

CHEMICAL AND MECHANICAL EVALUATION OF POLYMER PIPES TO DETERMINE REMAINING LIFE

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ABSTRACT

Asset management of water distribution networks is an important activity for water supply companies. This is to achieve and maintain the specified structural integrity of the network to minimise leaks and the continuity of water supply to the nationally defined quality standards. Key objectives are to achieve cost effective planning of the replacement of life-expired pipes with other maintenance work and extensions to the network whenever possible. This is particularly important when water pipes are beneath busy streets. An essential need is the ability to determine the end of life of installed pipes, of different materials, which relate to their different operational and environmental conditions.

In this study, results of accelerated testing have been used to predict in-service life of different polymer pipes. Actual life depends upon the working environment and operating conditions of the pipe. Precisely determining the end of life of polymer pipes, as they approach and go beyond their nominal life of 50 years, is difficult but important if planned replacement is to avoid frequent, costly and unpopular emergency repair activities. Some polymer pipes have now been in service for several decades and the expected life of these pipes is the main topic of this paper.

The research to be presented shows several different methods for assessing the age of pressurised polymer water pipes. These methods are divided into chemical evaluation and mechanical testing. The methodology of each of the analysis techniques is presented. The work looks specifically at the use of differential scanning calorimetry methods to identify degradation in the polymer. The use of oxidation induction time analysis for polyethylene and degree of fusion measurements for polyvinyl-chloride are shown as possible methods for examining the degradation of in-service pipes.

INTRODUCTION

Polymers have been used in the UK water distribution network since the 1950's when unplasticised polyvinyl-chloride (uPVC) started to be used instead of other materials. Over the next 20 years uPVC became the most common material for pipes to be made from. However there were problems with the new uPVC pipes, as they failed earlier than predicted and at

much lower pressures than first expected. A small amount of polyethylene (PE) was used, but the early materials were too weak and their use was limited.

Since the 1950's new and better types of uPVC and PE have been developed. The 1970's saw a better quality of uPVC being developed. While this reduced the number of failures, the earlier failures lead to further development of PE being proposed. In the 1980's this development saw the production of medium density polyethylene (MDPE) and high density polyethylene (HDPE). These new grades of PE started to take over as the dominant materials used in today's water pipe network.

The expected lifetime of these pipes is upwards of 50 years. The service life could be more or less than this expected figure. Hence a method of predicting the remaining lifetime of the pipe is essential for successful planning of replacement and maintenance. This can be done using large scale mechanical testing, but small scale chemical testing would be much more cost effective.

The major type of chemical degradation that occurs in high pressure PE water pipes is auto-oxidation which forms carbonyl groups (1). While in PVC water pipes the main form of degradation is dehydrochlorination (1). Both materials are also susceptible to other forms of degradation such as mechanical, biological and photo degradation by UV light (2). These forms of degradation will not be studied in this paper.

To resist the onset of chemical degradation the manufactures of the pipes add chemical stabilisers to the polymer resin. For PE the most important stabilisers are antioxidants, which cause other chemical reactions to occur, preventing any oxidation of the PE. Unfortunately the antioxidant agents continuously migrate to and leach from the surface of the material, meaning after an amount of time all of these agents are used and oxidation of the PE begins.

Bodycote (formerly Studsvik Material AB) (3-5) have studied these losses of antioxidants in PE pipes. This work did not obtain data on the wide range of different environmental, dynamic and static loads that can occur. This then highlights the need for an effective evaluation process for in-service pipes.

The research around PVC has been mainly the study of craze initiation, fatigue and gelation. Studies by Stahmer et al. (6) and Breen et al. (7) looked for physical deterioration of the pipes after they had been exhumed, this still leaves the need for a small scale test that can be performed quickly to identify deterioration.

TYPES OF CHEMICAL EVALUATION

As the polymers degrade, their structure, composition and chemical makeup change due to the chemical processes involved in the degradation. These changes can be measured using

several different techniques involving thermal analysis, infrared spectroscopy and weight distribution methods. The techniques used in this research and others investigated are briefly described below.

Oxidation Induction Time (OIT) measures the amount of time a polymer needs to oxidise at an elevated temperature. This gives an insight into the concentration of antioxidants remaining in the polymer matrix; the less time required the smaller the concentration of antioxidants present. OIT is found by heating a sample to above its melting temperature (for PE this is normally 200°C) and measuring the time taken for the exothermic oxidation to occur. This has been the standard method to measure the antioxidant concentration for some time; however it has its drawbacks (8). Instead of the standard OIT test this research used the Oxidation Induction Temperature (OIT*) this is a dynamic test of antioxidant concentration, and requires the temperature of the sample to be ramped until exothermic oxidation is observed. The OIT* method generally requires less time to perform and also reduces errors by removing the need to change the atmosphere that the sample is exposed to. PVC cannot be tested in this way because of the dangerous by-products which would be formed.

Thermal analysis of the polymer allows an insight into the phases of the polymer matrix. Using a Differential Scanning Calorimeter (DSC) it is possible to examine the crystallinity and the melt temperature (T_m) of the polymer. For PVC the gelation can also be measured. The crystallinity is the measure of the amount of heat required to melt the crystalline part of the polymer matrix (the heat of fusion). The higher the percentage of crystalline material in the polymer matrix the more degradation has occurred. Melt temperature allows investigation of the polymers thermal stability, the higher the melt temperature the more thermally stable the polymer. Gelation is a measurement to examine the degree of fusion in the rigid polymer. Gelation measures the amount of entanglement in the PVC resin. This begins with the production of the polymer, but also continues as the PVC ages. Gelation is closely related to mechanical strength and craze initiation (7).

Infrared Spectroscopy (IR) can be used to examine the makeup of the polymer. This is done by looking at the absorption of infrared radiation at certain wavelengths. Bonds in the polymer absorb the radiation, hence the more radiation absorbed at a particular wavelength the more of that particular bond is present. Using this process, by-products of the oxidation and degradation of the polymer can be examined. Carbonyl groups can be easily identified and have been used in polymer degradation investigations before. These absorptions are converted into a carbonyl index which can be compared between samples. The carbonyl groups are by-product produced by the oxidation of polymer chains. During this production polymer chains are shortened and hence weakened; another definitive marker indicating that degradation has occurred in the polymer.

Using Gel Permeation Chromatography (GPC) the weight and weight distribution of the polymer can be determined. If scissoring has occurred then the weight distribution is lowered, due to the increase in lower order polymer chains. GPC can be used as a comparative tool between old and new samples, however due to the method, absolute results are less accurate.

METHODOLOGY

OXIDATION INDUCTION TEMPERATURE

There is no standardised methodology for OIT* analysis except in Finland (9), the methodology used was that described by Schmid et al (10) and is similar to that used in the Finnish standard. Using a Perkin Elmer Pyris 1 DSC, samples were heated at 10°C/min from 50°C in an atmosphere of air at a flow rate of 50ml/min. Samples were taken from films sliced from the thickness of the pipe. These films were then punched into discs of 2.5mg (\pm 0.25mg) and placed into aluminium pans with loose lids. The loose lids allow the oxidising atmosphere to be in maximum contact with the sample. The sample was heated until an exothermic oxidation reaction was observed; the temperature where the onset of oxidation occurred, was then measured as the intersection between the baseline and the exothermic line

CARBONYL INDEX

A carbonyl index can be used to determine the amount of each of the carbonyl groups present. This was done by collecting spectra using a Perkin Elmer Spectrum One FT-IR Spectrometer fitted with an ATR attachment, a spectrum was taken between the frequencies of 4000cm⁻¹ and 1200 cm⁻¹. The values at 1740cm⁻¹ (Ester group), 1715cm⁻¹ (Ketone group) and 1705cm⁻¹ (Acid group) were normalised by the methyl group at 1415cm⁻¹ to produce the carbonyl index. For this investigation the Ester group was used.

MELT TEMPERATURE & CRYSTALLINITY

The melt temperature and crystallinity can be calculated using one test. Crystallinity is calculated using the total enthalpy method (11), while the melt temperature corresponds to the peak of the curve. Samples punched from films taken through the thickness of the pipe wall and weighing 2.5mg (\pm 0.25mg), were placed in regular aluminium pans that were then sealed. The samples were tested on a TA DSC Q2000 where they were heated from 60°C to 180°C in a nitrogen atmosphere at a flow rate of 50ml/min. The data was then analysed using the connected TA Analysis software, where the enthalpy of fusion (ΔH_f) and the melt temperature (T_m) were determined. Using the enthalpy of fusion of a 100% crystalline material quoted by Wunderlich (12) as 293 J/g the percentage of crystalline material in the polymer was calculated.

The tests were carried out on sections of PE 80 (diameter 63mm of SDR 11) which were aged using a bath of 2% Arkopal N100 in distilled water at 80°C. These pipes were aged for 50, 120 and 500 hours and compared to a section of virgin, un-aged pipe. As this type of pipe has only been used for the last 10 years, no pipes have yet been exhumed due to failure, hence no comparisons could be made with pipes from service.

GELATION

Although several methods to measure the gelation of PVC have been presented in the past, the method chosen was that of Vanspeybroeck and Dewilde (13). Samples of approximately 3mg were taken from the PVC pipe and measured using a TA DSC Q2000. The samples and reference were heated at 10°C/min from 80°C to 220°C in a nitrogen atmosphere at a flow rate of 50ml/min. The data was then analysed using the software attached to the DSC. Gelation was then calculated using Eq (1):

$$Gelation = \frac{A}{A+B} * 100\% \quad (1)$$

Region A is taken from the glass transition (T_g) to the fusion temperature where the plot inflects. Region B is taken from the inflection to 210°C. The value of 210°C was chosen as it was the value used by Vanspeybroeck and Dewilde (13), though other values have been used. Figure 1 shows a typical plot with regions A and B refined.

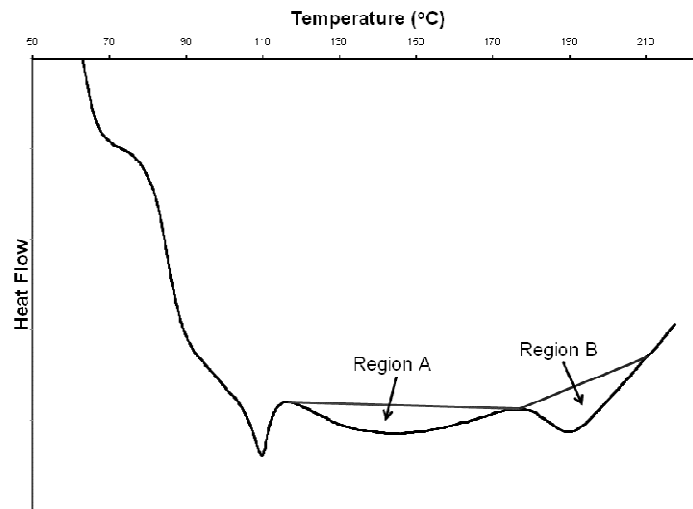


Figure 1 Determination of the gelation from a typical DSC plot.

The PVC samples were taken from a section of pipe used in service for a short amount of time (approximately 2 years), these were then aged further in the Arkopal solution for 120 and 500 hours. This was then compared to pipe that had been in service for approximately 50 years and the original short service pipe.

RESULTS & DISCUSSION

Figure 2 is the OIT* profiles for the four PE pipe sections. The profiles through the thickness show a steady decrease in oxidation temperature (and hence a reduction in antioxidant concentration) and then a large decrease for the sample aged for 500 hours. The profiles are symmetrical due to the outer and inner surfaces being in contact with the same environment, in real life conditions these environments would be different and hence an unsymmetrical profile would be expected.

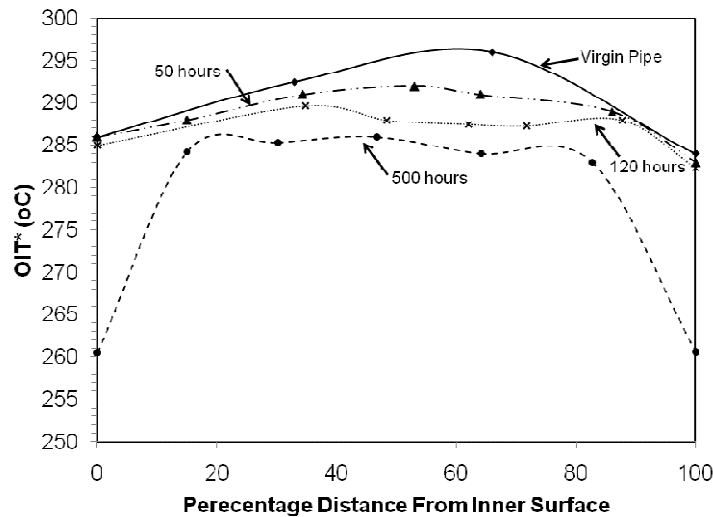


Figure 2 Oxidation induction temperature (OIT*) profile versus distance from inner wall for: 0 hours (♦), 50 hours (▲), 120 hours (X) and 500 hours (●).

Figure 3 shows the carbonyl index for the PE pipes. This test can be done on PVC pipes as well, but due to the different chemistry the signals obtained are much weaker and hence background noise can strongly influence the results. Because of this the results for the PVC pipes are not presented. The results in Figure 3 are inverted from those expected from theory; more oxidation would be expected at the surfaces of the wall than in the middle of the wall thickness. No comparable data using Arkopal as an aging agent has been found, hence the expected reason for this is that oxidation degradation has occurred throughout the thickness of the pipe. The carbonyl products have then been leached into the aging fluid from the surfaces of the pipe. At present this is just a hypothesis and needs to be tested further to be confirmed. The results do show a steady increase in the carbonyl products as time increases. The carbonyl index is also the only non-DSC technique examined in this work. The downside to this as an indicator to the remaining in-service life of a pipe is that degradation has already occurred when carbonyl products are formed.

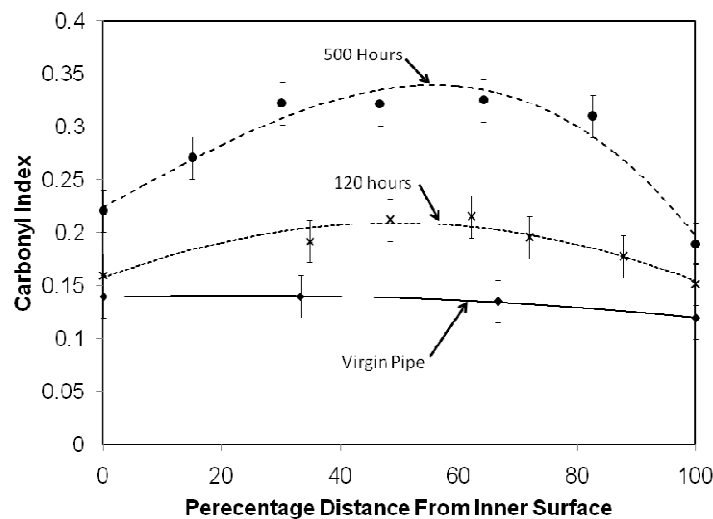


Figure 3 Carbonyl index (ester) versus percentage distance from inner wall for PE80 aged in Arkopal at 80°C: 0 hours (♦), 120 hours (X) and 500 hours (●). Trends through the pipe are shown by the dashed lines.

Figure 4 shows the percentage crystalline material in the polymer matrix of the PE samples. There is a marked difference between the virgin pipe and the aged pipe, but there is little difference between the aged samples. This suggests that all the aging has occurred in the first 50 hours of aging and minimal aging has occurred after this. There is also a noticeable slope from the inner wall to the outer wall of the pipe, even though both walls were subjected to the same environment. A sensible explanation for this would be that outer surface of the pipe is water cooled at manufacture, whereas the inner wall is allowed to cool in air. This causes a higher crystallinity at the inner wall of the virgin pipe as it has longer to cool. This then suggests that the increase in crystallinity has occurred uniformly over the thickness of the pipe. This would also support the results of the carbonyl index testing, that degradation has occurred throughout the pipe thickness.

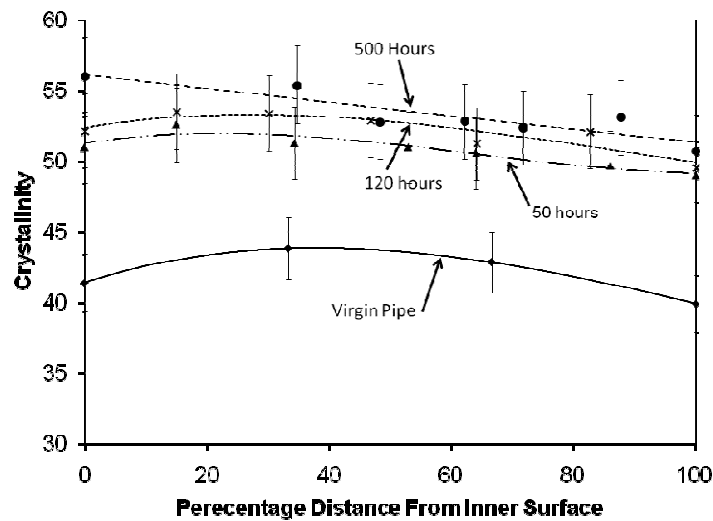


Figure 4 Percentage crystalline material of PE80 aged in Arkopal at 80°C versus distance from inner wall for: 0 hours (◆), 50 hours (▲), 120 hours (X) and 500 hours (●). Trends through the pipe are shown by the dashed lines.

Figure 5 shows the melt temperature of the four PE samples. There is a steady trend from the virgin pipe to 500 hours aged, however the results do seem to suggest that the melt temperatures at the two surfaces are very similar in all cases and the only differences between the samples can be seen at 10% and 90% of the wall thickness. Again there is a trend from the inner wall to the outer wall which is consistent with the trend seen in the crystallinity results above. The similar results at the surfaces and the limited difference (less than 0.5°C) between the aged samples make this a less suitable method for determining the remaining in service life of a PE pipe. It could however be useful in certain circumstances as secondary test.

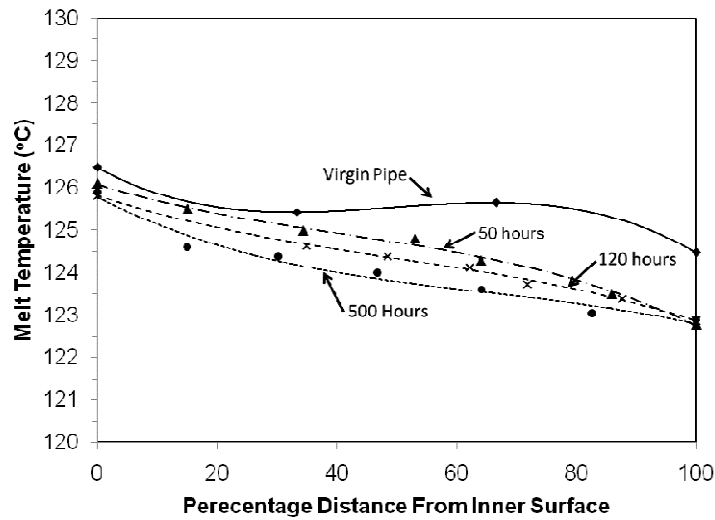


Figure 5 Percentage crystalline material of PE80 aged in Arkopal at 80°C versus distance from inner wall for: 0 hours (◆), 50 hours(▲), 120 hours (X) and 500 hours (●). Trends through the pipe are shown by the dashed lines.

The results of the gelation tests performed on PVC are shown in Figure 6. They show a vast difference between the gelation of a pipe artificially aged to one that has had a full in-service life. The pipes aged in Arkopal for 120 and 500 hours show very similar results to that of the un-aged pipe (the pipe aged for 120 hours was so similar to the original results for the pipe it could not be included in Figure 6 clearly). The reduction of the percentage gelation of the pipe from service at the inner wall is promising, the pipe in question failed in-service and was exhumed. However problems do arise from these results; either the gelation in the PVC structure remains virtually constant until a rapid deterioration just before failure or the Arkopal solution is not accurately accelerating the pipes aging. Either of these could be the case and further investigation is required.

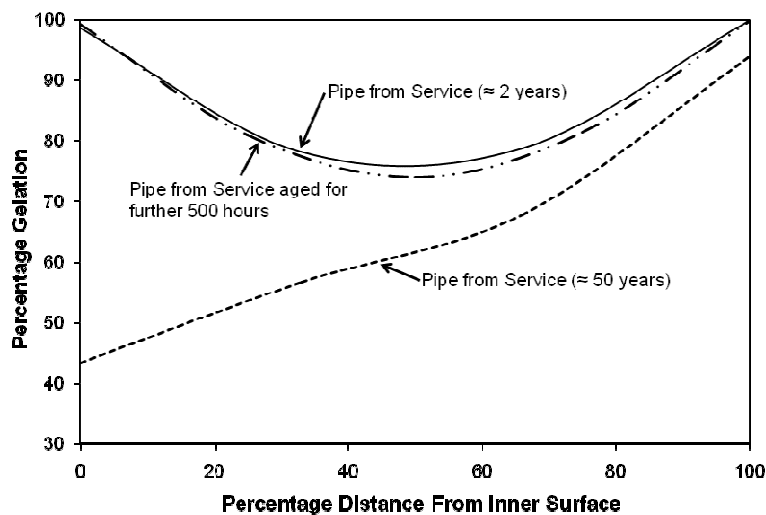


Figure 6 Percentage Gelation trends through the thickness of PVC pipes.

CONCLUSIONS

All of the techniques discussed above, have shown some ability for determining the remaining life of an in-service pipe. For these methods to be implemented fully, the failure conditions of these chemical markers need to be understood, as well as the rates at which these chemical markers deteriorate during different parts of the life of a high pressure water pipe.

Some of these methods however would be easier to implement than others in a commercial set-up. The changes that need to be monitored if using the melt temperature are very small and require precise measurements, whereas the changes seen in the OIT* and carbonyl index are much larger and would be easier to monitor when looking at the amount of data that could be collected from an entire water network. Of these two methods the OIT* has the advantage that the amount of stabilisers is being measured and hence this would give a good long term determination of the remaining service life.

The gelation results show promise, but there are other methods that could be explored such as the crystallinity of the PVC, using more accurate infrared spectroscopy or examining the fusion and melt temperatures from the gelation DSC plots.

What these results do show is that it is unlikely that one test would be capable of determining the remaining in-service life of all the polymer pipes that are currently in use. The data presented here shows just two of the many possible polymers used in pipe manufacture in the world. However the results do show that it may be possible to use the same instruments to obtain different chemical markers for these different polymers.

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References

1. T. Kelen, *Polymer Degradation*. Van Nostrand Reinhold Company, 1983.
2. W. Schnabel, *Polymer Degradation – Principles and Practical Applications*, Hanser International, 1981.
3. J Viebke and U. Gedde, *Polymer Engng. & Sci.*, 1997, 37(5), 896.
4. U. Gedde, J. Viebke, H. Leijstrom, M. Ifwarson, *Polymer Engng. & Sci.*, 1994, 34(24), 1773.
5. K. Karlsson, G. Smith, U. Gedde, *Polymer Engng. & Sci.*, 1992, 32(10), 649.
6. M Stahmer and A. Whittle, *Plastic Pipes XI*, 2001.
7. J. Breen, A. Boersma, P. Slaats and J Vreeburg, *Plastic Pipes XII*, 2004.

8. M. Schmid, A. Ritter and S. Affolter, *Journal of Thermal Analysis and Calorimetry*, 2006, 83(2), 367.
9. L. Koski and K. Saarela, *J. Thermal Anal.*, 1982, 25(1), 167.
10. M. Schmid and S. Affolter, *Polymer Testing*, 2003, 22(4), 419.
11. A. Gray, *Thermochimica Acta*, 1970, 1(6), 563.
12. B. Wunderlich, *Macromolecular Physics – Vol. 3 Crystal Melting*, Academic Press, 1980.
13. P. Vanspeybroeck and A. Dewilde, *Plastic Pipes XII*, 2004.