

Thermal ageing of PE 100 pipes for accelerated lifetime prediction under service conditions

Author(s): H. Vogt, H-F. Enderle, U. Schulte - Basell Polyolefine GmbH
J. Hessel - Hessel Ingenieurtechnik GmbH

Abstract:

It is widely accepted that the maximum lifetime of pipes made from bimodal HDPE types have reached a stage of development at which the service lifetime of the material is limited only by its resistance against thermal aging. The time until this degradation starts depends mainly on the stabilization package, the applied temperature, the oxygen concentration and the type and the flow rate of the media. However, a simple and fast method of determining the long term stability of HDPE pipes under service conditions is desirable.

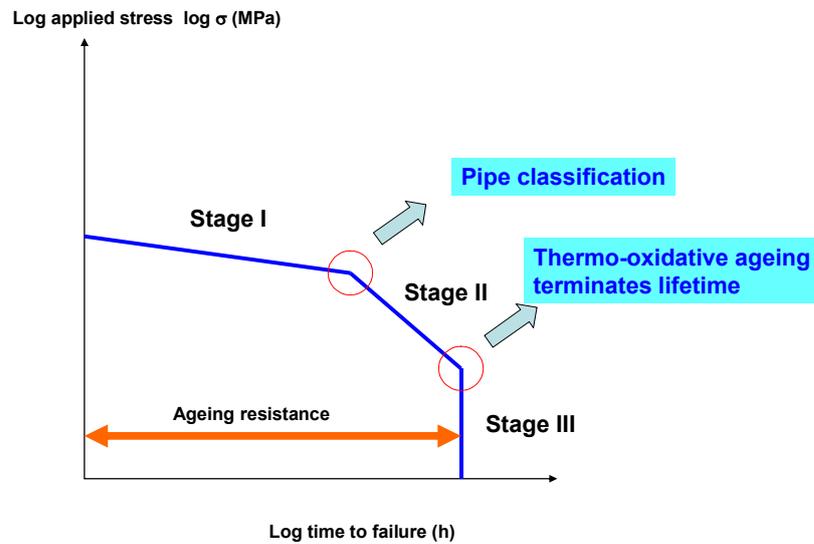
The resistance to thermal degradation was studied on pipes made from a PE 100 resin containing a usual antioxidant system in different concentrations. To simulate service conditions the heat ageing was performed under internal pressure with circulating or stagnant water at elevated temperatures until brittle failures occurred. The progress in ageing was studied on samples taken from the installed pipes and changes in molecular structure and antioxidant concentration were determined. The activation energies were calculated using the Arrhenius equation as a function of the fracture times and compared with those obtained as a function of other parameters such as loss in OIT.

Introduction:

Since the introduction of plastic pipes made from polyethylene, suitable accelerating test methods were needed to predict the maximum service lifetime of those pipes under multi-stress conditions (e.g. temperature, pressure, fluid or thermal degradation). It was very early recognized that hydrostatic pressure tests on pipes at different internal stress load and temperatures can be used as a reliable and proven method to estimate the service lifetime either by graphical or today by mathematical extrapolation based on the Arrhenius-law. Those creep rupture curves of polyethylene pipes according to ISO 9080 indicate different failure modes: In stage I ductile fractures occur due to yielding, whereas in stage II brittle fractures are dominating, which are mainly related to slow crack growth. And stage III limits the lifetime of the pipes by the extreme brittleness of the degrading polymer even under low stress levels (figure1) [1].

The time until the thermo-oxidative degradation starts depends on the polymer, its additive package and the environmental conditions, e.g. the temperature, the applied stress, the leaching of the additives by the medium/fluid and the concentration of the oxidant. Therefore a simple and fast method of determining the long term ageing stability of HDPE pipes under service conditions is desirable which takes into account all of the components of long term stabilization and service conditions.

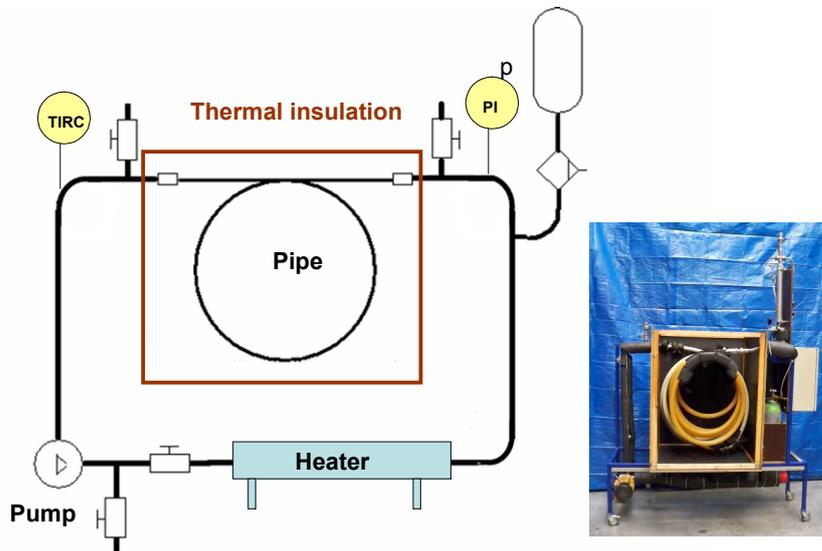
Figure 1 Hydrostatic pressure behaviour of PE Pipes



Experimental

For this purpose new test equipment was developed to study the progress in ageing of PE 100 pipes. A schematic drawing of the equipment is shown in figure 2. It simulates the most relevant ageing parameters under service conditions: Temperature, oxygen concentration, water flow rate and hoop stress.

Figure 2: Principle of Pipe Ageing Test



The test procedure is described in table 1. To accelerate the time to failure, PE 100 pipes (Dimension 32x3mm) produced with different additive levels were installed. The ageing resistance was investigated at different temperatures (80°C -110°C) with circulating water inside and hot air outside, with weekly water change. The hydrostatic pipe pressure was only 1 bar and 1.4 bar for $T = 110^{\circ}\text{C}$ respectively to simulate stage III mode as shown in figure 1.

Table 1: Test procedure

• Resin:	PE 100
• Additive level:	100%, 50%, 25%, 0%
• Pipe size:	32 x 3 mm
• Fluid:	Drinking water
• Mode:	Circulating water
• Fluid change:	Weekly (only in circulating mode)
• Velocity:	1 m/s ~ 32 l/min
• Temperatures:	80°C, 90°C, 100°C, 110°C
• Applied pressure:	1 bar (1.43 bar at 110°C)
• Applied stress:	~ 0.5 – 0.8 MPa
• Testing time;	Until brittle failure occurred

Results

To date the pipe ageing has achieved more than 25.000 h. The brittle failures are listed in table 2. As expected, the brittle failures occurred previously at higher ageing temperatures and previously at lower additive levels in the pipes. By far the shortest ageing resistance had the non stabilized pipes. Picture 1 shows a pipe under test with this type of brittle failure.

Picture 1: Brittle Failures due to Chemical Ageing

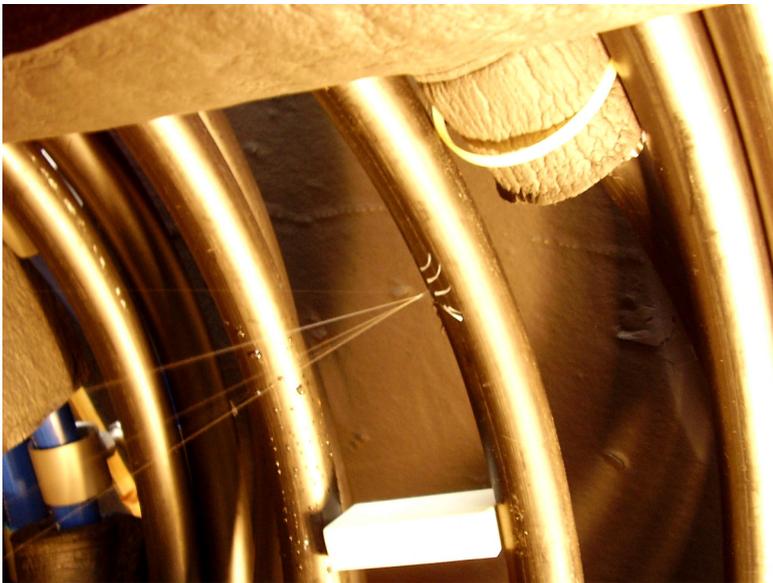


Table 2: Time to failure of PE 100 Pipes

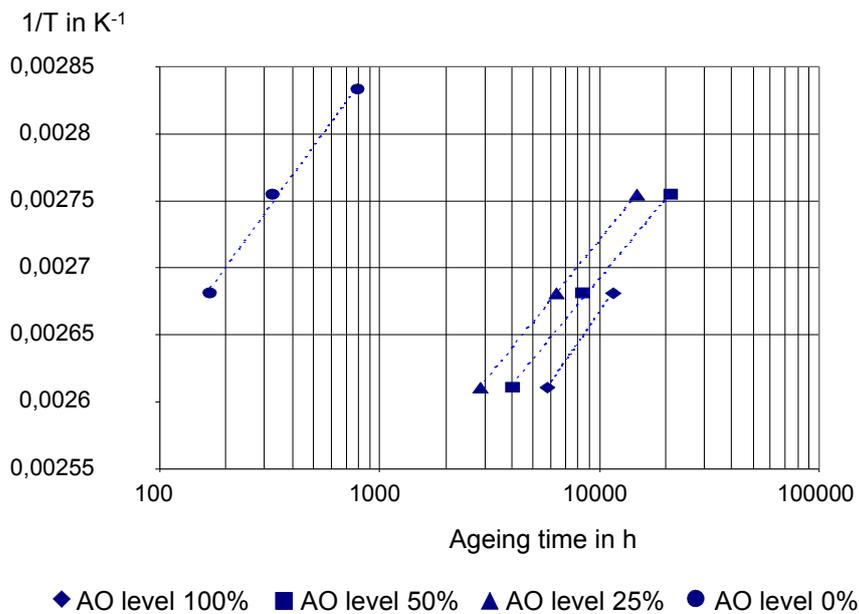
Mode: Circulating water

Pipe resin	PE 100	PE 100	PE 100	PE 100
Colour	black	black	black	natural
Additive level	100%	50%	25%	0%
80 °C	- *	- *	- *	799 h 806 h
90 °C	- *	21.188 21.642	13.876 h 15.927 h	301 h 352 h
100 °C	11.295 h 11.742 h	8.369 h 8.492 h	6.302 h 6.511 h	169 h 173 h
110 °C	5.650 h 6.012 h	3.993 h 4.072 h	2.833 h 2.914 h	Not tested
ΔH_{Ageing} [kJ/mol]	82	92	92	87

* No failure (actual testing time: 25.000 h)

The Arrhenius plot obtained experimentally from failure times at different temperatures is shown in figure3.

Figure 3: Time to Failure of PE 100 pipes with different AO level



The activation energy ΔH for the thermo-oxidative ageing of PE was calculated from the fracture times using the Arrhenius equation:

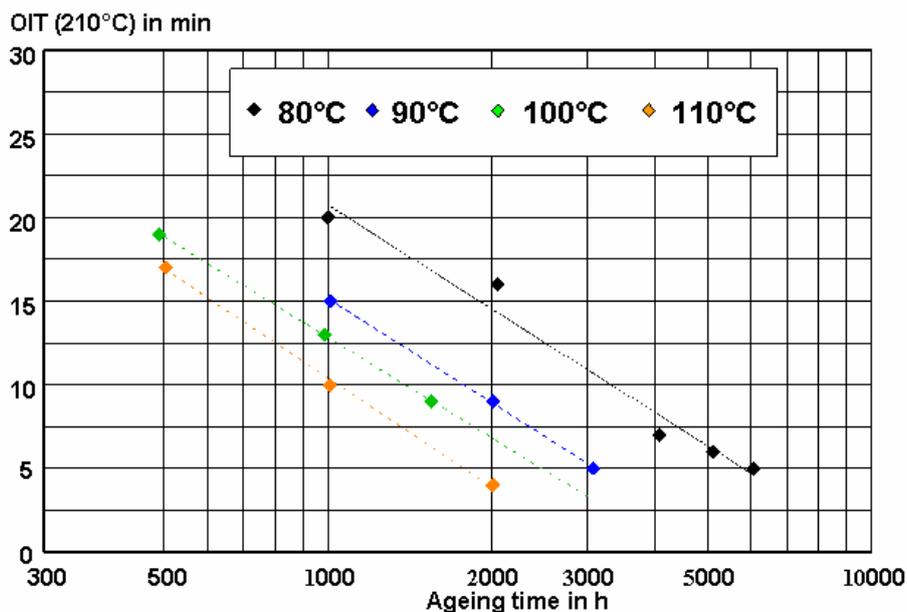
$$\Delta H = 1.9152 \cdot 10^{-2} \frac{\log t_1 - \log t_2}{1/T_1 - 1/T_2} \quad \text{kJ/mol}$$

t_1 and t_2 are the failure times at temperature T_1 and T_2 .

No significant difference in the activation energy ΔH ageing for stabilized and none stabilized pipes could be found. The ΔH ageing deduced from the slope was approximately 90 kJ/mol. It indicates that the degradation process for the stabilized and non stabilized pipes is the same. Furthermore, from pipe pressure tests performed in the presence of strong oxidants like Cl_2 and nitric acid, similar activation energies ΔH_{Ageing} of 96 and 94 kJ/mol respectively were obtained. That makes it plausible that the thermo-oxidative degradation process of PE follows the same chemistry which is well understood [2]. When initiated the rate determinant step might be either the formation of chain radicals via hydrogen abstraction or at least chain scission. The more effective the stabilization, the better it retards the ageing process. The presence of strong oxidants such as O_2 , Cl_2 or nitric acid accelerates the consumption of the additives and therefore the degradation process starts earlier.

Additionally the progress in ageing was studied on samples cut of the installed pipes and changes in molecular structure (viscosity number, MFR) and additive concentration were determined. No significant changes in MFR close to the time to failure could be found. Therefore these properties do not allow a prediction of failure times. In contrast the OIT values drop very rapidly with the ageing time as shown in figure 4 for pipes with an additive level of 50%. The calculated activation energies ΔH for the OIT drop are only approximately 50 kJ/mol. That's obvious; otherwise the additives couldn't retard the ageing process of the polymer.

Figure 4: OIT drop as a function of ageing time for pipes with 50% AO level

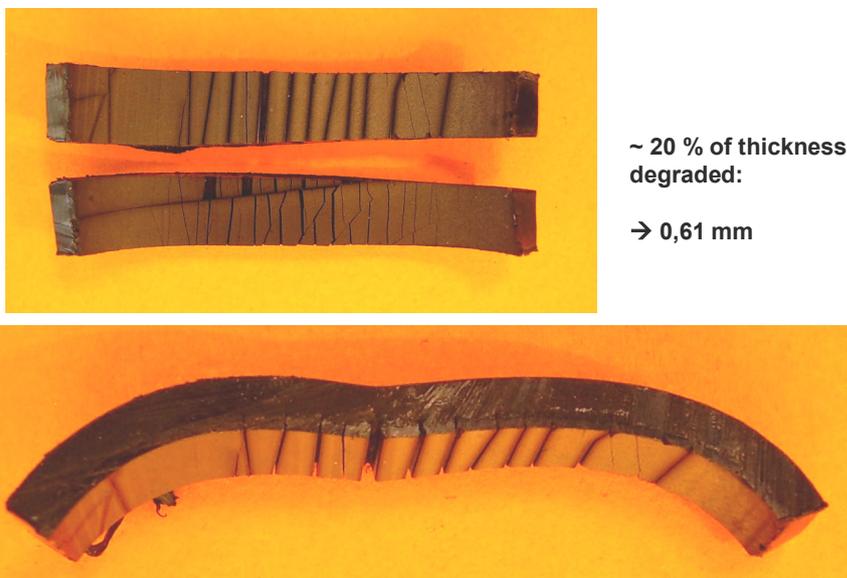


Yet it has to be considered that the loss of OIT is not an adequate method to describe the progress of ageing. In general the OIT drop can not be allocated to changes in the

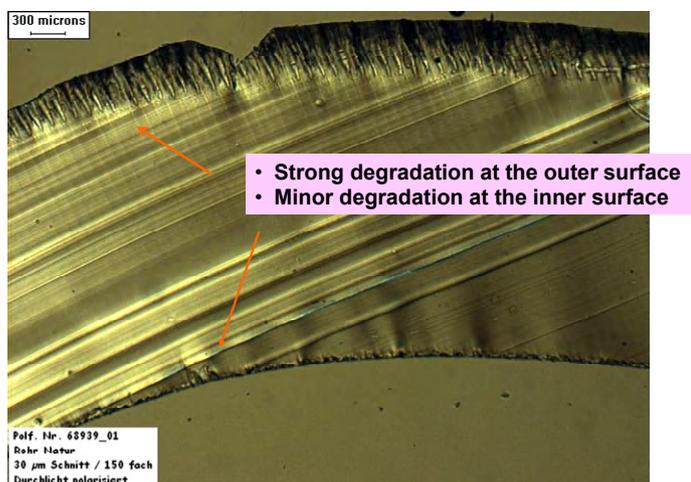
concentration of the present additives. Furthermore the changes in OIT during ageing can be affected either by the leaching of the additives by the medium or by scavenging free radicals.

As shown in picture 2 the degradation starts preferred at the internal pipe surface. That's obvious because the circulating hot water leaches the additives from the surface and enhances the chemical attack by the oxygen. The embrittled layer of the internal pipe surface was identified by light microscopy to be about 20 % or 0.6 mm of the total wall thickness of 3 mm. But this is only valid for the stabilized pipes! Beside this the external surface of non stabilized pipes is more degraded than the internal surface as shown in picture 3. This may be due to the greater rate of oxidation on the external surface as more oxygen is available than at the internal surface of the pipe, which may explain the very short failure times of the non stabilized PE 100 pipes.

Picture 2: Degradation of the internal pipe surface



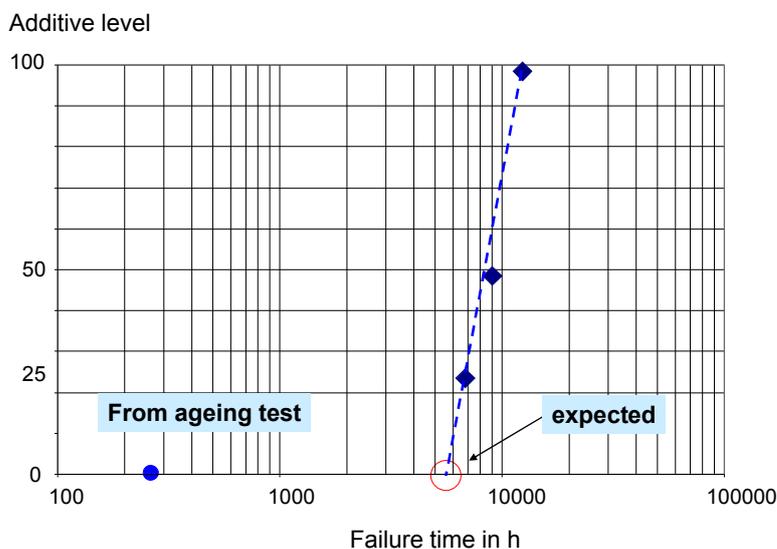
Picture 3: Embrittlement of the external surface of non stabilized PE 100 pipes



It also indicates that at the internal surface of the stabilized pipes the leaching of the additives by the circulating hot water is predominating and the loss of the additives accelerates the ageing process. As in the non stabilized pipes no leaching of the additives at the internal surface can take place; the embrittlement of the external surface is inevitable due to the higher oxygen concentration in the air.

From this observation, it is understandable that the very short failure times of the non stabilized pipes do not fit within the linear correlation of those from the stabilized pipes as shown in figure 5. According to the linear regression the time to failure for the non stabilized pipe should be around 5800 h at $T = 100^{\circ}\text{C}$ and much longer as the 170 h, which have been the result of the ageing experiment.

Figure 5: Correlation between failure time and additive level for $T = 100^{\circ}\text{C}$



A ΔH_{Ageing} of 95 kJ/mol was calculated from the Arrhenius plot of the rate constants which resulted from the linear correlation of failure times at different aging temperatures versus additive level in the pipes.

Summary:

Test equipment was developed to study the progress in ageing of PE 100 pipes at different temperatures and circulating water/ air mode. To accelerate the time to failure pipes with different additive levels were tested. It could be found that the activation energy ΔH_{Ageing} is about 90 kJ/mol either for non stabilized or stabilized pipes. The key parameters for the time to failure are: ageing temperature, leaching of additives (flow rate of the water), additive package and level, concentration of the oxidant. Loss of OIT is not an adequate method to describe the progress of ageing.

References:

- [1] E. Gaube, *Kunststoffe*, **49** (1959)
- [2] F. Gugumus, *Polymer Degradation & Stability*, **52** (1996), p131-144