 was tested in the E direction, unaged and after 3 and 6 months ageing. One of the FU-80 P samples did not break during the test, marked with a cross at the end of the curve. The values of toughness, maximum strength and strain at break are presented in Table 2.

Despite a decrease in the mean for most properties of aged samples can be seen for most properties, a two-sample t-test with a significant level of 0.05 was undertaken for all toughness aged/unaged pairs, which showed that the results are not statistically different.
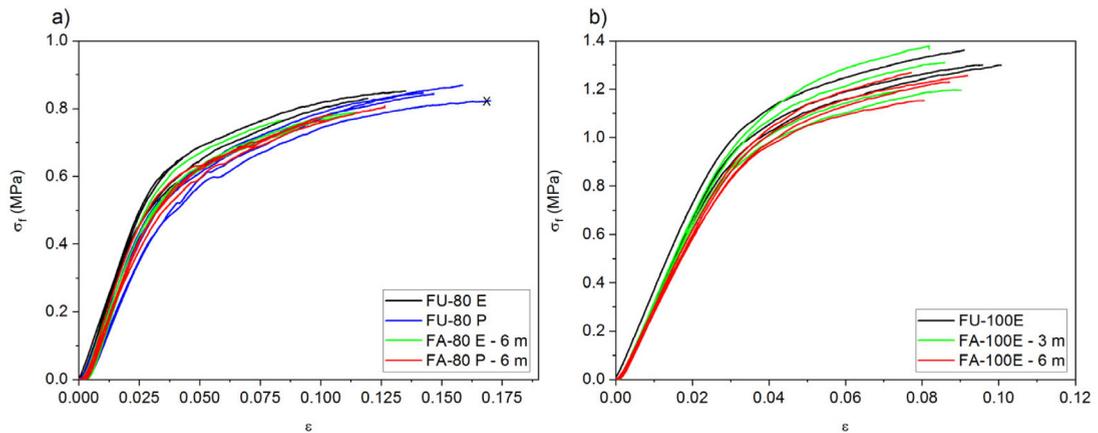
Fig. 4. Bending stress–strain curves for foam 80 (a) and 100 (b).

Table 2. Mechanical Properties derived from flexural tests.

	$\sigma_{f,max}$ (MPa)	U (MJ/m^3)	ε at break	E modulus (MPa)	$\Delta\sigma_{f,max}$ (%)	ΔU (%)	$\Delta\varepsilon$ at break (%)	ΔE modulus (%)
FU-80E	0.76 ± 0.10	0.05 ± 0.03	0.091 ± 0.04	21.84 ± 1.30	n.a	n.a	n.a	n.a
FU-80P	0.78 ± 0.14	0.07 ± 0.04	0.12 ± 0.06	18.9 ± 1.78	n.a	n.a	n.a	n.a
FU-100E	1.28 ± 0.07	0.08 ± 0.01	0.092 ± 0.01	35.00 ± 3.05	n.a	n.a	n.a	n.a
FU-100P	1.29 ± 0.08	0.1 ± 0.02	0.106 ± 0.02	33.52 ± 1.85	n.a	n.a	n.a	n.a
FA100E - 3 m	1.27 ± 0.09	0.07 ± 0.01	0.083 ± 0.01	35.32 ± 1.50	−1.1	−11.7	−10.3	0.9
FA100E - 6 m	1.23 ± 0.05	0.07 ± 0.01	0.084 ± 0.01	32.46 ± 1.13	−4.9	−14.1	−8.6	−7.2
FA80E - 6 m	0.77 ± 0.02	0.05 ± 0.01	0.1 ± 0.02	20.99 ± 0.55	1.5	4.2	9.5	−3.9
FA80P - 6 m	0.76 ± 0.05	0.05 ± 0.02	0.101 ± 0.02	19.87 ± 2.59	−2.6	−24.3	−15.8	5.1

4. Discussion

The acting cyclic loads in DH pipes could be a cause of fatigue for the constituent materials. While this is widely considered for the steel pipe, only a few studies evaluate its effect on the insulating foam [8,21]. A foam is not a material, but a structure, and repetitive expansion and contraction and related flexure of the cell walls could lead to cracking events [22]. Cell anisotropy [23] and hysteresis intrinsic to polymers may exacerbate irreversible changes in the cellular structure. A previous study with PU foam at high temperature reports that the cell expansion is wider

in the direction parallel to the foam direction and original shape is only partly recovered [24]. One contributor to the foam thermal expansion is the expansion of polymer itself. The second contributor is the expansion of the gas inside the cells, applying pressure to the cell walls [24]. With increasing temperature, the expansion of the gas coincides with the reduction of the strength of the polymer matrix. We have found no effect of the applied cycles on the mechanical properties of the PET foam. This is related to the low thermal expansion of PET, of $9.1 \cdot 10^{-5}$ K^{-1} [25] vs $15 \cdot 10^{-5}$ K^{-1} for PU [22]. Due to the semicrystalline nature of PET, a further change in the mechanical properties could arise from temperature induced changes in crystallinity. No significant changes in crystallinity were detected after the applied thermal cycles. The results from the static tests under temperature (Section 3.2) suggest that the 75 min temperature hold time was not long enough to allow for thermal crystallization. The hold time was selected in order to achieve a manageable trial duration for the 250 cycles, which ascended to 8 weeks.

It is seen in Fig. 3(a) and (c) that the strength and E modulus decrease with increasing temperature, consistent with previous observations in PET [5] and other polymeric foams [22,26]. However, it can be seen that the strength at 100 °C can increase by 130% with time under temperature. This indicates that during this period the crystallinity degree increased. The intermolecular bonding is higher in the crystalline phase than in the amorphous, increasing the strength of the polymer [27]. This effect is expected to occur in DH networks, which are held at high temperature for long periods of time. Therefore, limiting the PET foam for networks operating below 100 °C due to the softening of the foam at its T$_g$ (∼80 °C) [5] is proven conservative, as the $\sigma_{10} = 0.3$ MPa required by EN 253 can be exceeded at 100 °C (Fig. 3b). It should be noted that in any case the standard requires this σ_{10} at room temperature. Foaming semicrystalline polymers is a recent development, and its particularities i.e. crystallinity degree changes with time and temperature should be taken into account when selecting the materials properties at the design point of the piping network.

As for moisture-induced ageing, no effects have been found after 6 months accelerated ageing. While the obtained data does not allow us to predict long term behavior, at the ground temperature all involved processes will be slower. It should be noted that the samples were left to stabilize at ambient conditions prior mechanical testing, since the focus of the study was to evaluate irreversible degradation. Therefore, loss of mechanical properties due to the plasticization effect of moisture would not be detected in this experimental plan. Equivalently only permanent effects related to swelling. i.e. deformation of the cells, would be detected. It has been seen during the study that moisture uptake by PET foam is very low, reaching only 0.3% weight increase after over 2600 h of 80% moisture exposure at 40 °C. The details on the moisture uptake and its in-situ and long-lasting effects will be discussed in another publication [28]. This very low moisture uptake limits to a great extent the degradation. It is known that PET is susceptible to hydrolysis at temperatures above its T$_g$ and has been widely studied [13,14]. The chain scission produced by hydrolysis leads to embrittlement, conditioning the service life of the material. Therefore, bending tests were selected to better detect embrittlement, which was not found after the applied 6 months hygrothermal ageing. We have found that the cellular structure of the foam produces no deviation in the hydrolysis reaction rate from that occurring in films [29]. According to models developed by previous authors based of PET films [14], service life at 40 °C and 50% r. H would be 30 years, assuming an Arrhenius relationship. Since all the experimental data is collected above T$_g$, it is likely that deviations are encountered in the glassy state, leading to an underestimation of the service life below T$_g$ [14]. Since the temperature gradient through the insulation thickness keeps the insulation in contact with the medium pipe dry, high humidity levels would only be found at low temperatures. Degradation through hydrolysis is hence not foreseen an issue for steel PET-insulated pipes.

5. Conclusions

The ageing of PET foam has been studied, in order to confirm its suitability as insulation for DHC pipes. No degradation due to thermal cycling or hygrothermal exposure has been detected, related to the low coefficient of thermal expansion and moisture sorption of PET. Previously determined service temperature limit to PET's T$_g$ at around 80 °C has been proven conservative, due to the thermally induced crystallinity increase and its impact on the material's strength. Therefore, PET foam could be a sustainable replacement for PU, eliminating the use of toxic chemicals in the DH piping manufacturing and supporting the transition to the Circular Economy.

CRediT authorship contribution statement

Lucía Doyle: Study design and conception, Data collection and analysis, Preparing the manuscript, Critical discussion of the results, Editing of the manuscript. **Ingo Weidlich:** Scientific supervision, Critical discussion of the results, Editing of the manuscript.

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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