

LIFETIME PREDICTION OF A BLUE PE100 WATER PIPE

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ABSTRACT

The lifetime prediction of a well established PE100 water pipe has been investigated using chemical analysis on pipes exposed to hydrostatic pressure at various test temperatures (maximum 80°C) in water for durations up to 9 years. The depletion of antioxidants (AO) and the build up of oxidative hydroperoxide degradation products (ROOH) have been monitored using oxidative induction time (OIT) and Iodometry respectively. An empirical model based on the Arrhenius fit of the data has been developed to extrapolate the lifetime of the PE100 pipe material at various service temperatures (10 – 25°C). Lifetime was found to be far in excess of design (50 years). The combination of pressure testing and measurements of OIT and ROOH build up proved to be a very powerful tool to extrapolate the lifetime of plastic pipes.

1. INTRODUCTION

Typical requirements for gas and water pipes are roughly 50 years. The traditional method to assess the lifetime of plastic pipe materials is based on hydrostatic pressure testing. Hydrostatic rupture tests are conducted in a specified internal and external environment (usually air or water), at various pressure levels and at different temperatures. The time to failure is recorded and the data are presented as log (hoop stress) versus log (failure time) that results in stress rupture or creep rupture schematics as illustrated in Figure 1.

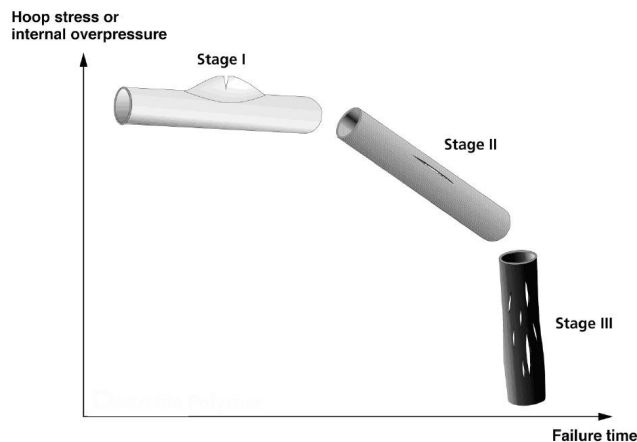


Figure 1. Stress rupture schematic.

Stress rupture curves can be divided into three failure modes: stage I, stage II and stage III. During Stage I, the pipe will fail mainly in a ductile manner under mechanical overload (high hoop stress levels). Initiation of micro-cracks in the pipe walls will occur in Stage II which

will lead to mainly brittle failures at intermediate stress levels. The slope of the curve increases during Stage II and a “mechanical knee” can be observed. In Stage III, failures are generally brittle and will occur under low stress levels due to the predominant chemical degradation process taking place. The failure time is virtually independent of the hoop stress and a “chemical knee” can be observed. The lifetime of a plastic pipe is controlled by three main factors: material, environment and loading. The material factor includes the resins, the additives, the manufacturing processes, etc. Environmental factors include gases, liquids, UV radiation, radioactive radiation, microbiological effects, etc. The effect of chlorinated water environment has been recently investigated by Hassinen et al (1) and proved to affect the lifetime of plastic pipes. Finally loading factors comprise temperature, temperature cycling, static and dynamic loading, notches and scratches, etc.

Current standards for extrapolation of the lifetime of PE pipes are based on an Arrhenius relationship between logarithm of time (t), logarithm of pressure (P) and inverse absolute temperature (T). However, this approach can be very expensive and time-consuming. Furthermore, extensive PE pipes pressure testing in water conducted by Ifwarson et al (2) in accordance with the current standards suggested that elevated temperatures data (above 80°C) cannot be extrapolated to predict PE pipes lifetime at room temperature. The purpose of this study was to use a different approach based on antioxidants depletion and initiation of thermo-oxidative degradation in a PE100 pipe material exposed to hydrostatic pressure in water at low test temperatures (maximum 80°C). The depletion of antioxidants due to leachage by water and consumption reaction to protect the pipe against thermal oxidation was monitored by the oxidative induction time (OIT) testing. In addition, the level of hydroperoxide oxidative degradation products was assessed by the iodometric method.

2. EXPERIMENTAL

2.1. Materials

The polyethylene pipe grade material tested was a blue high-density polyethylene (PE100 classification) produced by Basell Polyolefine GmbH predecessors in 1994 and intended for the use for drinking water application. The density of the PE material (granule) was 0.949 g/cm³ and its MFR (190°C/5 kg) was 0.20 g/10 min. The outer diameter of the PE pipe material was 32 mm and the wall thickness was 3 mm. The pipe material was stabilised with a primary sterically hindered phenolic antioxidant and a secondary processing phosphite antioxidant. The pipe material was also stabilised with a HALS (hindered amine light stabiliser) and a UV absorber in order to prevent photo-oxidation during outdoor storage.

2.2. Long-term hydrostatic pressure testing

Hydrostatic pressure testing was conducted in accordance with ISO 1167-1973 by Bodycote Polymer AB, Sweden. Both internal and external test medium was deionised water. Lengths of 350 mm of PE pipes were tested at 20, 40, 60 and 80°C using Beulco (type A) fittings. Pipes tested at 80°C were exposed up to 79 000 hours, i.e. approximately 9 years. Pipes tested at other temperatures, i.e. 20, 40 and 60°C, were exposed up to 20 000 hours, i.e. approximately 2 years.

2.3. Oxidative induction time (OIT)

Oxidative induction time (OIT) is widely used for the determination of the thermal oxidative resistance of polyethylene materials. A linear relationship exists between the concentration of phenolic antioxidant (and also phenolic/phosphite mixtures) and the observed OIT in

polyethylene. The OIT testing only provides a relative measure of the level of antioxidants remaining in the pipe material but is a suitable analytical technique to monitor the degree of depletion of antioxidants from the pipe surface. OIT was determined at the internal, middle and external surfaces of PE pipe samples exposed at various temperatures under hydrostatic pressure testing using a Jade DSC (Perkin Elmer) fitted with an auto-sampler. The samples were tested at 200°C in an oxygen atmosphere in accordance with ISO/TR 10837.

2.4. Determination of hydroperoxides

The iodometric method based on the oxidation of iodide ions is the most widely used of all colorimetric methods for hydroperoxide analysis and has been extensively used with PE materials by Hoàng et al (3,4). The level of hydroperoxides was determined at the internal, middle and external surfaces of PE pipe samples exposed at various temperatures under hydrostatic pressure testing. A mass of 0.50 g of film fragments (around 100 µm thick) was then refluxed for 30 minutes with 10 cm³ of a mixture of glacial acetic acid (100%, GPR™ BDH) and propan-2-ol (99.8%, HiPerSolv VWR BDH Prolabo, HPLC grade) at a ratio by volume of (5:95/acetic acid:propan-2-ol) in the presence of 0.10 g of sodium iodide (99.99%, Suprapur®, Merck). The I₃⁻ formed during the peroxide decomposition was finally determined using a Lambda 7 UV/Vis spectrophotometer (Perkin Elmer) at 420 nm. The relative level of total hydroperoxides was reported in terms of Absorbance at 420 nm.

3. RESULTS AND DISCUSSION

3.1. Hydrostatic Pressure Testing

Pressure regression data at 80°C are presented in Figure 2. Stage I was clearly apparent in the plot obtained from experimental data until approximately 30 000 hours, i.e. when brittle failures started occurring consistently; a “mechanical knee” could clearly be observed, thereby indicating the onset of stage II. Pressure regression data were also recorded at 20, 40 and 60°C but no brittle failures were observed over the period of investigation.

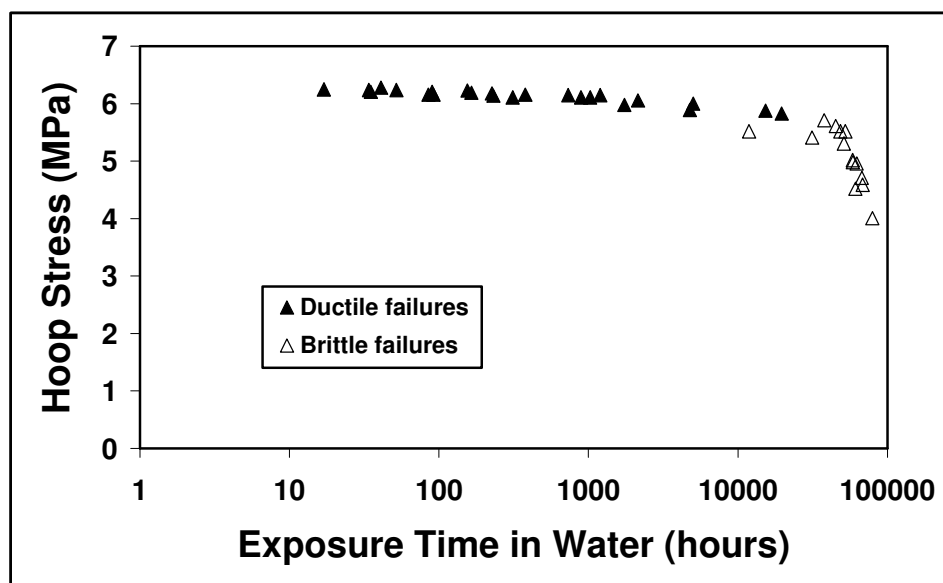


Figure 2. Pressure regression data at 80°C

3.2. OIT

OIT results at the external surface at all test temperatures are compiled in Figure 3.

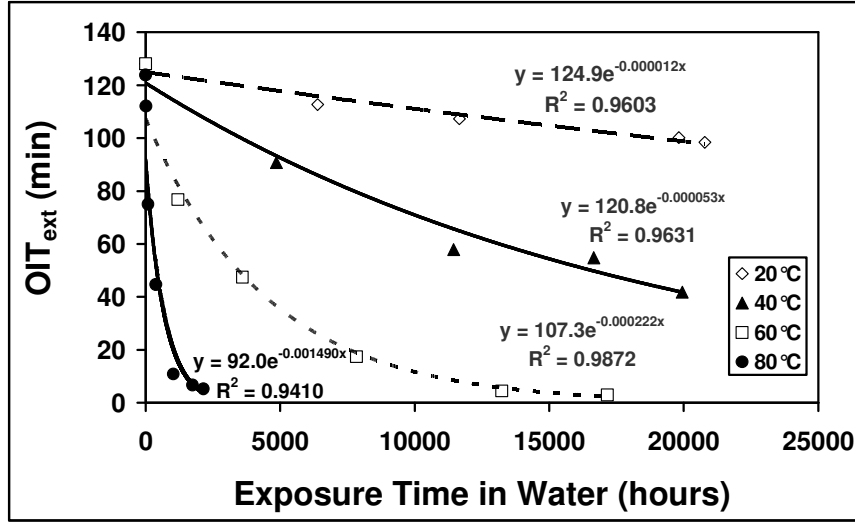


Figure 3. OIT data at all test temperatures for external surface of the pipe and exponential fits.

According to the regression coefficients, there was a good exponential fit for the rate of antioxidants depletion at the external surface at all test temperatures. The exponential pattern for the rate of depletion of antioxidants is in line with studies conducted on the lifetime of HDPE geo-materials by Hsuan et al (5) and Rowe et al (6). The OIT data were subsequently plotted as a logarithmic (Ln) scale. The logarithmic plot is shown in Figure 4.

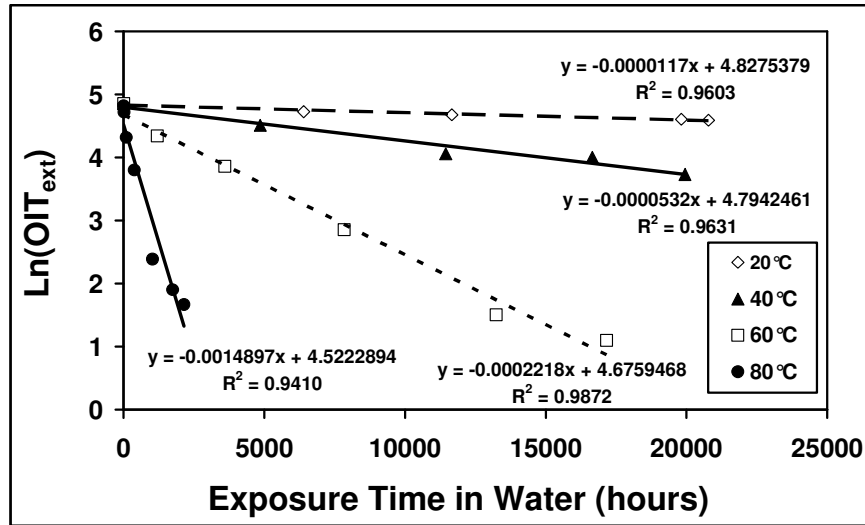


Figure 4. Logarithmic plot of OIT data at all test temperatures for external surface of the pipe.

As expected, straight lines were observed. The linear regression can be defined as:

$$\ln(OIT) = S_T \times t + \ln(OIT_0) \quad (1)$$

where OIT is the OIT value for the pipe exposed at test temperature T and exposure time t , S_T is the rate of depletion of antioxidants (reaction rate) at test temperature T , t is the exposure time at test temperature T , OIT_0 is the initial OIT value for the unexposed pipe, i.e. at $t = 0$.

Although the mechanisms of antioxidants loss is known to be more complex the results show that the antioxidants loss essentially follows a first order kinetic from which the rate constant can be determined. Therefore reaction rates S_T , which are the slope of the linear regression lines, could be determined graphically at all test temperatures. The rates of depletion of antioxidant S_T are compiled in Table 1. These reaction rates could then be fed into an Arrhenius model. The Arrhenius equation is defined as follows:

$$\ln(S_T) = -\frac{E_a}{R} \times \frac{1}{T} + \ln C \quad (2)$$

where S_T is the reaction rate (rate of depletion of antioxidants) at test temperature T (Kelvin K), E_a is the activation energy of the reaction (depletion of antioxidants) (kJ/mol), R is the gas constant ($8.31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), C is a constant independent of test temperature T .

Table 1. Reaction rates S_T for the depletion of antioxidants (OIT) and the formation of ROOH at various test temperatures

Test Temperature (°C)	Reaction rate S_T		
	OIT		ROOH
	External	Internal	External
20	-0.0000117	-0000098	-
40	-0.0000532	-0000462	0.0000053
60	-0.0002218	-0002150	0.0000209
80	-0.0014897	-0015597	0.0000418

This Arrhenius relationship can be interpreted as a linear correlation between the rate of depletion of antioxidants (Logarithmic scale) at different test temperatures and the inverse temperature ($1/T$). The Arrhenius plot obtained experimentally from OIT data at the external surface is shown in Figure 5.

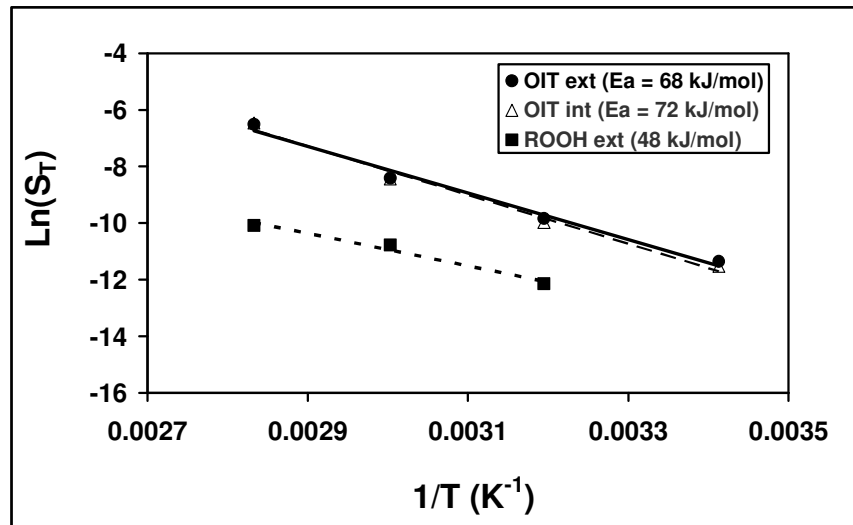


Figure 5. Arrhenius plot for OIT data for external and internal surface of the pipe and for ROOH data for external surface of the pipe.

The Arrhenius equation for the rate of depletion of antioxidants at the external surface of the pipe obtained from experimental OIT data could therefore be expressed as:

$$\ln(S_T) = -8214.3856 \times \frac{1}{T} + 16.5243 \quad (3)$$

The activation energy (E_a) for the antioxidant depletion at the external surface of the pipe could be deduced from the slope and was found to be 68 kJ/mol. The rate of depletion of antioxidant S_T at the external surface of the pipe could subsequently be extrapolated to service temperature of 10°C with Equation (3). This extrapolated rate of reaction S_T at service temperature of 10°C was then fed into Equation (1) in order to predict the time required for the total depletion of antioxidants at the external surface of the pipe. If it is considered that the OIT value is 1.0 min when no antioxidant remains at the surface of the pipe, the time to total depletion of antioxidants would be 1 304 491 hours, i.e. approximately 150 years. Therefore, from the Arrhenius model applied to the OIT data it is predicted that the antioxidants will be totally depleted at the external surface of the pipe after approximately 150 years at a service temperature of 10°C. The time to total depletion at the external surface of the pipe was also extrapolated at other service temperatures, i.e. 20 and 25°C, and results are compiled in Table 2.

Table 2. Extrapolated time to total depletion of antioxidants (OIT) and to critical ROOH level at various service temperatures

Service Temperature (°C)	Extrapolated Time (years)		
	OIT		ROOH
	Internal	External	External
10	194	151	234
20	69	56	117
25	42	35	84

The OIT data from the internal surface of the exposed pipes were also fed into the Arrhenius model. The Arrhenius equation for the rate of depletion of antioxidants at the internal surface of the pipe obtained from experimental OIT data was:

$$\ln(S_T) = -8613.7284 \times \frac{1}{T} + 17.6908 \quad (4)$$

The activation energy E_a for the antioxidant depletion at the internal surface of the pipe was found to be 72 kJ/mol. The rate of depletion of antioxidant S_T at the internal surface of the pipe was extrapolated to service temperature of 10°C and is shown in Table 1. By feeding the data into Equation (1), the antioxidants would be totally depleted at the internal surface of the pipe after approximately 195 years at a service temperature of 10°C. The time to total depletion at the internal surface of the pipe was also extrapolated to other service temperatures, i.e. 20 and 25°C, and results are compiled in Table 2. The rate of depletion of antioxidants appeared to be greater at the external surface of the pipe. This may be due to the greater rate of oxidation at the external surface of the pipe as oxygen was more available than at the internal surface of the pipe.

3.3. Hydroperoxides

The level of oxidative hydroperoxide products (ROOH) was determined at the internal, middle and external surface of the pipes exposed at 80°C and compared to the pressure regression data. ROOH and pressure regression data are shown in Figure 6.

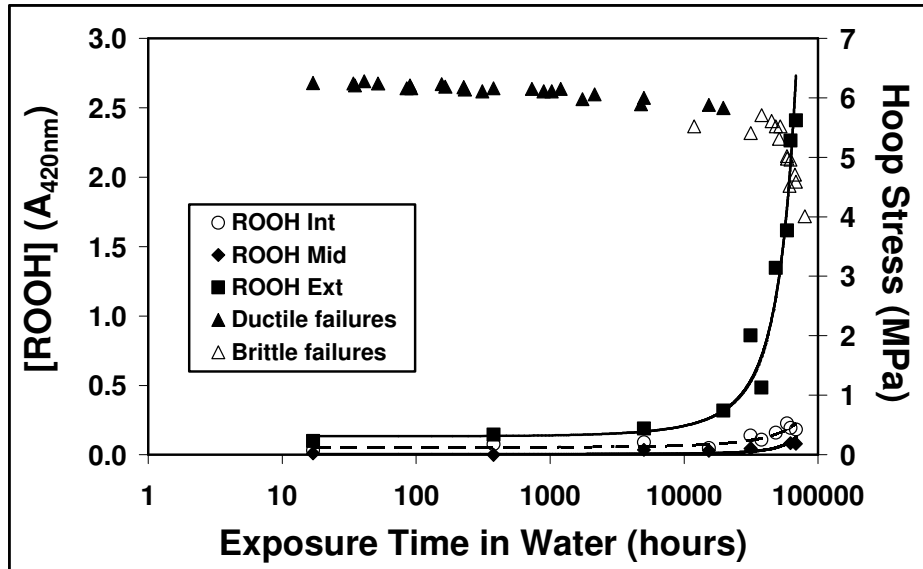


Figure 6. ROOH data and exponential fits at 80°C (left axis) and pressure regression data at 80°C (right axis)

The first important feature is that the level of ROOH at the external surface of the pipe appeared to increase significantly at the same time as the occurrence of the ductile/brittle knee, i.e. from around 30 000 hours. On the other hand, the surfaces least exposed to oxygen, i.e. the internal and middle surface of the pipe, did not show any significant increase in ROOH formation over the period of investigation. However, data suggest that the level of ROOH appeared to have reached a critical value at the external surface of the pipe to promote brittle failures of the whole pipe.

Another important feature is that the rate of formation of ROOH appeared to follow an exponential build-up pattern. This exponential formation of ROOH after an induction period is in good agreement with the known thermo-oxidative degradation mechanism of PE material observed by Gugumus (7). The level of ROOH was therefore determined at the external surface of the pipe at various test temperatures, i.e. 40, 60 and 80°C. Data at 20°C were not included as no significant hydroperoxide build-up could be detected (the error on measurements was too high relative to the values obtained). The logarithm (Ln) of ROOH was plotted versus exposure time at these various test temperatures and shown in Figure 7. As expected straight lines were apparent which support the exponential build-up of ROOH. Therefore data could be fitted into an Arrhenius model in the same manner as for OIT data using the rate of formation of ROOH shown in Table 1.

The Arrhenius equation for the formation of ROOH at the external surface of the pipe obtained from experimental data plotted in Figure 5 could be expressed as:

$$\ln(S_T) = -5735.2 \times \frac{1}{T} + 6.2622 \quad (5)$$

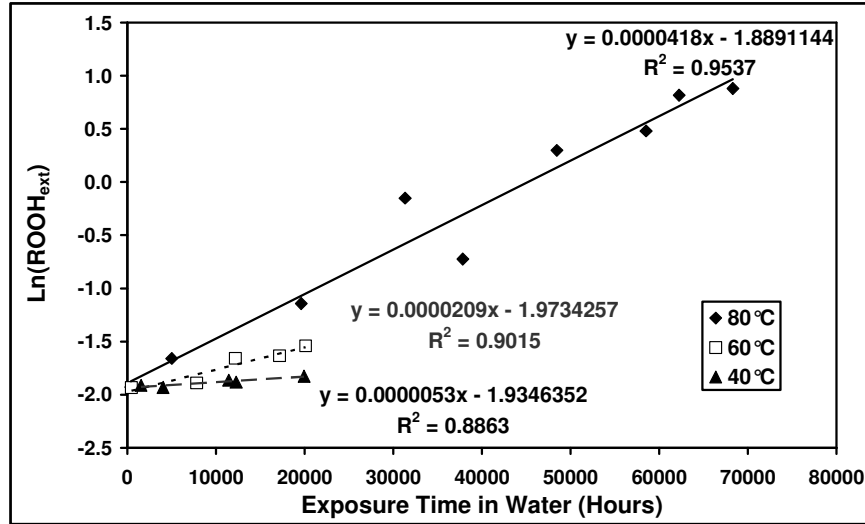


Figure 7. Logarithmic plot of ROOH data at various test temperatures for external surface of the pipe.

The activation energy E_a for the formation of ROOH at the external surface of the pipe could be deduced from the slope and was found to be 48 kJ/mol. The rate of formation of ROOH S_T at the external surface of the pipe could subsequently be extrapolated to service temperature of 10°C using Equation (5). The extrapolated rate of reaction S_T at service temperature of 10°C was fed into Equation (6) in order to predict the time required to reach the critical level of ROOH at the external surface of the pipe.

$$\ln(\text{ROOH}) = S_T \times t + \ln(\text{ROOH}_0) \quad (6)$$

where ROOH is the ROOH value for the pipe exposed at test temperature T and exposure time t , S_T is the rate of formation of ROOH (reaction rate) at test temperature T , t is the exposure time at test temperature T , ROOH_0 is the initial ROOH value for the unexposed pipe, i.e. at $t = 0$.

According to Figure 2, it is considered that the critical level of ROOH to lead to brittle failures is 0.5 (Absorbance at 420 nm). Therefore the extrapolated time to reach this critical level would be 2 019 595 hours, i.e. approximately 235 years. From the Arrhenius model applied to the ROOH data it was predicted that brittle failures would occur after approximately 235 years at a service temperature of 10°C. The time required to reach the critical level of ROOH at the external surface of the pipe was also extrapolated to other service temperatures, i.e. 20 and 25°C, and results are compiled in Table 2.

3.4. Discussion

Both Arrhenius models based on OIT and ROOH data were in agreement with each other. On one hand the total loss of antioxidants at service temperature of 10°C was about 150 years at the external surface of the pipe, i.e. the surface the most exposed to water and air, and about 195 years at the internal surface of the pipe. This is in line with recent studies by Lundbäck et al (8) which demonstrated that for PE samples exposed to water the depletion of antioxidants was faster for samples exposed to water saturated with air. On the other hand, extrapolation at this service temperature suggested that ROOH would increase significantly to reach a critical level at about 235 years at the external surface of the pipe, leading to brittle failures. This is in line with expectation as brittle failures would occur once no antioxidants remain to protect the pipe against oxidative degradation. As oxidation initiates and proceeds,

formation of ROOH becomes more significant and reaches a critical level where the pipe material loses its physical properties and fails in a brittle manner.

A time lag of about 85 years was recorded between the time to total loss of antioxidants at the external surface of the pipe at service temperature of 10°C (i.e. 150 years) and the time required to reach the critical level of ROOH at the external surface of the pipe at this service temperature (i.e. 235 years). This induction period preceding oxidative degradation may be due to the positive contribution of the HALS which protects the pipe material against long-term thermo-oxidation once all phenolic and phosphite antioxidants have been consumed. HALS can actually act as long-term heat stabiliser in polyolefin materials as demonstrated by Gijssman (9) and are most effective at low temperatures. However Schulte (10) showed that these stabilisers do not influence OIT but improve the long-term stability of blue HDPE pipes. Gensler et al (11) observed a more gradual deterioration with polymers stabilised with HALS. Once HALS have been consumed themselves by chemical reaction or physical loss, initiation of oxidation can proceed and the formation of hydroperoxides builds up significantly.

At higher service temperatures, the extrapolated lifetime still exceeded the 50 years lifetime requirement. According to results compiled in Table 2, the extrapolated time to total depletion of antioxidants at 20°C was 56 years at the external surface of the pipe and the extrapolated time required to reach the critical level of ROOH to lead to brittle failures exceeded 100 years. At the service temperature of 25°C, total depletion of phenolic and phosphite antioxidants was predicted to occur after approximately 35 years at the external surface of the pipe, whilst the time to brittle failures was approximately 85 years. Therefore, it is expected that this PE100 grade would also be able to meet 50 years lifetime requirement in warmer countries (ca. Southern Europe or Middle East). It is worth noting that the approach used in this paper simulated a worst-case scenario. First of all, both internal and external environment were water, whilst during service the internal surface of the pipes only is exposed to water. Furthermore, the test water was deionised. Practical experience proved that deionised water accelerates the degradation of the pipe compared to non-deionised water. Therefore it is expected that the service lifetime of this PE100 pipe material is greater than the lifetime figures determined in this paper.

4. CONCLUSION

A new approach that combines hydrostatic pressure testing and chemical analysis for depletion of antioxidants (OIT) and formation of hydroperoxide oxidative products (ROOH) was used to predict the lifetime of a blue PE100 water pipe material. An empirical model based on the Arrhenius fit of the data was developed to extrapolate the lifetime of the PE pipe at various service temperatures. Lifetime prediction over the range 10 - 25°C proved to exceed the 50 years lifetime requirements. Furthermore the rate of antioxidant depletion is strongly related to the type and level of antioxidant mixtures. As a matter of fact not only the extractability resistance of the antioxidant will affect the rate of depletion, but also its susceptibility to hydrolyse as it has been recently demonstrated by Nagy et al (12). On the other hand, the use of other stabilisers such as HALS has the ability to prolong the service lifetime of PE pipes. The empirical model presented in this paper could be applied to other plastic pipe materials and to other environments (ca. water chlorinated with sodium hypochlorite or chlorine dioxide, etc.). Furthermore the lifetime prediction based on OIT could be obtained with 2 years pressure testing data only. Finally the model may be used for evaluating changes in AO packages and/or the degree of deterioration of pipes in the field.

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