New Developments in Strain Hardening Modulus for Polyethylene Pressure Piping Applications

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Abstract

Strain Hardening Modulus (SHM) is of increasing international interest for its capability to provide a useful index of the slow-crack growth (SCG) performance of polyethylene (PE) materials. Recently, a broad industry initiative has started to formalize an ASTM International test method to measure SHM. This effort likely is driven by several benefits to industry including the significant reduction in time required for SHM measurement in comparison to traditional SCG test methods. This paper will update the literature establishing the capabilities of SHM to replace traditional SCG test methods and provide a progress report in creating a North American standard for this useful test.

Introduction

PE piping has three distinct advantages over archaic pipe materials; 1) reduced lifetime costs 2) installation complexity and installation sensitivity are dramatically reduced resulting in faster construction especially when trenchless methods are utilized, and 3) very low failure rates per mile of installation when installed using industry best practices. PE pipe has the added benefit of being essentially inert across a broad range of fluids including market penetration in drinking water distribution, natural gas distribution and hydrocarbon production. Based on these benefits and others, PE piping has captured significant infrastructure market share in North America over the past decades. Market share gains in Western Europe for plastic piping have been faster, deeper and continue to grow due to an ever increasing application to new materials to new application environments.

Aside from occasional poor installation practices and third party damage, the ultimate limit on the lifetime of high-density PE (HDPE) piping systems is slow crack growth (SCG) resistance. A variety of index tests have been developed that industry uses for both material qualification and new material development including the Notched Pipe Test[1] (NPT), the Cracked Round Bar (CRB) Test[2] and Full-Notched Creep Test (FNCT)[3]. The latter two tests, CRB and FNCT have received attention due in part to reduced testing times.

North America regulations are summarized in ASTM D3350 "Standard Specification for Polyethylene Plastics Pipe and Fittings Materials"[4]. In this standard, HDPE resins used for pressure pipe rely solely on qualification according to ASTM F1473 "Standard Test Method for Notch Tensile Test to Measure the Resistance to Slow Crack Growth of Polyethylene Pipes and Resins", more commonly called the PENT test[5]. A new index test based on elevated temperature tensile testing called Strain Hardening Modulus (SHM) test has been formalized by the 2015 publication of ISO 18488[6]. This test proposes to provide slow-crack growth (SCG) performance information in a fraction of the time required for all other methods. In 2016, I provided a review and presentation at the Polyolefins Conference which provided a detailed consideration of the microstructural relationship between SCG resistance and strain hardening modulus[7]. In this review, we will illustrate two critical improvements of the SHM when compared to PENT. The SHM test provides a test method with a strong correlation to PENT in a fraction of the time required for PENT. Also, the SHM test provides a reliable index of SCG well beyond the level of performance when PENT is no longer reliable – for example for PE100 RC materials with PENT testing times in excess of 1 year. However, the next section will review the meaning of the term SHM within the context of the more familiar tensile coupon testing found in ASTM D638[8].

Strain Hardening Modulus

A series of familiar features are observed in the load / displacement plot obtained when polyethylene tensile bars are elongated in a cross-head displacement testing station (see Figure 1). Initially, the modulus of elasticity is observed to start at the origin as the load quickly rises with increasing displacement. After yielding, the strain localizes and the material shows strain softening followed by neck stabilization and drawing of the material into the neck region[9]. This is followed by an extended drawing or necking region with the load becoming fairly stable under further elongation resulting in the gage section of the test specimen converting into a long fiber. The drawing region is terminated at a strain we will refer to as the Natural Draw Ratio (NDR) when the load is observed to increase significantly with incremental elongation. Eventually, the test specimen will rupture or break with the ultimate load sometimes exceeding the load at yield. It is this final feature which is the focus of the ISO 18488 test method[6]. In our previous Polyolefins paper[7], we discussed the early literature starting in the 1990s which documented a relationship measure of slow crack growth resistance and drawing characteristics from the tensile curve. We also summarized the results of a significant 2001 paper published in the Plastic Pipes conference[10] which related a lower value of NDR to an increased failure time in NPT testing. Most importantly, our previous Polyolefins paper underlined the nearly universal acceptance of mechanical reinforcement of the damage zone ahead of the crack tip is by "tie molecules" which participate in two crystalline regimes and improve SCG resistance. Generally speaking, as tie molecule density increases, the SCG resistance of the PE material also increases. More recent literature suggests that the strain hardening regime is also mainly governed by the density of tie molecules and entanglements. Thus, the SHM can be used as indirect measure for the SCG resistance.

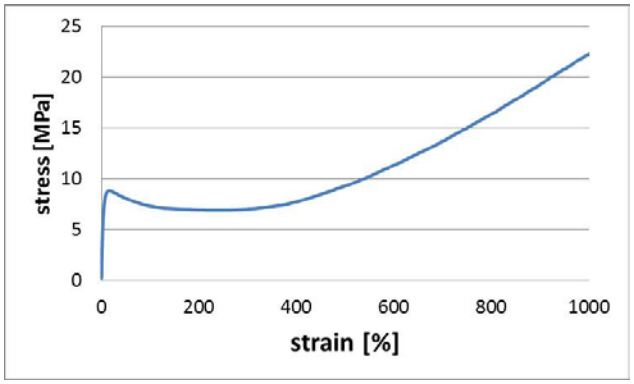

Figure 1. Drawing of a typical PE stress-strain curve illustrating the broad region of fiber drawing that follows yielding.

The Origins of ISO 18488

In fact, the ISO test method reworks the familiar features of Figure 1 into a report of true stress and true strain assuming volumetric conservation. Then a linear fit of the slope of the true stress–strain curve above the NDR is created and this value is referred to as SHM. As stated in the test method "the strain hardening modulus . . . is used as a measure for the resistance to slow crack growth of polyethylene. The strain hardening modulus is obtained from stress-strain curves on compression moulded samples . . . and . . . provides a method that is valid for all types of polyethylene. . . that are used for pipes and fittings applications".

The ISO test method is clearly based on the 2005 publication[11] by researchers from Sabic and DSM and closely mirrors several elements originated in that work including 120°C annealing of the polyethylene sheet prior to stamping out specimens, 80°C elevated temperature during testing, slight modification of an ISO37 type 3 tensile bar, and the preference for optical extensometer measurement. Table 1 contains the data from the 2005 paper and the data is plotted in Figure 2. It is potentially important to note that the authors refer to the testing they conducted as ESCR testing (we continue that terminology) but the testing is not equivalent to the familiar ASTM test method D1693 in several ways[12]. The reader is referred to the original paper for the details of this testing. However, the high value for goodness of fit illustrates the quality of the correlation between SHM in MPa and the log of the time to failure in ESCR testing reported in hours.Our interest in this alternative testing approach is underlined in this quotation from the publication "The slow crack resistance of polyethylene is usually . . . time consuming . . . the findings reported in this publication offer a possibility to assess the information on slow crack propagation in much simpler and faster way".

ESCR (hrs)	G_p, MPa	Log ESCR
58	18.8	1.763
103	20.6	2.013
10	13.1	1.000
20	15.4	1.301
50	19.0	1.699
47	19.5	1.672
112	26.0	2.049
300	30.7	2.477
1000	35.8	3.000
>2000	47.2	NA

Table 1. Data from Reference 11. The data point reported as ">2000 hrs" was not including in the analysis in Figure 2.

While this 2005 publication provides the first correlation of SHM to ESCR values, the pressure piping industry is more interested in other measures of stress crack resistance aside from ESCR commonly applied to pressure pipe resins. In North America, the most commonly applied test method is PENT.

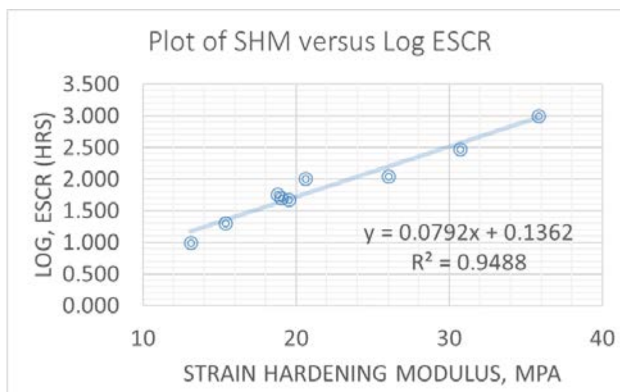

Figure 2. Plot of the log ESCR values against the strain hardening modulus from Reference 11.

SHM and Statistics

Of course, one of the most important considerations for establishing a correlated relationship between SHM and any other measures of SCG resistance will be the statistical variation in the measurement of both values. One of the best publications[13] on this subject was provided during the Plastic Pipes XVI conference by authors from Kiwa Technology. These authors reported the findings of a round robin study conducted on three generations of pressure pipe resins; PE80, PE100 and PE100RC. Eight laboratories conducted testing on all three materials with individual replicate measurements varying in number from a minimum of three to a maximum of nine. The reader is directed to the publication for further details but the results summarized in Table 2 are worthy of further discussion.

	Resin A	Resin B	Resin C
G_p, MPa	82.7	46.6	25.1
Stan. Deviation	8.0	2.3	1.1
% Stan. Deviation	9.7	4.9	4.4

Table 2. Summary of Statistical Data from Reference 13.

For a start, it is worth mentioning that the paper describes some reasons for exclusion of some data results from the round robin which fairly significantly reduce the standard deviation for Resin A. The standard deviation for Resin A is then reported to drop to 4.4% of the average value. For the sake of simplification, let us consider that the standard deviation for all three resins was approximately 5% and does not increase significantly as the value for SHM increases. In this data, the standard deviation appears fairly constant over a range of SHM that extends over nearly all modern pressure pipe resins and covers greater than a 300% change in the value. Perhaps a standard deviation value of 5% reflects a good estimate for the experimental error in multiple replicate studies. We will return to this standard deviation value later in the discussion.

SHM and PENT Correlations

In 2015, a case study was published[14] that explored the potential for a correlated relationship between SHM and Log PENT failure times. Unfortunately, the data we are interested in are not published in the paper directly in table format. Instead, the data for both SHM and PENT failure time is estimated here based on Figure 6 from the paper. Table 2 contains the data from the 2015 paper and the Log PENT versus SHM is plotted in Figure 3. The high value

PENT (est.) (hrs)	Est. G_p, MPa	Log PENT
35	28.0	1.544
225	32.2	2.352
230	33.4	2.362
475	34.5	2.677
600	33.9	2.778
950	34.4	2.978
1250	37.6	3.097
1875	38.0	3.273
2000	37.4	3.301
3025	36.9	3.481

Table 2. Data estimates prepared based on Figure 6 of Reference 14

for goodness of fit illustrates the quality of the correlation between SHM in MPa and the log of the time to failure in PENT testing reported in hours. This implies that one can assess the likely failure time of pipe resins in PENT testing, likely taking thousands of hours in some cases, by conducting the quick and low cost SHM test.

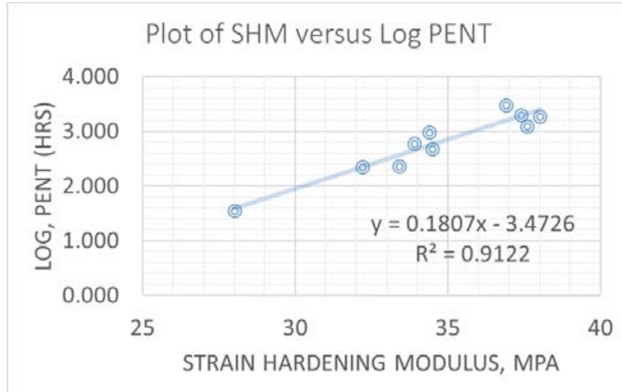

Figure 3. Plot of the log PENT values against the strain hardening modulus from Reference 14

There are other interesting details to mention regarding this case study. The researchers from Rey Juan Carlos University in Spain stated that the resins used in the study were "polyethylene grades from blow molding up to PE-80, PE-100, and higher resistant to crack grades". However, the values of SHM reported reach a maximum of 36.9 MPa which does not address the full range of SHM values available in the current market or in their later publications. Tensile tests were conducted on ISO37 type 3 tensile bars in an 80°C chamber at a rate of displacement of 10 mm/min measured using an optical extensometer. But it is interesting to note that the thickness used for tensile specimens in this paper was 2 mm which does not comply with the requirements of ISO 18488 which allows a maximum of 1.0 mm and recommends 0.3 mm. Also, it was not mentioned if there was annealing done after initial molding in spite of the fact that this is required by ISO 18488. Otherwise, the details of sample preparation and testing are aligned with the ISO test method. It should be clearly stated that the testing in this paper is not conducted in strict accordance with ISO 18488 and, therefore, the absolute correlation between log PENT and SHM by ISO 18488 provided in Figure 3 must remain in doubt. Additionally, it is unfortunate that , in spite of the fact that the researchers mention that they measured SHM in triplicate, there are no error bars provided in Figure 6.

An additional important case study was provided by the researchers from Rey Juan Carlos University at the 2016 Plastic Pipes Conference[15]. In this case study, "a wide range of PE resins grades" was studied using the ISO 18488 test method and compared to PENT testing. As discussed below, this publication introduces additional complexity to the 2015 case study. Shown below is Figure 4 from that paper in which the SHM is compared to the log of PENT failure times for three families of resins; 1) Ziegler-Natta (ZN) resins made using a 1-butene comonomer, 2) chromium catalyzed resins made using a 1-hexene comonomer and 3) an extrusion blended system prepared from two component polymers. The paper further clarifies that an un-named "iron based catalyst" was the source of a homopolymer PE blended with a low density ethylene-hexene copolymer made using an un-named metallocene catalyst. The paper makes the point that is clearly illustrated in Figure 4, not all polyethylene materials follow an identical relationship between SHM and Log PENT.

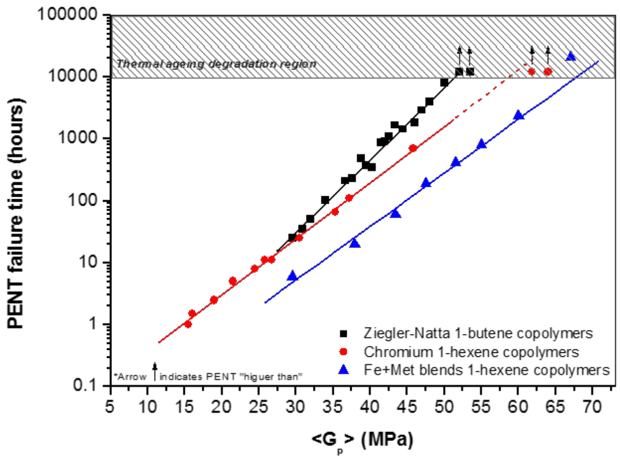

Figure 4. Reprint of the log PENT values against the strain hardening modulus which originally appeared as Figure 4 in Reference 15.

While the paper concludes "Correlation between SH method and classic SCG tests are reported on this work. It is proved that the method guarantees a rapid and accurate evaluation" it is also clear that there is an apparent relationship to the precise nature of the polymer which is not fully explained. It is possible that the SHM may differ for two PE materials with essentially equivalent PENT values due to some relationship to either the catalyst (and its effect on the microstructure of the polymer) and/or the co-monomer. However, for the most common commercial systems, the differences between families of resins is relatively minor up to a PENT failure time of 100 hours or even 500 hours. Perhaps even more critical is to understand if the amount of statistical variation is low when SHM is measured, then this might allow industry to accept a conservative value for SHM in order to obtain a result that is essentially equivalent to a PENT testing time (that may take thousands of hours to generate) by SHM testing consisting of a very rapid tensile test.

Statistical Implications for SHM Correlations

If we now apply the statistical conclusion from the Kiwa publication to the 2015 case study, then the results become even more interesting. If we assume that the errors in these measurements of SHM are normally distribution about the mean, then 3 times the standard deviation should account for 99.7% of the sample population being studied.

It might therefore be reasonable to multiply 15% by the SHM should then account for approximately 99.7% of the measured value for SHM to estimate a measure of statistical relevance that may be applied to our previous Figure 3. It is important to recall that the standard deviation value incorporates both positive and negative variations. These values have been provided in Table 3 as a new column that was not present previously. Next we can superimpose an oval on our previous Figure 3 to represent the positive and negative statistical variation about the mean value for SHM. Then lines are drawn to define the positive and negative boundary for the data variation. These changes to figure 3 are illustrated below as Figure 5.

PENT (est.) (hrs)	Est. G_p, MPa	3 X Est. Stan. Deviation, MPa	Log PENT
35	28.0	4.2	1.544
225	32.2	4.8	2.352
230	33.4	5.0	2.362
475	34.5	5.2	2.677
600	33.9	5.1	2.778
950	34.4	5.2	2.978
1250	37.6	5.6	3.097
1875	38.0	5.7	3.273
2000	37.4	5.6	3.301
3025	36.9	5.5	3.481

Table 3. Data Estimated from Figure 6 of Reference 11 including an estimated standard deviation column equal to 15% of the SHM.

Let us consider the implications of Figure 5 for an illustrative example - a Log PENT value that is equal 2.0 would represent a PENT value of 100 hours. If we wish our SHM values to represent 99.7% of all outcomes, then we must acknowledge that values falling between approximately 28.2 MPa and 32.5 MPa are statistical results one might obtain for that resin.

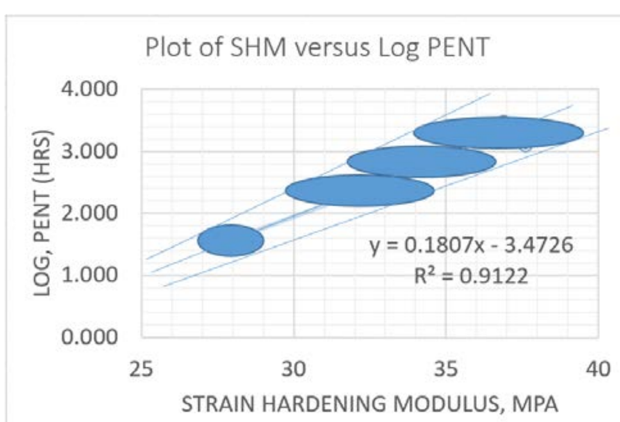

Figure 5. Re-plot of the log PENT values against the SHM for Figure 3 of this paper including superposition of ovals on top of some previous data points to illustrate error bars equal to 15% of the SHM measured value.

Conversely, if one wished to set a minimum SHM value such that statistics provided a 99.7% likelihood that a PENT result would be obtained that exceeds 1000 hours, then one first substitutes 3.0 for the value of y in the equation in Figure 4 and solving for x obtains a value of 35.8 MPa. However, then one must increase this value by 7.5% to account for the possible statistical negative variation. This leads to a calculated value of 38.5 MPa. To those who are more gifted in statistical analysis, it will be clear that the above discussion assumes no variation in the measured value of PENT which is obviously not correct. ASTM F1473 precision statement indicates that standard deviation of the average values within laboratories for round robin testing was +/-16 % while the standard deviation of the average values between laboratories was +/-26 %. In other words, substantially greater standard deviation than observed for SHM. However, it is hoped that the above discussion illustrates that the statistical consequences of the data analysis are not intractable.

As already noted previously, it is uncertain that the testing conditions in this case study match the ISO 18488 conditions, but for the sake of illustration we will use the values provided in Figure 3 of this paper as if they were reliable without attempting to assure their correctness. If one wished to provide reasonable statistical assurance of a PENT value greater than 1000 hrs by first measuring SHM, the minimum acceptable average value is 38.5 MPa once the possibility of statistical variation is accounted for. While this approach might not be appealing in all circumstances, the opportunity to obtain this result in perhaps 72 hours rather than waiting 1000 hours for the PENT result is likely attractive in some scenarios. intractable but are, rather, merely complex. Perhaps the attractiveness of such an approach becomes more clear if the desired PENT value is 2000 hours, 5000 hours or 10,000 hours. It should also be mentioned that such an approach unlocks the possibility of selecting SCG resistance that is currently unamenable to PENT testing by thoughtful application of the SHM test.

Current Efforts Underway

The publication of test method ISO 18488 removed a critical barrier to North American industry acceptance of the SHM. The two case studies presented here from 2015 and 2016 remove another barrier by providing a detailed correlation between SHM and log of PENT. Finally, the publication from Kiwa researchers removes an additional barrier by providing confidence that a version of ISO 18488 can be conducted with relatively reasonable statistical variation. What then is lacking for North American industry to start the adoption of SHM into PE piping standards.

One answer might be merely familiarity with the ISO 18488 test method. The author of this review has solicited independent quotations from six North American laboratories to conduct ISO 18488 testing and received back four valid quotations. One laboratory declined to provide quotation due to limitations relating to the elevated temperature oven required during testing. One laboratory shifted the quotation to a European laboratory. In a very interesting development, this European lab asked if it was necessary for the laboratory to compression mold the initial sheet of material indicating that clients often provide the sheet of material directly and the lab only conducts in-house annealing as required in ISO 18488.

At first glance, this seems an odd response since the compression molding is written as a mandatory component of the ISO test method. However, on further consideration, it seems plausible that the required sheet annealing steps (ie. 1 hour at 120°C followed by slow cooling at a rate less than 2°C / minute) may reasonably be expected to remove any processing history from the initial sheet molding. Perhaps the mandatory conditions for the initial compression molding of the PE sheet are not critical to performance of the testing with high statistical relevance.

It seems that a critical barrier which persists is to obtain an ASTM test method which is vetted by an industry consensus process and eliminates any overly proscriptive requirements that can be shown are not critical to the results of testing. Therefore, the author has initiated a project to create an ASTM test method titled "Measurement of Strain Hardening Modulus on Polyethylene Materials used in the Manufacture of Stress-Rated Pipe". It is hoped that this effort will provide ASTM participants access to a test method which meets the needs of industry. At the point that the test method reaches finalization, it is anticipated that a round robin study will again be conducted on the strict scope of the ASTM SHM test method. A particularly favorable outcome would be to obtain an ASTM test method that retains any critical aspects of the ISO test method.

Discussion and Conclusions

In this review, we have provided some critical case studies to update the reader on the SHM literature. To all appearances, the potential continues to exist to replace traditional SCG test methods such as PENT with SHM and obtain results in less than a 100 hours which can be used to verify thousands or tens of thousands of hours of PENT performance. Additionally, the author has introduced his own efforts at ASTM as a progress report in creating a North American standard for SHM testing. Although the path may take several years and much effort, the pathway for progress seems reasonably straight-forward.

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Key Words: Strain Hardening Modulus, ISO 18488 Test Method, ASTM F1473 Test Method.