THE LIFETIMES OF PE AND PVC MATERIALS FOR USE IN SODIUM HYPOCHLORITE AND HYDROGEN PEROXIDE ENVIRONMENTS

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ABSTRACT

Hydrostatic pressure testing at elevated temperatures was undertaken in order to determine the lifetimes of a PE 100 pipe grade including welds and a PVC-U pipe grade when exposed to two different fully-formulated products. Each product contains active chemical constituents that may affect the lifetime of these materials in their application; one product has sodium hypochlorite as a major constituent and the other hydrogen peroxide. Lifetime predictions were made from the results using different extrapolation techniques, such as combining multiple linear regression with Miner's rule. The data obtained demonstrate that the testing equipment and methodology developed for use with these formulated products was successful. When appropriate extrapolation techniques are used, this methodology is shown to be a useful design tool for determining lifetimes in an industrial application giving confidence for the use of different thermoplastics in these specific chemical environments.

INTRODUCTION

Unilever's product portfolio includes cleaning fluids based on sodium hypochlorite and hydrogen peroxide. Both are potentially corrosive, and managing the risk of corrosion with metallic material usually requires dedicated plant. Titanium is the preferred choice for handling sodium hypochlorite and its products, whilst stainless steels are adequate for handling hydrogen peroxide and product derivatives. Titanium corrodes in hydrogen peroxide and stainless steel corrodes in sodium hypochlorite, and in both cases corrosion causes product decomposition and gassing. Engineering thermoplastics potentially offer lower costs and the flexibility to manufacture both types of product on the same plant, without the risk of product decomposition and gassing due to metal ion pick-up. However, little mechanistic understanding and few relevant data were available, and a programme of work was established to investigate the performance of plastics in these environments.

The project described in this paper formed one key part of a larger study of plastics performance prediction in these environments [1]. In this case, two candidate materials, a PE 100 pipe grade, including welds, and a PVC pipe grade were considered. The aim of the project was to study how the two different chemical environments affect the lifetimes of these plastic piping materials. The lifetimes of these materials may not only be affected by the major active chemical constituents, sodium hypochlorite and hydrogen peroxide but both products also contain a number of unspecified perfumes, dyes and surfactants that may also have an effect. Hydrostatic pressure tests were initiated at elevated temperatures in order to develop data that could be extrapolated to operational temperatures. The basis for these tests was the chemical testing methodology developed earlier by Bodycote [2] so that by using different extrapolation techniques, such as combining multiple linear regression with Miner's rule, preliminary lifetime predictions could be made. Results will be presented which demonstrate the potential for using polymer pipe grade materials to replace metallic components in these applications. The predictions indicate that plastics could offer the option for making both products at the same plant, whereas metallic options require dedicated facilities.

MATERIALS INVESTIGATED

The tests presented here were undertaken on two commercial pipe materials, a black PE 100 and a grey PVC-U. Chemical testing should usually be conducted on pipes with smaller dimensions such as 12 mm outer diameter by 2 mm wall thickness in order to reduce costs and increase safety. However these tests were performed on PE 100 pipes with nominal dimensions of 20 x 2.5 mm and PVC-U with nominal dimensions of 20 x 1.5 mm, as these were the smallest readily available commercial pipe sizes.

The fully-formulated products were designated Chemical A, for the product where the major active chemical constituent is sodium hypochlorite and Chemical B, for the product where the major active chemical constituent is hydrogen peroxide.

EXPERIMENTAL PROCEDURES

All tests were performed at the polymer laboratory at Bodycote Polymer AB, using hydrostatic pressure testing equipment designed and built by Bodycote Polymer AB. The testing was carried out with one or other of the formulated products on the inside of the pipe in each case. The external environment was air. The pipe specimens were fitted with specially made PVDF or PTFE fittings manufactured by Bodycote Polymer AB. The general testing conditions follow ISO 1167:1996 [3].

The fully-formulated products used in the tests contain active chemicals which dilute quickly and therefore the products required changing once a week. In order to obtain failures in a reasonable time the tests would normally be accelerated by increasing the temperature. However in this case degradation of the chemicals occurs at high temperature thus tests could be conducted at no higher temperature than 60°C.

Initially 16 tests were started on PE 100 pipes. These tests consisted of duplicate samples at each of two different initial stress levels, 4 and 2 MPa, at two different temperatures 40 and 60°C for each formulated product. Later the test programme was expanded to include testing of four PE 100 pipes that included welds and 12 PVC-U pipes. Duplicate samples of welded PE pipes were tested at 4 MPa and 60°C and PVC-U tests were started under all the same conditions as for the PE 100 apart from the tests at 2 MPa and 60°C.

GENERAL FAILURE MECHANISMS FOR PLASTIC PIPES

Before presenting the individual test results, a more general discussion of the degradation mechanisms for plastic pipes in aqueous environments is given. When plotted on a logarithmic hoop stress versus failure time basis a creep rupture curve for a thermoplastic material can usually be divided into three regions, termed Stage I, Stage II and Stage III, as shown in Figure 1 [4].

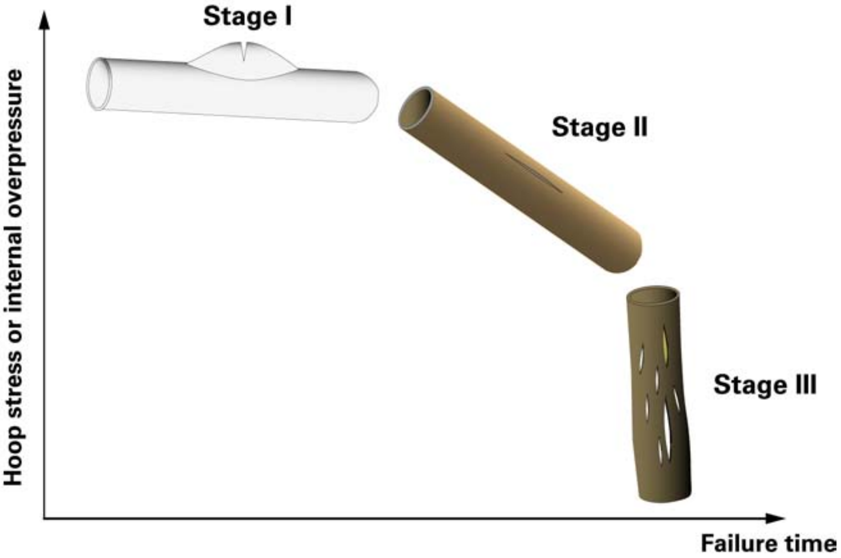

Figure 1 *The three stages of a creep rupture lifetime plot for plastic pipes*

At a given temperature, at high hoop stress levels and short failure times the predominant failure mechanism is Stage I where ductile failures occur by gross plastic deformation, rather than from defects within the material. The slope of regression of Stage I data is very shallow and can often be extrapolated to give very long lifetimes with only a small decrease in stress carrying capacity from that obtained at short times, providing that the failure mechanism does not change.

Often however after some period of time the failure mechanism changes to Stage II, where failure occurs by the growth of cracks from small defects within the material. The intersection of this mechanism with the Stage I regression curve is often referred to as the mechanical knee. The position of this knee and the Stage II regression slope are determined by the slow crack growth performance of the material. Failures in this region are usually brittle in character allowing the successful application of the principles of linear elastic fracture mechanics. Chemical factors can also affect this predominantly mechanical process. Stage II is characterised by a much steeper slope than Stage I, however within this region there is still a strong stress dependency, enabling a significant increase in lifetime to be obtained by reducing the stress level.

Eventually as stress levels are reduced still further chemical degradation processes will begin to dominate the failure mechanism. Ultimately, at very low stress levels and extremely long times, a second knee will occur. Below this chemical knee Stage III failures occur. These are often characterised by a multitude of small brittle cracks all over the pipe where the pipe ceases to have any load bearing capacity due to complete chemical degradation. The regression slope of Stage III data is so steep as to be almost vertical. In other words this slope has very little stress dependency and even significantly reducing the stress level will give little benefit in pipe lifetime. The pipe has really reached its lifetime limit by this Stage.

The three Stages described are only a general model and although some materials display all three stages, the exact curve for a given material is highly material and environmentally specific.

RESULTS

The results of the hydrostatic pressure tests with Chemical A as the internal test medium are presented in Table 1. The pipes that failed during the tests are highlighted in bold, with those that were terminated without having failed in normal type. All the PE 100 pipes tested failed in a brittle manner. The higher stress level and higher temperature gave shorter failure times as would be expected. There is quite a significant difference in failure time between the different stress levels at the same temperature, showing a stress dependency indicative of a Stage II regime. When plotted as in Figure 2, it can be seen that the data lie on approximately parallel slopes. The PE 100 pipes that included welds both failed at the weld at a significantly shorter time than for pipes without welds tested under the same conditions. All the PE 100 data are seen to be reasonably consistent.

Table 1 *Hydrostatic pressure testing results with Chemical A as the internal test medium*

Pipe Material	Temperature °C	Hoop Stress MPa	Exposure Time h	Comments
PE 100	40	4.0	**2 412**	Brittle failure
	40	4.0	**2 292**	Brittle failure
	40	2.0	**12 690**	Brittle failure
	40	2.0	**9 147**	Brittle failure
	60	4.0	**1 068**	Brittle failure
	60	4.0	**1 452**	Brittle failure
	60	2.0	**4 344**	Brittle failure
	60	2.0	**6 012**	Brittle failure
Welded PE 100	60	4.0	**584**	Brittle failure
	60	4.0	**538**	Brittle failure
PVC-U	40	4.0	**3 440**	Brittle failure
	40	4.0	6 096	Terminated
	40	2.0	6 096	Terminated
	40	2.0	6 096	Terminated
	60	4.0	**3 776**	Brittle failure
	60	4.0	**3 944**	Brittle failure

The PVC-U tests give an indication of longer lifetime than the tests on the PE-100 material as shown in Table 1. However these results are less consistent, particularly noting the somewhat surprising failure at 4 MPa and 40°C. On visual inspection it was considered that this had been caused by a stress concentration produced by one of the fittings and therefore this result was not used in the subsequent lifetime estimations. Also three pipe tests were terminated before failure after only 6 096 h, making extrapolation for realistic lifetime predictions difficult.

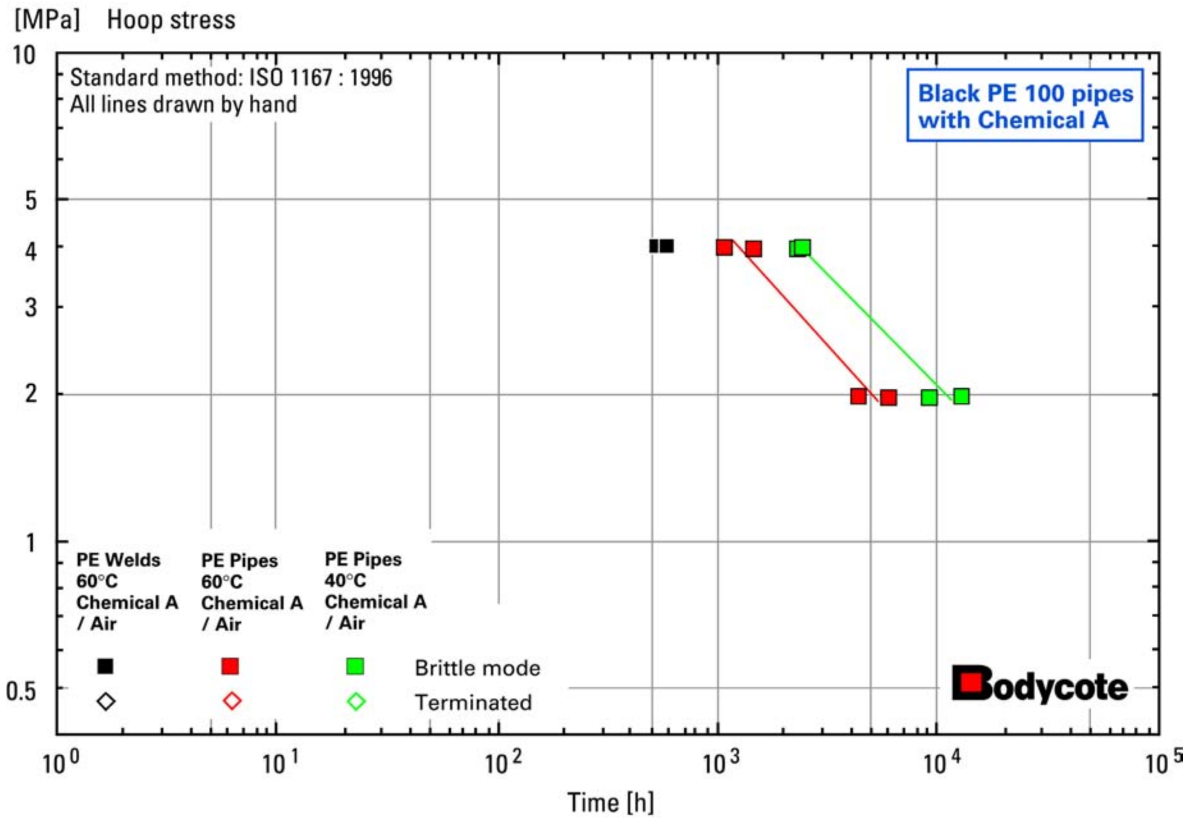

Figure 2 *Creep rupture diagram for PE 100 pipes and welds tested with Chemical A*

The results of the hydrostatic pressure tests with Chemical B as the internal test medium are presented in Table 2. Again the pipes that failed during the tests are highlighted in bold, with those that were terminated without having failed in normal type.

Table 2 *Hydrostatic pressure testing results under different conditions with Chemical B*

Pipe Material	Temperature °C	Hoop Stress MPa	Exposure Time h	Comments
PE 100	40	4.0	19 344	Terminated
	40	4.0	19 344	Terminated
	40	2.0	19 344	Terminated
	40	2.0	19 344	Terminated
	60	4.0	**4 500**	Brittle failure
	60	4.0	**4 936**	Brittle failure
	60	2.0	**17 469**	Brittle failure
	60	2.0	**18 780**	Brittle failure
Welded PE 100	60	4.0	**1 377**	Brittle failure
	60	4.0	**1 256**	Brittle failure
PVC-U	40	4.0	6 096	Terminated
	40	4.0	6 096	Terminated
	40	2.0	6 096	Terminated
	40	2.0	6 096	Terminated
	60	4.0	6 096	Terminated
	60	4.0	6 096	Terminated

All the PE 100 pipes tested at 60°C failed in a brittle manner with the higher stress level and higher temperature tests giving shorter failure times. There is quite a significant difference in failure time between the two different stress levels used at 60°C, again showing a stress dependency indicative of a Stage II regime. However all four PE 100 pipes tested at 40°C were terminated after 19 344 h exposure before any failures had occurred. The long exposure times do though give an indication of a large temperature dependence for this failure mechanism. The PE 100 pipes that included welds both failed at the weld at much shorter times than for pipes without welds tested under the same conditions and all the PE 100 data are seen to be reasonably consistent. These features can be observed in Figure 3.

Figure 3 *Creep rupture diagram for PE 100 pipes and welds tested with Chemical B*

The results of the PVC-U testing again give an indication of longer lifetime than the tests on the PE-100 material as shown in Table 2. However these results are not very conclusive as they were all terminated after 6 096 h before any failures occurred, thus making any subsequent extrapolation for a realistic lifetime prediction difficult and not very reliable.

LIFETIME EXTRAPOLATIONS

Providing that sufficient data have been obtained it may be possible to predict the lifetime of pipes exposed to different operational conditions. In this case it could be done by using the technique of multiple linear regression combined with a Miner's rule analysis using the operational conditions specified by Unilever. However when insufficient data has been obtained it is not possible to perform a multiple linear regression analysis. In such cases a preliminary lifetime prediction can be made using a general acceleration factor for polymer materials.

The multiple linear regression method used for the determination of the time to failure (t_{fi}) is based on model Q in ISO/TR 9080 [5]. The equation of Model Q contains three unknown regression coefficients A, B and C and two independent variables, temperature (T_i) and stress (σ_i):

Model Q according to ISO/TR 9080

$$\log(t_{fi}) = -A - (B/T_i)\log(\sigma_i) + C/T_i \qquad \textit{Equation (1)}$$

Equation 1 can be used for calculations of the expected failure time at any fixed combination of temperature and pressure (hoop stress) under constant service conditions.

For the PE 100 pipes with Chemical A it was possible to establish a proper fit to this set of data, with the following constants obtained for Equation 1; A = 1.295, B = 676.201, and C = 1 867.491, leading to the multiple linear regression extrapolations shown in Figure 4.

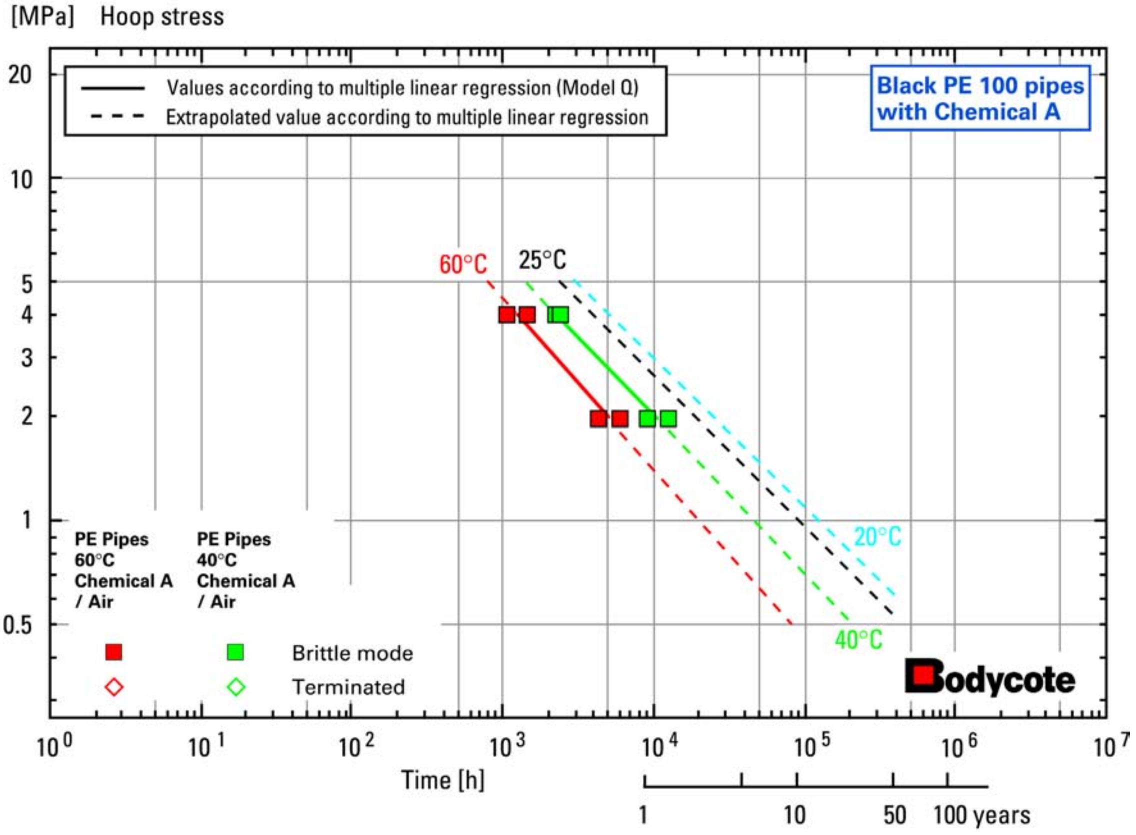

Figure 4 *Multiple linear regression applied to PE 100 pipes tested with Chemical A*

For the PE 100 pipes with Chemical B it was not possible to perform any true evaluation as there were only four failures. However a preliminary multiple linear regression analysis based on the failures at 60°C and the two terminated pipes at 40°C at the high stress level was made which gave an initial indication of the minimum lifetime of this PE 100 pipe material exposed to this chemical environment. Using these assumptions it was possible to establish a proper fit to this set of data, with the following constants obtained for Equation 1; A = 5.946, B = 647.070 and C = 3 591.548 enabling calculation of the multiple linear regression extrapolations shown in Figure 5.

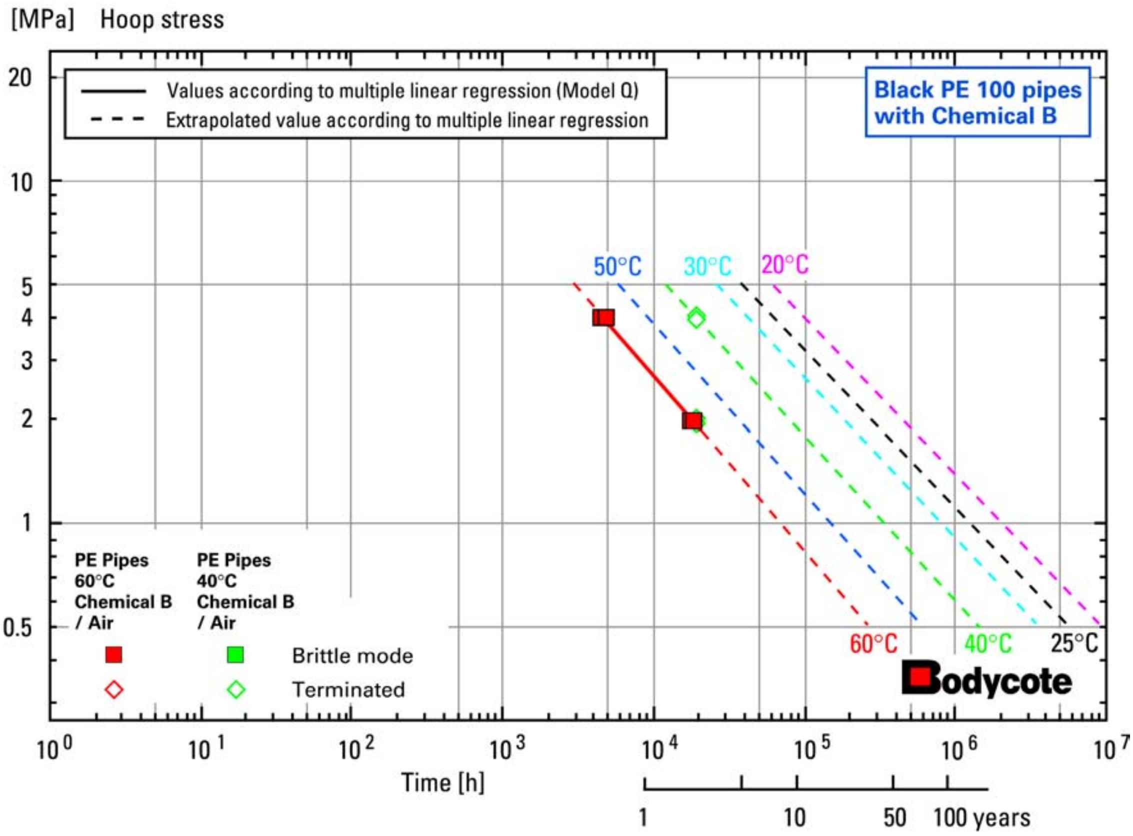

Figure 5 *Multiple linear regression applied to PE 100 pipes tested with Chemical B*

Normally design is based on fixed service conditions where there is a constant maximum stress level at one specific temperature allowing multiple linear regression extrapolations such as these to predict lifetime. However in many applications one or both of these conditions vary during the lifetime rendering a multiple linear regression analysis alone inadequate. In this case Unilever estimated that the materials are expected to spend 6/7 of their service life at 25°C and 1/6 of their service life at 40°C. Therefore a Miner´s rule analysis was undertaken for these two conditions. Assuming that each damage (caused by a constant service condition) is proportional to the duration of attack (“proportionality rule”) and the damages from different service conditions “i” may be cumulatively added (“additivity rule”) Miner’s rule appears in ISO 13760:1998 [6] as:

Miner’s rule according to ISO 13760

$$1/t_f = \sum_{i=1}^{i=n} \left[(t_i / t_{tot}) / t_{fi}(T_{i,} \sigma_i) \right] \qquad \textit{Equation (2)}$$

where:

t_f	Lifetime at various conditions
$t_{fi}(T_i,\sigma_i)$	Failure time for condition “i”
n	Number of service conditions
t_i	Exposure time at condition “i”
t_{tot}	Total exposure time

Combining Equations 1 and 2 provides the tool for the determination of the expected lifetime of plastic materials subjected to varying service conditions, i.e. alterations in temperature and stress. If the constants determined for Equation 1 for the PE 100 pipes tested with Chemical

A are used in combination with a Miner’s rule analysis for two conditions according to Equation 2, the following preliminary minimum expected lifetime could be determined, for example for two conditions at 2 MPa: By applying Equation 2 to 25°C for 6/7 of the time at σ = 2 MPa, and 40°C for 1/7 of the time at σ = 2 MPa the following is obtained, as shown in Figure 6:

$$\frac{1}{t_f} = \frac{6}{7\times19316} + \frac{1}{7\times10437}$$

Therefore: *Lifetime* t_f *= 17 223 h (2.0 yrs at 2 MPa)*

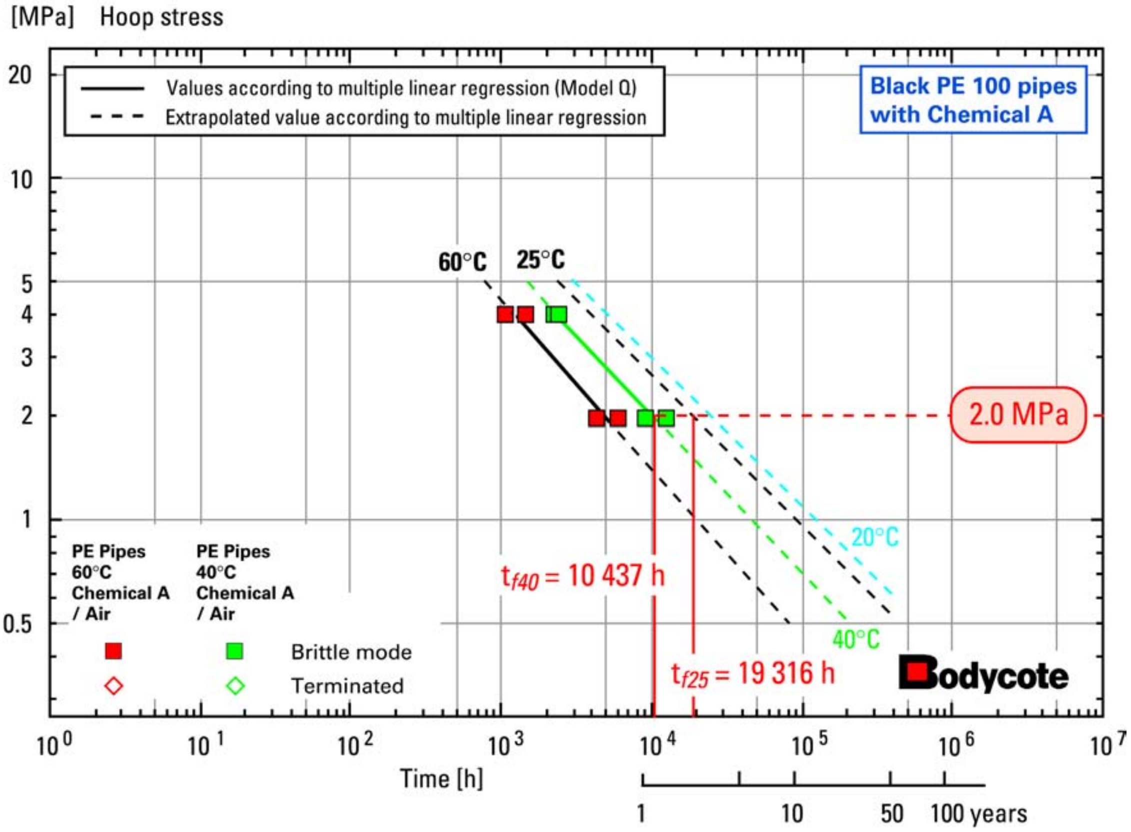

Figure 6 *Miner’s rule for two conditions applied to PE 100 pipes tested with Chemical A*

A similar calculation was made at 4 MPa and also for the PE 100 pipes tested with Chemical B at both stress levels, see Table 3. For the results with the welded pipes, the best estimate that could be performed with the limited data available was to apply a welding factor, which was simply a function of the relative average failure time for the pipes without welds tested at the same temperature and stress level. This was then applied to the estimations made for two conditions at each stress level for each chemical, as shown in Table 3.

For the PVC-U pipes it was not possible to perform multiple linear regression analyses and therefore no true evaluation could be made. However using the results obtained, highly preliminary estimations of expected lifetime in the application could be determined. The acceleration factor for most polymer materials is between 2-3/10°C. Using the assumption that the acceleration factor was 2.5/10°C [7] enabled calculation of very preliminary lifetimes in these cases. Preliminary lifetime estimations, at both 2 and 4 MPa for an operational temperature of 25°C for 6/7 of the time and 40°C for 1/7 of the time, calculated for all the pipe materials and welds are summarised in Table 3:

Table 3 *Preliminary estimated lifetimes at different stress levels*

Environment	Pipe Material	4 MPa	2 MPa
Chemical A	PE 100	0.4 years	2.0 years
	Welded PE 100	≈ 0.2 years*	≈ 0.9 years*
	PVC-U	> 7.7 years*	> 7.7 years*
Chemical B	PE 100	> 5.4 years	> 23.5 years
	Welded PE 100	≈ 1.5 years*	≈ 6.6 years*
	PVC-U	≈ 12.1 years*	> 12.1 years*

**The estimated lifetimes of PE welds and PVC pipes are very preliminary since no true evaluations can be made*

These estimations were only possible due to the application of the chemical testing methodology developed earlier at Bodycote Polymer AB [2]. One significant difference is that in the previous work extrapolations were based on the Arrhenius relationship rather than the multiple linear regression approach adopted here.

CONCLUSIONS

- The data obtained demonstrate that the test equipment and methodology developed for use with these formulated products was successful.

- When appropriate extrapolation techniques were used the methodology was shown to be a useful design tool for determining lifetimes in specific chemical environments.

- The methodology was shown to be particularly effective for the PE material, however conclusions for PVC were limited by the low number of tests and short exposure times. More comprehensive testing programmes are required in order to give full confidence.

- The predictions made indicate that plastics can offer more manufacturing flexibility than metals for these applications.

- A flexible methodology for testing in different chemical environments has proven to be very useful in a specific industrial application, with obvious potential for use in other industrial applications and chemical environments.

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