J Mater Sci (2009) 44:4683–4691
DOI 10.1007/s10853-009-3719-x

Methods for determining the in-service life of polymer water pipes

**J. M. B. Sanders · M. A. Shepherd ·
H. M. S. Belmonte · J. P. Dear**

Received: 27 March 2009 / Accepted: 1 July 2009 / Published online: 21 July 2009

Abstract A key requirement for polymer pipes, in having the ability to achieve a long in service life, is the retention by the polymeric material of its anti-oxidants. In dry air and other favourable environmental conditions the life-span of the polymer material can be many decades. However, when polymer pipes are transporting water and the pipes need to be installed in all kinds of ground conditions then the loss of anti-oxidant from the polymer can become more of a problem. To maintain integrity of water distribution networks, companies aim to plan for replacement of water pipes before they are likely to fail. This paper presents ways in which small scale evaluations of aged pipe material can be employed to assess remaining in-service life of water pipes. Small-scale chemical and physical evaluations have been devised to provide indicators of the ageing process with associated loss of mechanical properties. The presented studies were performed using MDPE and PE80 pipe materials. These materials were evaluated before and after ageing to identify which chemical and physical evaluations were the most appropriate to assess the remaining life of in service polymer pipes.

Introduction

The use of medium density polyethylene (MDPE) and high density polyethylene (HDPE) has increased rapidly since it was first used for high pressure water distribution in the 1980s. This pipe material can last upwards of 50 years under some operating conditions. However, the expected lifetime will relate to the severity of the operational and environmental stresses to which a pipe is subjected and this can vary in different parts of water distribution networks. There is also the point that minerals present in drinking water vary depending on its source. Hence, the need is to be able to determine the remaining lifetime of pipes in different locations. Planned sampling of pipe material as part of maintenance programs and other opportunities is helpful in providing the needed sampling required. This is for monitoring the degradation of pipe material in different locations and identifying those pipes approaching the end of their reliable in service life. This sampling of pipe material for laboratory studies can help in identifying areas that for different reasons have higher than average pipe deterioration. This information can also help for better planning of pipe replacement needs, which are linked to planned maintenance, new installations and other opportunities.

The major type of degradation that occurs in pipes is a type of oxidation called auto-oxidation, where the polymer reacts with oxygen to form carbonyls and hydro-peroxides. The degradation causes chain scission which is a reduction in the polymer chain length [1]. This scission in turn causes a decrease in the strength of the polymer and the formation of cracks, both of which result in a pipe made of this material being more susceptible to failure. Other forms of degradation [1, 2] such as chemical degradation will also take place, but the reduction in properties will be similar. This article describes the different chemical/physical markers that can

J. M. B. Sanders (✉) · J. P. Dear
Department of Mechanical Engineering, Imperial College
London, London SW7 2AZ, UK
e-mail: joseph.sanders02@imperial.ac.uk

J. P. Dear
e-mail: j.dear@imperial.ac.uk

M. A. Shepherd · H. M. S. Belmonte
Thames Water Utilities, Research & Development, Innovation
Centre, Reading STW, Island Road, Reading RG2 0RP, UK

be identified and the experimental procedure that is used to measure each of the different chemical properties. Initial results are then presented as well as a discussion into their suitability and repeatability for pressurised water pipe distribution systems.

To resist degradation, the polyethylene pipe material is saturated with anti-oxidants during its production. The anti-oxidants used depend upon the polyethylene supplier. It is important that a high degree of anti-oxidant is retained in the polyethylene during pipe manufacture. The retention of anti-oxidant during the in-service life of pipes is one important factor in this study. End of life failure of polyethylene pipes often starts with hair-line axial cracks being generated on the pipe's inner surface. Anti-oxidants protect polymer chains from scission and other oxidising effects. This is in the amorphous regions of the material because oxygen does not penetrate the crystalline regions so easily. A problem is that the anti-oxidant agents in, for example, polyethylene continuously migrate to and are lost from the surface of the material. Unfortunately, water is particularly proficient in the removal of the anti-oxidant from the surface of the material with the result of increasing loss of anti-oxidant from the polymer. Also, the diffusivity of the anti-oxidant in the polymer is affected as the polymer absorbs water. Bodycote Polymer formerly Studsvik Material AB [3–11] has studied these loss processes of anti-oxidant from polyethylene pipes. From these accelerated studies, it was indicated that polyethylene pipes would have a life, in standard water distribution systems, of about 50 years.

Studies have also been performed using different methods to extrapolate the lifetime of polymeric material. These include studying the thermal stability of the polymer [3, 5, 12, 13], as well as studying the carbonyl content of the polymer after degradation has occurred [5, 14, 15].

However, these studies did not obtain data related to the wide range of dynamic, static and environmental stresses to which water distribution systems can be subjected. They did, however, show the relevance of different analytical techniques to polymer water pipes. Hence, there is a need for accurate evaluation procedures which can be applied to pipes in-service.

Types of chemical/physical evaluations

The degradation of polymers generates chemical and physical changes (or markers) that can be measured. One marker is the formation of carbonyl groups which include the ester, ketone and acid compounds formed by the oxidation of a polymer [16, 17]. The greater the degree of oxidation the more of these different carbonyl functional groups are present and identifiable.

The presence of chain scission can be determined by examining the molecular weight distribution and molecular mass (M_w); scission is associated with a decrease in the molecular weight. Then by comparison of the virgin material and the aged material's molecular weight distribution, the number of lower molecular weight molecules can show the degree of scission.

The crystallinity of a polymer can also show how much degradation has occurred; the percentage of the material that is crystalline increases as the polymer degrades [18].

The melt temperature (T_m) of the crystalline polymer can also be determined and this gives an insight into the thermal stability of the polymer. The higher the melt temperature the more thermally stable the polymer.

These markers can indicate that degradation has already begun and there may already be weaknesses in the material. Examining the stabilisers added to the polymer at manufacture can give an insight into the time to the onset of degradation. One of the most important of these is a group of additives known as anti-oxidants. The higher the concentration of remaining anti-oxidants shows the length of time remaining to the onset of degradation.

Experimental

The following are the different experimental techniques employed to find the chemical markers required.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) uses a differential scanning calorimeter to measure the change in heat flux between a sample and a reference that is held at the same temperature. This allows observations into any phase changes as well as any thermal changes during reactions.

The amount of crystalline polymer is determined using the total enthalpy method [19]. The procedure follows that of the ISO 11357-3. The samples used were discs punched from films taken from through the thickness of the pipe and these were of mass 2.5 ± 0.25 mg; this is smaller than the standard due to the thickness of the film. These were placed in regular aluminium pans and sealed. The samples were then tested using a TA DSC Q2000, heating them from 60 to 180 °C, this allows for the change in melt temperature between the different pipe samples. The data are then analysed using the connected TA Analysis software, where the enthalpy of fusion (ΔH_f) (the area under the curve) and the melt temperature (the peak of the curve) are determined. Using the enthalpy of fusion of a 100% crystalline material quoted by Wunderlich [20] as 293 J/g, the percentage of crystalline material in the polymer can be determined.

The other use of the DSC is to determine the remaining anti-oxidant concentration in the polymer resin. The current standard for this is ISO 11357-6:2002, which describes the Oxidation Induction Time (OIT). This uses the fact that oxidation is an exothermic reaction and hence can be recorded by the DSC. Anti-oxidant loss is determined by measuring the OIT at 200 °C for samples subject to different ageing conditions (for example, the initial OIT at 200 °C for MDPE is ca. 70 min). This isothermal method for testing the anti-oxidant concentration, as described by Schmid et al. [21], has its problems. The change in gas can cause an error and the identification of the oxidation point can be difficult to achieve.

There is, however, a dynamic method for testing the anti-oxidant concentration. Unlike the OIT, where the polymer sample is kept at 200 °C in an air atmosphere, the oxidation induction temperature (OIT*) [22] ramps the temperature. The temperature at which the oxidation occurs is then recorded. The OIT* is not standardised except in Finland, but is being considered as part of a revision to ISO 11357-6:2002. The method employed for this study was that used by Schmid and Affolter [23], using a Perkin Elmer Pyris 1. The samples were punched from films (2.5 ± 0.25 mg) and placed in aluminium pans with the lid loosely fitted. The loosely fitted lids allow the air to get full contact with the sample. The sample is heated in air at a flow rate of 50 mL/min. Starting at 50 °C, the sample is heated at a constant rate of 10 °C/min, until the sample oxidises and the oxidation peak is observed (an initial test of the material at 50 °C/min was used to give a rough end point). The procedure was seen to give oxidation points that were easily identifiable and also took less time to obtain than with normal OIT evaluation. The oxidisation temperature can then be measured at the onset of decomposition; this is calculated by finding the temperature at which the base-line and the tangent to oxidation intersect.

The degree of depletion of the anti-oxidant, through the thickness of the pipe wall, can be determined by taking thin microtome wafers through the thickness of each pipe wall and then subjecting each wafers to DSC.

Infrared spectroscopy

Infrared spectroscopy (IR) is a common tool used to look at the structure and composition of polymers particularly PE. Infrared radiation is passed through the sample and each different type of bond absorbs a different frequency of radiation. The type of bond present can then be determined by examining tables of known frequencies. The tables by Bellamy [24, 25] were used in this research.

The absorbance of each bond can also be determined, allowing an insight into the abundance of that particular bond and hence a particular group. The carbonyl groups are identified by peaks at 1,740 cm^{-1} (Ester group), 1,715 cm^{-1} (Ketone group) and 1,705 cm^{-1} (Acid group). The absorbencies at these peaks are normalised by the methyl group at 1,465 cm^{-1}, this allows scans to be compared and a carbonyl index to be calculated, showing the abundance of the carbonyl groups and hence how much oxidation has occurred.

Spectra for all the samples were obtained using a Perkin Elmer Spectrum One FT-IR Spectrometer fitted with an ATR attachment. The scans were performed between frequencies of 4,000–1,200 cm^{-1} and 10 scans were performed on each sample. Software connected to the spectrometer was then used to evaluate the peaks of interest, and the carbonyl index calculated.

Gel permeation chromatography

Gel Permeation chromatography (GPC) is used to calculate the molecular weight of polymers as well as the molecular weight distribution. If chain scission has occurred then the molecular weight would have been reduced and this can be detected by GPC. The molecular weight distribution can be used to examine the length of the polymer chains and by using weighted averages this can be examined further. GPC works by using the size exclusion phenomena, with the sample flowing down a column packed with porous glass beads. The molecules are trapped by the glass beads, the smaller ones less so than the larger ones and hence slowing the larger molecules. The number of polymer chains are then calculated at the bottom and compared to a sample of known molecular weight.

GPC evaluation was done by Dr Steve Holding of RAPRA Technology Limited. Samples of 15 mg of the polymer was dissolved in 15 mL of 1,2,4-trichlorobenzene with anti-oxidants. This mixture is then heated to 190 °C for 20 min and then cooled to 160 °C and filtered prior to testing. The data were then analysed and the average molecular weights calculated. Higher average molecular weights can also be calculated. As these are more sensitive to higher molecular weight molecules, this is done by increasing the order of the molecular weight used when finding the average as given in Eqs. 1 and 2:

$$M_{\mathrm{w}} = \frac{\sum N_i M_i}{\sum N_i} \tag{1}$$

$$M_z = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{2}$$

where M_i is the molecular weight of a chain and N_i is the number of chains that have the molecular weight M_i. A decrease in M_{w} would suggest a decrease in the size of the chains in general; whereas a decrease in the number of larger chains would be visible when comparing M_z. This weighted averaging can be taken further by increasing the order of the molecular weight. Other researchers have found it useful when studying PEs, which have variable polydispersity, to use the *Z*-average molecular mass (M_z) particularly for comparing different grades. In this study, only one grade of PE was assessed and hence it was acceptable to use M_w.

Mechanical tensile studies

For the mechanical studies, polyethylene dumb-bell shaped specimens, of thickness 2 mm, were obtained from the inner wall of MDPE pipes. These specimens conform to the standard shape required for mechanical tensile tests as specified in Type A test piece in BS 2782 Method 320A (1976). Several specimens were obtained from each section of pipe and these were used to obtain the elongation to failure of the material before and after ageing. All specimens were taken from along the axis of the pipe. For each study of pipe degradation, these specimens provided consistent results.

For the PE80 material also studied, tensile tests were performed on dumb-bell shaped specimens, of thickness 0.5 mm. These were taken 1.5 mm from the inner surface and 1.5 mm from the outer surface. Three samples from along the axis of the pipe were obtained for each aged sample and an average taken. The elongation to failure, yield stress and failure stress were then used as the parameters in the evaluation of the mechanical properties of the pipe.

Effect of chlorine on stressed pipes

Studies of creep rupture by hydrostatic pressure were performed, with chlorinated water, on MDPE pipes (diameter 90 mm with SDR 11 and SDR 17.6) using the WIS 4-32-03 standard. The lengths of the pipe were 1 m and their ends were capped with electro-fusion seals as specified by WIS 4-32-08. After these sealed pipes had been charged with the appropriate pressurised chlorinated water, they were immersed in water baths maintained at elevated temperature. The level of chlorine concentration of the water in the sealed pipes was monitored and maintained. These pressurised pipe experiments continued until the pipes failed or completed the test period. After failure, 2 mm thick dumb-bell specimens were taken from the inner wall of the pipe and these specimens were subjected to tensile tests to measure yield stress and elongation to failure.

Chlorine penetration

For the chlorinated stressed pipe studies, energy dispersive X-ray analysis (EDAX) was used to determine the depth of penetration of chlorine into the inner wall of the polyethylene pipe. This was to perform an EDAX measurement at different depths from the inner wall surface of a cross section of the pipe wall. The EDAX experimental data were confirmed by subjecting a number of specimens to pyrolysis-gas chromatography (PGC), and that revealed the concentration of chlorine at different through-thickness points in the specimen. This was achieved by taking thin microtome wafers through the thickness of each pipe wall and subjecting each wafer to PGC.

Results and discussion

Ageing experiments on MDPE

For one series of experiments on MDPE, chlorine was added to the water to accelerate the ageing process [26]. The accelerated evaluations, to study the degradation of complete pipes (diameter 90 mm of SDR11 and SDR17.6), were performed at 80 °C, with pressurised chlorinated water of different concentrations. The chlorine concentration on the inside of the pipe was varied from 500 to 120,000 mg L^{-1} [changed every 672 h (4 weeks)]. Three groups of experiments were performed, using different hydraulic pressures that produced hoop stresses in the pipe wall of 2.7, 3.1 and 4.6 MPa. The pressurised pipes were immersed in large tank of unchlorinated water at 80 °C. It is necessary to note that at high temperatures there can be changes in crystallinity and mechanical properties of the pipe material. This needs to be taken into account when relating the results obtained at high temperature to the working temperature of pipes. Also, to be noted, there are partial correlations, for example, between the effects of temperature, stress and chlorine concentration.

For the pipes which failed, Fig. 1a shows a plot of Log_{10} (hoop stress) versus Log_{10} (time to failure). All of the failures for pipes evaluated in this study were of a macroscopically brittle nature. The reference line shown on Fig. 1a is, however, for both ductile and brittle failures in MDPE at 80 °C when the water inside the pipe is not chlorinated. This reference line was based on the same conditions as originally employed by Gedde et al. [4]. Ductile failures exhibit drawn or yielded material about the failure site whereas brittle failures show little or no evidence of yielding or drawing and failures are mostly due to axial cracks. The ductile failure processes are mostly controlled by the viscoelasticity of the MDPE and hence the ductile failure line has a gradual slope. The brittle failure line, however, has a much sharper slope and shows that brittle failures occur at stress levels below those for ductile failures. For the same hoop stress in the pipe wall,

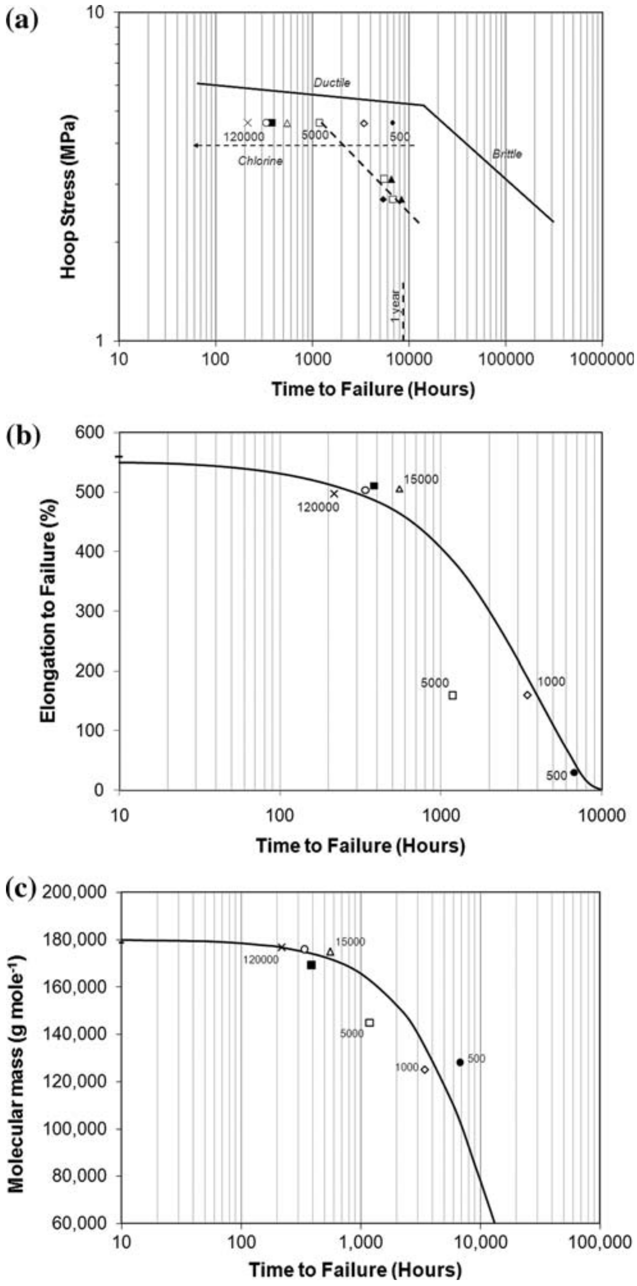

Fig. 1 Failure of chlorinated stressed MDPE pipes when internally pressurised at 80 °C for chlorine concentrations in mg L^{-1}: 500 (●), 1,000 (◇), 3,000 (▲), 5,000 (□), 10,000 (◆), 15,000 (Δ), 30,000 (■), 45,000 (○), 120,000 (×): **a** Hoop stress versus time to failure—a *reference* line is shown for *ductile* and *brittle* failures at 80 °C when the pressurised water inside the pipe is not chlorinated, **b** elongation to failure versus time to failure for a hoop stress of 4.6 MPa, **c** molecular mass (M_w). *Note*: Symbol (–) relates to the measurement of the properties of the pipe material prior to ageing of the pipes

pipes will fail earlier when exposed to a higher chlorine concentration, as indicated by Fig. 1a.

It was to be expected that the brittle failure lines, related to the pressurised chlorinated water, would have the same slope as the brittle failure line for unchlorinated water. This was verified by subjecting pipes to different pressures of chlorinated water, which was at a set concentration (5,000 mg L^{-1} at 80 °C), and drawing a dotted line through these brittle failure points (see Fig. 1a). The dotted line was parallel to the brittle failure line for the pressurised unchlorinated water.

After subjecting the sealed pressurised pipes to different concentrations of hot chlorinated water at 80 °C, dumb-bell shaped specimens (*BS 2782: Method 320A-Type A dimensions*) of 2 mm thickness were taken from the pipe's inner wall. These specimens were tensile loaded to obtain yield stress and elongation to failure data. For those pipes subjected to hot chlorinated water and a hoop stress of 4.6 MN m^{-2}, Fig. 1b shows a plot of the elongation to failure of the aged pipe material versus time to failure. Each plot point is coded using a different symbol for each chlorine concentration. For high chlorine concentrations, those greater than 15,000 mg L^{-1}, the time to failure of the pipe is <1,000 h, but the elongation to failure of the aged specimen is little affected. However, for chlorine concentrations of 5,000 mg L^{-1} or less, the time to failure is longer and there is a marked reduction in the elongation to failure of the aged specimen. Figure 1c shows the molecular mass (M_w), measured using GPC, for the aged specimens plotted against time to failure. This reveals that M_w decreases as the exposure time to the hot chlorinated water increases. The reduction in M_w by chain scission would occur mostly in the amorphous material and relates to the individual concentrations of chlorine and oxygen, as well as the level of stress in the working pipe. This is similar (though smaller) to the decrease in M_w seen by Hassinen et al. [27]. The pipes assessed by Hassinen et al. [27] were in a circulation loop configuration, while the pipes analysed in this research were hydrostatically loaded. Differences in test temperatures, pressures and material could also account for the differences seen.

Figure 2 shows examples of OIT profiles that were obtained from the aged pipes that failed. In these plots, the vertical dashed line shows the extent of the penetration of the chlorine as measured by EDAX. The upper horizontal dotted line relates to the anti-oxidant level prior to ageing of the pipe and the lower solid line shows the anti-oxidant profile after ageing. Figure 2a relates to a pressurised pipe, with a hoop stress of 4.6 MPa and aged with a chlorine concentration of 120,000 mg L^{-1}, which failed after 216 h. Figure 2b relates to a pressurised pipe, with a hoop stress of 4.6 MPa and aged with a chlorine concentration of 15,000 mg L^{-1}, which failed after 552 h. For both cases, there is a sharp loss of anti-oxidant from the inner wall of the pipe and the diffusion of anti-oxidant to the inner wall has increased. This loss of anti-oxidant via the inner wall surface is much greater than the loss via the

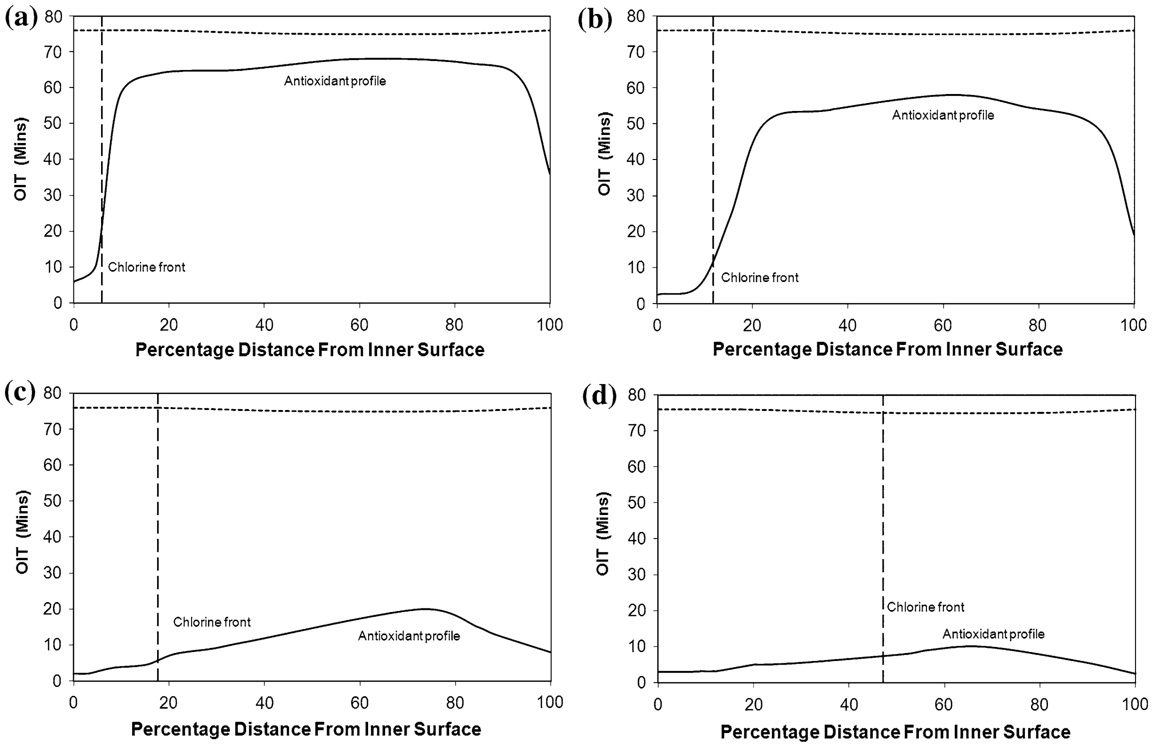

Fig. 2 Anti-oxidant concentration by OIT versus distance from inner wall for failures of aged MDPE pipes (hoop stress 4.6 MPa) with *vertical dashed line* showing penetration of chlorine by EDAX: **a** chlorine concentration 120,000 mg L^{-1} and time to failure 216 h, **b** chlorine concentration 15,000 mg L^{-1} and time to failure 552 h, **c** chlorine concentration 5,000 mg L^{-1} and time to failure 1176 h, **d** chlorine concentration 1,000 mg L^{-1} and time to failure 3432 h

outer wall surface, which is only exposed to unchlorinated water. Initially, a substantial proportion of the anti-oxidants diffusing to and lost from the wall surfaces will be the more mobile anti-oxidants. Figure 2c, d relates to two examples of OIT profiles for aged pipe samples that failed after longer periods of time. Figure 2c relates to a pressurised pipe, with a hoop stress of 4.6 MPa and aged with a chlorine concentration of 5,000 mg L^{-1}, which failed after 1,176 h. Figure 2d relates to a pressurised pipe, with a hoop stress of 4.6 MPa and aged with a chlorine concentration of 1,000 mg L^{-1}, which failed after 3,432 h. For both cases, the consumption of anti-oxidant is much more marked. In particular, Fig. 2d shows that the penetration of the chlorine is nearly halfway through the thickness of the pipe wall and that the anti-oxidant depletion is considerable both behind and ahead of the chlorine front. This data can be easily compared to Hassinen et al. [27], but with the outer surface being in a water environment there is a greater reduction on the outer surface. This makes direct comparison difficult with respect to the rate of chemical consumption of the anti-oxidants as chemical degradation occurred at inner and outer surfaces.

Ageing experiments on PE80

For the second series of experiments on PE80, pipes (diameter 63 mm of SDR 11) were placed unstressed into a bath with a 2% Arkopal N100 in distilled water at 80 °C. Virgin pipe material and pipes aged for 50, 120, and 500 h were evaluated. These times were decided upon by studying research performed by Pinter et al. [28].

Samples were taken throughout the thickness and evaluated as explained in the "Experimental" section. Figure 3 shows the carbonyl index through the pipe for the various exposure times. It is notable that there is a steady increase in the carbonyl index from the virgin pipe to the aged pipe for 500 h. The carbonyl index through the pipe wall exhibits a higher carbonyl index in the middle rather than near the surface. No other carbonyl testing has been found using Arkopal and so there is no other research data with which to compare the data obtained. A possible process is thought to be due to the Arkopal encouraging oxidation to occur and then the carbonyl products being leached out. This would explain the shape of the graph.

Figure 4a shows the percentage crystalline material in the polymer matrix and Fig. 4b displays the results obtained

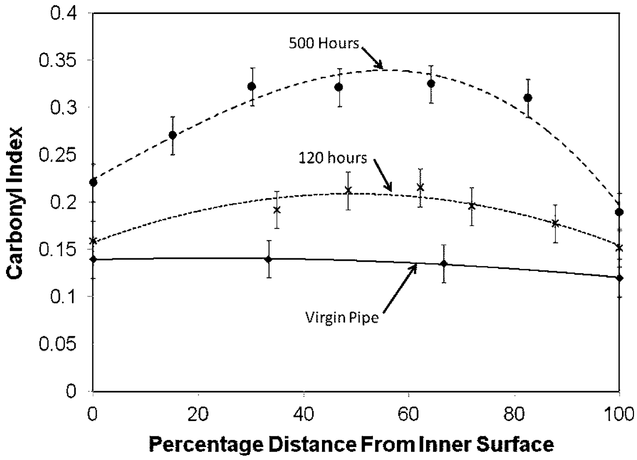

Fig. 3 Carbonyl index (ester) versus percentage distance from inner wall for PE80 aged in Arkopal at 80 °C: 0 h (◆), 120 h (×) and 500 h (●). Trends through the pipe are shown by the *dashed lines*

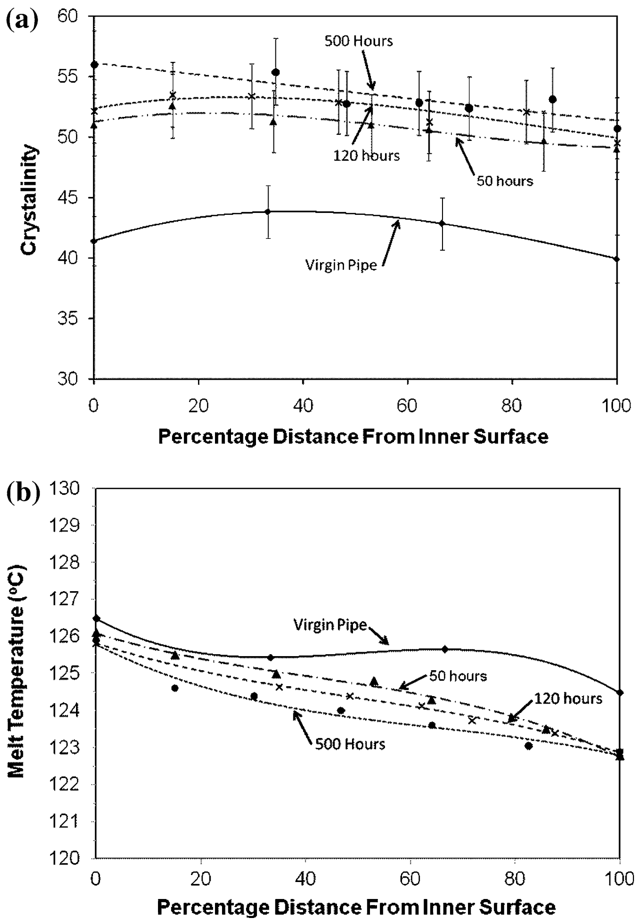

Fig. 4 Thermal properties of PE80 aged in Arkopal at 80 °C versus distance from inner wall for: 0 h (◆), 50 h (▲), 120 h (×) and 500 h (●). Trends through the pipe are shown by the *dashed lines*. **a** Percentage crystalline material of matrix and **b** melt temperature of polymer

for the melt temperature through the pipe wall thickness. The changes in the crystallinity are most evident between the virgin pipe and the samples that have aged; however, there is less difference between the aged samples at different times. A possible reason is that the changes in crystallinity have occurred in the first 50 h of ageing and after this, there has been limited change. The trend lines all go from the inner surface to the outer surface. This is expected, when the pipes are extruded the outer layer is water cooled while the inner surface is allowed to cool in air. Crystallinity increases while the pipe is cooling hence the inner surface has a higher crystallinity. Figure 4a shows that this trend continues in the aged samples, which suggests that the ageing has occurred uniformly over the wall thickness. The melt temperature shows a stronger correlation; there is a steady trend from the inner to outer surface which is due to the manufacturing process that the pipe has undergone. Again as with the carbonyl index, there is a steady trend from the virgin sample to the aged pipe. These changes are very small though and it would be hard to repeat to the required accuracy to determine the predicted life of the pipe. However, when the crystallinity and melt temperature are compared to the results found by Hassinen et al. [27] they show a comparable degradation for a PE100 pipe aged at pressure in chlorine. These results too show a large increase of crystallinity between virgin and aged pipe, but only a small change between the two different ageing regimes used. The results differ at the inner surface and this is probably due to the chlorine environment that was used compared to the Arkopal environment.

Figure 5 shows the OIT* profiles through the thickness of the pipe; the aged samples show an obvious decrease in the temperature of oxidation, especially at the outside edges. Unlike the OIT profiles seen in Fig. 2 where the outer and inner surface have been exposed to different ageing regimes, the profiles in Fig. 5 are symmetrical as

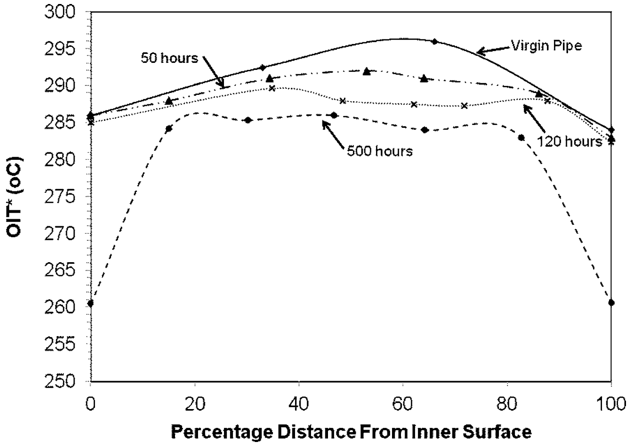

Fig. 5 Oxidation induction temperature (OIT*) profile versus distance from inner wall for: 0 h (◆), 50 h (▲), 120 h (×) and 500 h (●)

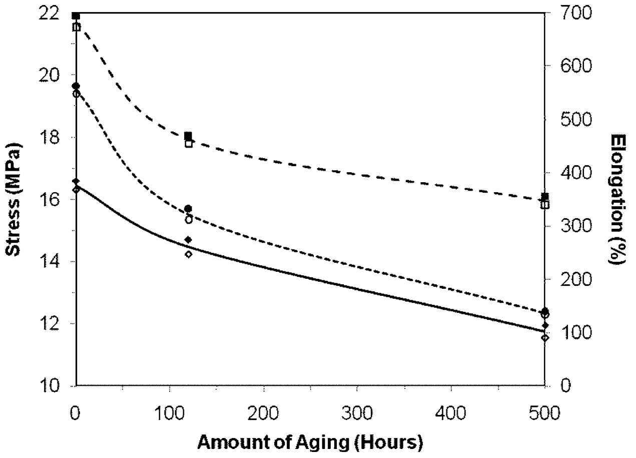

Fig. 6 Tensile strength of the samples compared with the ageing conditions. The failure stress [outer surface (●) and inner surface (○)] and yield stress [outer surface (◆) and inner surface (◇)] (*left hand vertical axis*) compared with the elongation to failure [outer surface (■) and inner surface (□)] (*right hand vertical axis*)

the outer and inner surface are subject to the same environment.

Figure 6 shows the results obtained from the tensile testing of the aged samples. A decrease in both failure stress and elongation is observable because the samples have been aged for longer.

Evaluation of analysis methods

The requirements of the water industry are that any test of pipe degradation and ageing can be performed easily and produce reproducible results that show a clear correlation between the chemical markers and the deterioration of physical/mechanical properties.

The melt temperature and crystallinity show a difference between the aged and non-aged pipes, but there was little change between the aged samples. This limited change means that these results for this methodology are not so suitable for determining the remaining lifetime in a commercial environment. They do, however, have a good comparison to the deterioration of the physical properties; the major deterioration occurring between 0 and 120 h. This is expected as crystallinity is known to be a factor when examining tensile strength.

The easiest chemical markers that show the most noticeable change between the aged samples were the carbonyl index and the OIT*. The carbonyl index shows a steady increase, which is proportional to the ageing time. This increase is most noticeable at the centre of the pipe with a major drop at the edges, where it is believed carbonyl products have leached into the ageing fluid.

The OIT and OIT* seen in Figs. 2 and 5, respectively, show another possible marker that could be used to determine the amount of degradation in the pipe. The OIT* showed a very good comparison to the tensile strength of the middle of the pipe with the major change in the central section of the wall thickness occurring between unaged pipe and pipes aged for 50 h. Comparison between the OIT and OIT* can also be made, the plateau can be seen in both cases and both represent the anti-oxidant profile of the pipe. On a functionality point, the OIT can take upwards of 70 min, whereas the OIT* only takes 20 min. The anti-oxidant profile also gives a give a pre-warning of any degradation occurring; the anti-oxidants will begin to be used up before oxidation occurs, indicating the start of degradation. This allows the degradation to be noticed early and plans made for the pipe to be replaced.

Being able to relate these chemical markers to the mechanical properties of the pipe would allow further evaluation that could help in determining the remaining life of the water pipe that is in service. This was achieved by finding the value of chemical markers (OIT* and carbonyl

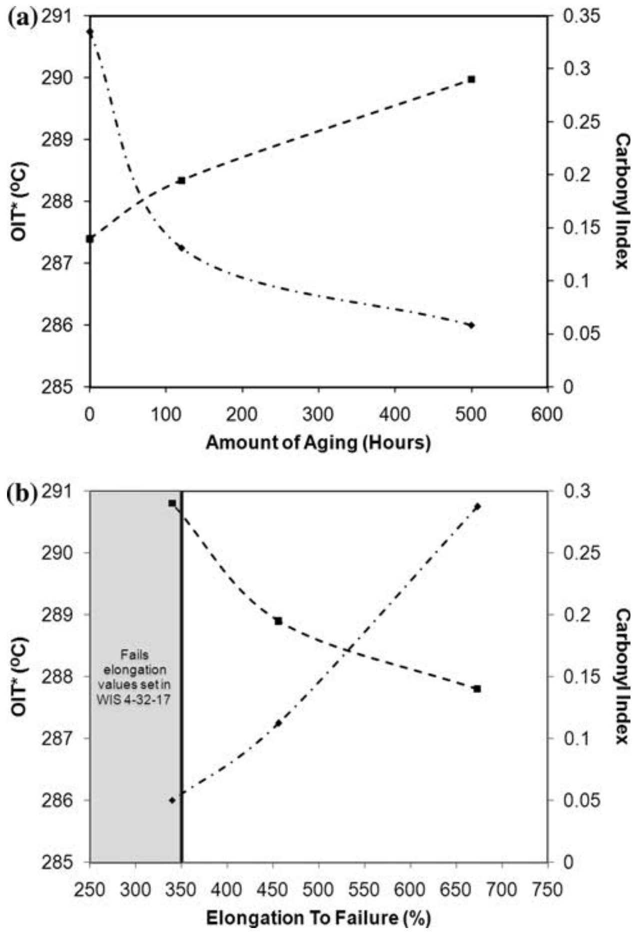

Fig. 7 Relating the chemical markers to the mechanical properties, carbonyl index (■) and OIT* (◆). **a** Relates the chemical markers to the amount of ageing. **b** Relates the chemical markers to the mechanical properties

index) at 1.75 mm from the inner surface. This was used as it is the middle of the mechanical test pieces used in Fig. 6. These values were then plotted against time of exposure as presented in Fig. 7a. Figure 7a can then be cross-referenced with Fig. 6 so that the chemical markers and elongation can be related to each other as seen in Fig. 7b. Figure 7b shows the grey area where the elongation is not sufficient to pass the requirements in WIS 4-32-17, this could be used to examine the suitability of a pipe in service to perform its required function. This would then give a lower limit of the chemical marker that could be used by the water companies to test the pipes that are in service.

Conclusions

Below is a summary list of the main findings:

- The anti-oxidant profiles determined by OIT and OIT* analysed through the pipe wall thickness both give good indication of loss of anti-oxidant from the pipe material.
- The OIT and OIT* showed a good correlation to the reduction in tensile strength and elongation to failure of the pipe material. The OIT* procedure was seen to give oxidation points that were easily identifiable and also took less time to obtain than with normal OIT evaluation and would be a good marker to be employed by the water industry.
- There is a steady increase in the carbonyl index with ageing of the pipe material. Carbonyl index is a sensitive indicator which also gave good correlations to changes in the mechanical properties of the pipe material, and would also be suitable to be used as a chemical marker by the water industry.
- The changes in crystallinity and melt temperature were more difficult to detect, but these provided complementary marker data which was relatively easy to obtain.
- The process developed of obtaining thin tensile specimens from inner and outer surface of a pipe to provide complementary tensile properties could also be used for marker assessment by the water industry. However, the physical/chemical evaluations can be applied to smaller samples and are more attractive in some cases.
- By relating the chemical and mechanical properties, a lower limit of suitability can be determined for the chemical markers that can be used to see if the in-service water pipe can be left or must be replaced.

Acknowledgements The authors wish to thank Ms. P. Carry for her help with the analytical treatments in this project. This research has been supported by ESPRC and Thames Water Utlities.

References

1. Kelen T (1983) Polymer degradation. Van Nostrand Reinhold Company, New York
2. Schnabel W (1981) Polymer degradation—principles and practical applications. Hanser International, New York
3. Gedde UW, Ifwarson M (1990) Polym Eng Sci 30:202
4. Gedde UW, Viebke J, Leijstrom H, Ifwarson M (1994) Polym Eng Sci 34:1773
5. Karlsson K, Smith GD, Gedde UW (1992) Polym Eng Sci 32:649
6. Verdu J, Colin X, Fayolle B, Audouin L (2007) J Test Eval 35:289
7. Viebke J, Gedde UW, Elble E (1996) Polym Eng Sci 36:458
8. Viebke J, Gedde UW (1997) Polym Eng Sci 37:896
9. Viebke J, Elble E, Ifwarson M, Gedde UW (1994) Polym Eng Sci 34:1354
10. Viebke J, Hedenqvist M, Gedde UW (1996) Polym Eng Sci 36:2896
11. Viebke J, Gedde UW (1998) Polym Eng Sci 38:1244
12. Woo L, Khare AR, Sandford CL, Ling MTK, Ding SY (2001) J Therm Anal Cal 64:539
13. Woo LC, Ling MTK, Eu B, Sandford C (2006) Thermochim Acta 442:61
14. Sombatsompop N, Sungsanit K, Thongpin C (2004) Polym Eng Sci 44:487
15. Kaci M, Sadoun T, Cimmino S (2000) Macromol Mater Eng 278:36
16. Allara DL (1975) Environ Health Perspect 11:29
17. White JR, Turnbull A (1994) J Mater Sci 29:584. doi:10.1007/BF00445969
18. Graice IM, Younan MYA, Naga SAR (2005) J Pressure Vessel Technol Trans ASME 127:70
19. Gray AP (1970) Thermochim Acta 1:563
20. Wunderlich B (1980) Macromolecular physics—vol 3, Crystal melting. Academic Press, New York
21. Schmid M, Ritter A, Affolter S (2006) J Therm Anal Cal 83:367
22. Koski L, Saarela K (1982) J Therm Anal 25:167
23. Schmid M, Affolter S (2003) Polym Test 22:419
24. Bellamy LJ (1975) The infrared spectra of complex molecules, vol 1. Chapman and Hall, London
25. Bellamy LJ (1975) The infrared spectra of complex molecules, vol 2—advances in infrared group frequencies. Chapman and Hall, London
26. Mason NS (1998) PhD thesis, Imperial College, London
27. Hassinen J, Lundback M, Ifwarson M, Gedde UW (2004) Polym Degrad Stab 84:261
28. Pinter G, Haager M, Balika W, Lang RW (2007) Polym Test 26:180