

# **TECHNICAL REPORT**

## **MODELLING MECHANISMS OF BRITTLE OXIDATIVE DEGRADATION TO ENSURE PLASTIC PIPE MATERIAL PERFORMANCE**



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# MODELLING MECHANISMS OF BRITTLE OXIDATIVE DEGRADATION TO ENSURE PLASTIC PIPE MATERIAL PERFORMANCE

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## Abstract

With material evolution, the projected service lifetimes of plastic piping materials continues to increase. This has led to an increasing interest in characterization of the brittle-oxidative resistance of these materials to define the ultimate lifetime. In this paper, the mechanisms associated with brittle failure of polyolefin piping materials are examined. The competing mechanisms of oxidative and mechanical crack initiation and propagation are found to control the ultimate mechanism of failure. Four different possible failure modes are identified and examples of the failure modes observed in laboratory testing are provided. Identification of the different failure modes and methodologies for forecasting and validating pipe oxidative performance are discussed.

## Background

Plastic piping materials have enjoyed a long and successful history. Since the introduction of the first commercial thermoplastic pipe in the 1940's, plastic pipe usage and applications have continued to expand. Certainly the inherent characteristics of the materials themselves; such as resistance to corrosion, ductility, ease of handling and installation, etc., have played a large part in this success. Another key factor, however, in their acceptance and successful application has been the development and refinement of methodologies for forecasting the long-term strength of these materials<sup>1</sup>. These methodologies enabled the transformation of plastic piping into an engineering material – a material with predictable and reproducible properties.

In the development of methodologies for forecasting long-term strength of plastic piping materials, three distinct failure regimes have typically been distinguished. These three regimes are typically referred to as Stage I, Stage II and Stage III, representing Ductile-Mechanical, Brittle-Mechanical and Brittle-Oxidative failure modes, respectively. Stage I failures typically occur at higher stresses and shorter times. For some materials there is a potential for transition to Stage II failures at longer times. If a material does not fail by Stage I or Stage II failure in service, Stage III brittle oxidative performance is believed to represent the ultimate lifetime of the piping material.

Characterization of Stage I performance is used to define a plastic pipe materials pressure rating or mechanical strength. In North America, the methodology

defined in ASTM D2837, Standard Test Method for Obtaining Hydrostatic Design Basis for Thermoplastic Pipe Materials<sup>2</sup>, has been successfully applied for over thirty years. A similar methodology, ISO 9080, Plastics Piping and Ducting Systems – Determination of the Long-Term Hydrostatic Strength of Thermoplastics Materials in Pipe Form by Extrapolation<sup>3</sup> has also been successfully applied in Europe and, more recently, in North America.

Early in the implementation of the methodologies used to forecast long-term strength based on Stage I performance, reports appeared of pipes that were failing prematurely by brittle-like slits even though the pipes were subjected to operating pressures that were significantly below the projected safe value (based on characterization of Stage I performance). The recognition of these Stage II type failures led to significant advances in both material durability and in the methodologies to characterize this type of failure mode<sup>1</sup>. Current pressure rating requirements preclude materials prone to brittle-like Stage II type failures and ensure ductile performance of plastic piping materials.

With current generation plastic pipe materials and the current methodologies for characterization of the Stage I and Stage II regimes, service lifetimes, dependant upon the application, in excess of 100 years<sup>4</sup> are often referred to. This, and the expansion of plastic pipe into ever more demanding applications, has resulted in a growing focus on the characterization of Stage III brittle oxidative performance of plastic piping materials. An ASTM Standard, ASTM F2023, Test Method for Evaluating the Oxidative Resistance of Crosslinked Polyethylene (PEX) Tubing and Systems to Hot Chlorinated Water<sup>5</sup>, has recently been developed and used as the basis for establishing minimum oxidative resistance for PEX pipe materials for potable water applications as a requirement in the product standard (ASTM F876, Standard Specification for Crosslinked Polyethylene (PEX) Tubing<sup>6</sup>). A similar test methodology for polyethylene (PE) piping materials has also been developed (ASTM F2263, Standard Test Method for Evaluating the Oxidative Resistance of Polyethylene (PE) Pipe to Chlorinated Water<sup>7</sup>).

In this paper, the mechanisms associated with brittle oxidative degradation of polyolefin piping materials are examined. The competing mechanisms of oxidative and mechanical crack initiation and propagation are found to control the ultimate mechanism of failure. The different possible failure modes are identified and examples of those failure modes observed in laboratory testing are provided. Identification of the different failure modes and

methodologies for forecasting and validating pipe oxidative performance are discussed.

## Experimental

Testing was conducted on commercially available polyolefin piping materials. Standard hydrostatic pressure testing was conducted in accordance with ASTM D1598<sup>8</sup>. Chlorine resistance testing was conducted in general conformance with the ASTM F2023<sup>5</sup> or ASTM F2263<sup>7</sup> methodologies.

## Results and Discussion

### *Characterization of Failure Modes*

In accelerated performance testing of polyolefin piping materials to characterize Stage III behavior, several possible failure modes have been identified. These failure modes depend on the time-scale of the competing oxidative and mechanical degradation mechanisms in crack initiation and propagation. It is important to identify and distinguish between these different failure modes to ensure that the methodologies being applied to forecast long-term strength are valid for the failure mode in question and so that different failure modes are not inadvertently grouped together in the same analysis.

For crack initiation, initiation can be either Mechanical or Oxidative. Mechanical Crack Initiation is the typical initiation associated with Stage II performance testing. This initiation process is typically regarded as defect driven with the initiation time dependent on the specific stress state, the temperature and the material properties<sup>9</sup>. For Oxidative Crack Initiation, the initiation time is a function of the oxidative environment, the temperature, the stress and the material. Crack initiation occurs due to oxidative degradation of the inner surface leading to embrittlement<sup>10</sup>.

Similarly, for crack propagation, propagation can be either Mechanical or Oxidative. Again, Mechanical Crack Propagation is the typical propagation associated with Stage II performance testing. Crack propagation occurs due to a mechanical breakdown of the fibrils spanning the process zone in the crack front<sup>9</sup>. For Oxidative Crack Propagation, it appears that oxidative breakdown of the fibrils spanning the process zone in the crack front occurs.

Based on the specific test conditions and material properties there are, therefore, four possible overall failure modes:

Mode 1: Mechanical Initiation - Mechanical Propagation

Mode 2: Mechanical Initiation - Oxidative Propagation

Mode 3: Oxidative Initiation - Mechanical Propagation

Mode 4: Oxidative Initiation – Oxidative Propagation

Mode 1 is the typical failure mode associated with Stage II failures. Mode 2 behavior is potentially observed in some standard testing to characterize Stage II performance. Mode 3 failures appear to be a possible failure mode. This mode of failure has not however typically been differentiated. Mode 4 is the typical failure mode associated with Stage III failures. In characterizing oxidative performance of piping materials Mode 4 behavior is typically of primary interest. While the distinction has been made between modes in this paper to facilitate discussion, in reality there may be a continuum of failure modes progressing from pure mechanical to pure oxidative.

### *Observed Failure Modes*

As discussed previously, it is important to identify and distinguish between the different possible failure mechanisms. To that end, examples of the different failure modes observed in laboratory testing are examined below.

#### Mode 1: Mechanical Initiation – Mechanical Propagation

A typical fracture surface for a Mode I or Stage II type failure is shown in Figure 1A. The failure was generated in a polyolefin material in standard hydrostatic pressure testing with water internal/water external at 80 °C. The failure is typical of Mode I failures in that failure occurred at a single point and that the inner pipe surface remained ductile (i.e. no oxidative degradation) as evidenced by reverse bend testing (i.e. no crack or crazing of the inner pipe surface). The initiation point is shown in Figure 1B and 1C. Initiation occurred at an inclusion approximately 15 µm in diameter. As shown by EDX analysis in Figure 2, the inclusion composition is carbon based. The classic microfibril structure of the fracture surface is clearly shown in Figure 1D. This failure typifies the classic Mechanical Initiation – Mechanical Propagation failure mode.

#### Mode 2: Mechanical Initiation - Oxidative Propagation

Mode 2 failures have not been clearly identified in experimental testing to date. There is evidence reported in the literature, however, of oxidative effects observed in Stage II testing<sup>13</sup>. Current research projects at Jana Laboratories are attempting to generate and characterize Mode 2 type failures.

#### Mode 3: Oxidative Initiation - Mechanical Propagation

Figure 3 shows a plot of log (failure time) versus log (stress) for a polyolefin pipe tested in two different oxidative environments. The Mode I failure lines were generated by standard hydrostatic pressure testing according to ASTM D1598<sup>8</sup> with water internal/air external at 80 °C. The Mode III failure line was generated

by testing in general accordance with ASTM F2263<sup>7</sup>, which involves testing with oxidatively aggressive flowing internal water/air external at 80 °C.

The Mode I failures were as described above and shown in Figure 1. There was typically a single crack initiation-propagation point. There was also no evidence of inner surface oxidation and the fracture surfaces exhibited the typical microfibril structure seen in Figure 1.

The Mode 3 failures, on simple visual examination, appear similar to Mode I type failures. A comparison of typical Mode 1 and Mode 3 failures is provided in Figure 4. For the Mode 3 failures, there was typically a single crack initiation point and there was typically little or no visual evidence of inner surface oxidation. There was no evidence of bulk oxidation on examination by Fourier Transform Infrared (FTIR). The loss of inner surface ductility is clearly evident, however, on reverse bend testing or tensile elongation of the inner pipe surface (crazing and microcracking). The shift in initiation time is also clearly visible in Figure 3. At the test conditions, the failure curve is shifted a minimum of one log decade.

For the Mode 3 failures, SEM examination of the crack surface reveals the same microfibril structure observed for the Mode I failures, indicating Mechanical Crack Propagation. Crack initiation is, however, at the inner surface as opposed to near the inner surface and typically at a defect for Mode I failures. The slope of the Mode 1 and Mode 3 failure curves are similar, with the Mode 3 failure curve being somewhat steeper. This may be an indication that there is some oxidative component to the crack propagation or may simply reflect a different stress dependence of the oxidative and mechanical initiation mechanisms.

#### Mode 4: Oxidative Initiation – Oxidative Propagation

A typical Mode 4 type failure is shown in Figure 5. The sample is a polyolefin material tested in accordance with ASTM F2023, which involves testing with oxidatively aggressive flowing internal water/air external.

As previously reported<sup>10,11,12</sup>, the failure mechanism appears to be:

1. Oxidation of the inner surface.
2. Once sufficient oxidation and degradation of the inner wall occurs a combination of degradation induced and applied stresses on the inner pipe surface causes micro-cracks to form in the degraded inner layer.
3. The crack density and crack length increase with exposure time. The cracks propagate through the wall of the pipe material.
4. The cracks begin to coalesce to form larger cracks.
5. Ultimately a brittle slit or pin hole failure is observed when a crack propagates through the entire wall thickness.

The distinguishing features of a typical Mode 4 type failure (as shown in Figure 5) are a typically highly degraded inner surface with microcracking and multiple crack initiation points. The crack surface is also typically highly degraded and does not typically show the classic microfibril structure of Mode 1 and Mode 3 type failures.

#### Modeling Test Data

Mode 1 Mechanical – Mechanical (or Stage II) type failures have been successfully modeled using elevated temperature testing and the Rate Process Model<sup>14</sup> for over two decades. The results of this approach have also been correlated with field performance of plastic piping materials<sup>15</sup>.

Mode 2 Mechanical – Oxidative type failures have not typically been differentiated in analysis, although there are reports of an oxidative component in standard Stage II type testing.<sup>13</sup> The applicability of current modeling approaches for Mode I type failures applied to Mode 2 type failures should be examined.

Mode 3 type failures have also not typically been differentiated. Given that the initiation is chemically driven and the propagation appears to be predominantly mechanically driven, caution needs to be applied to utilizing the current accepted methodology of the Rate Process Model to this failure mode. Further work needs to be conducted to either validate the application of the current failure models or to develop alternate analysis methodologies.

Mode 4 (or Stage III) type failures have been successfully modeled using either the Rate Process Model or Arrhenius type extrapolations<sup>10,11,12</sup>. More recently this modeling approach has formed the basis for establishing minimum performance requirements for specific plastic piping materials<sup>5,6</sup>.

## Conclusions

The competing mechanisms of mechanical and oxidative crack initiation and propagation are found to control the ultimate mechanism of failure. The different possible failure modes were identified and examples of those observed in the laboratory were provided. Modeling of test data for Mode 1 and Mode 4 type failures has been successfully achieved using the Rate Process Model. For Mode 2 and Mode 3 type failures, further work needs to be conducted to either validate the application of the current models or to develop alternative analysis methodologies.

## Acknowledgements

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Figure 1: Mode I Fracture Surface: 1A: Fracture Point, 1B: Initiation Point, 1C: Initiation Point Detail, 1D: Detail of Microfibril Crack Surface

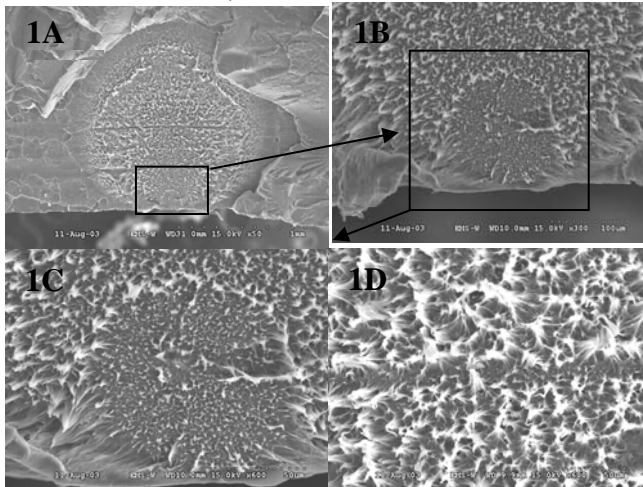


Figure 2: SEM EDX Analysis of Crack Initiation Point Inclusion

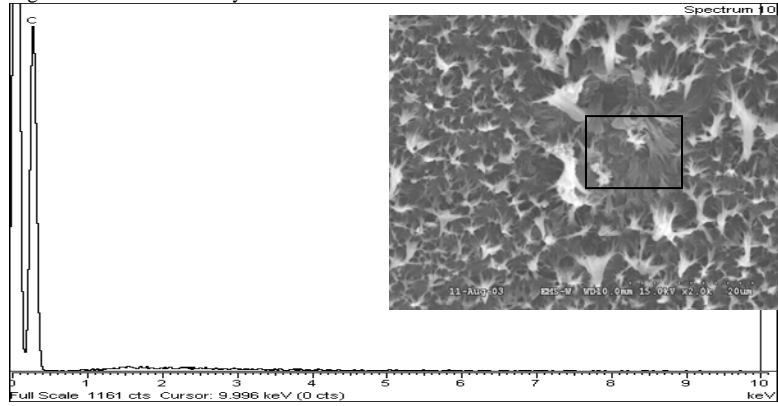


Figure 3: Comparison of Mode 1 and Mode 3 Failure Times

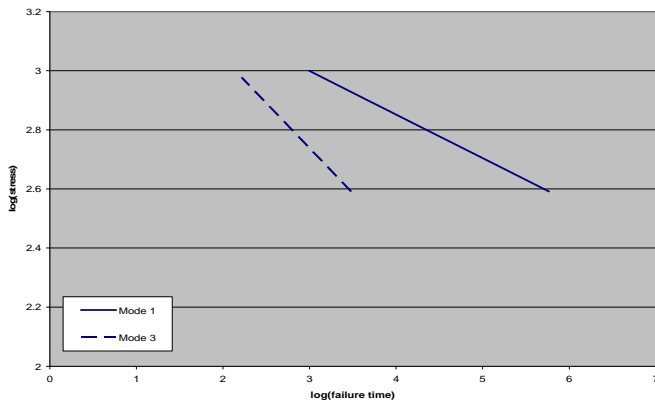


Figure 4: Visual Comparison of Mode 1 and Mode 3 Failures

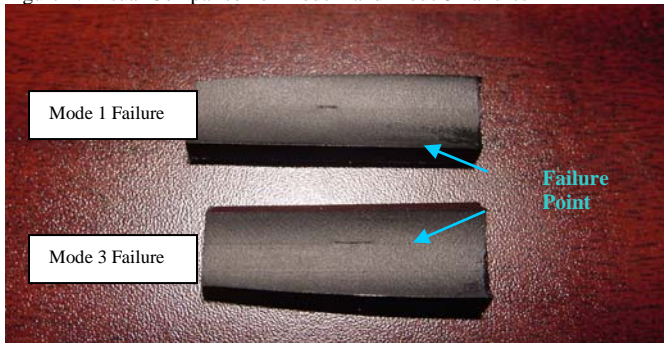
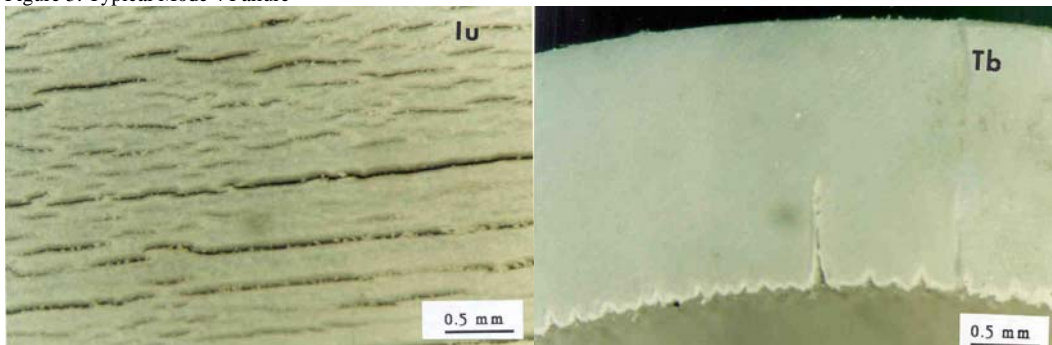


Figure 5: Typical Mode 4 Failure





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