

NEW ACCELERATED METHOD TO DETERMINE SLOW CRACK GROWTH BEHAVIOUR OF POLYETHYLENE PIPE MATERIALS

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ABSTRACT

Resistance to slow crack growth is an important material property of polyethylene especially for pipe applications. Slow crack growth resistance of polyethylene pipes and materials is usually assessed by tedious and time consuming testing methods (e.g. NPT, FNCT, PENT, ESCR etc.) performed on notched samples in contact with specific fluids at elevated temperatures.

In this paper we present a new test method to predict slow crack growth resistance in materials in a much simpler, more accurate and faster way. It will be shown that resistance to slow crack growth in polyethylene can be predicted from a simple tensile strain hardening measurement at 80°C. It is shown that for bimodal polyethylene materials for pipe applications the slope of the stress-strain curve above its natural draw ratio (i.e. strain hardening) correlates well with the measured stress crack resistance *via* traditional methods. The rationale behind this correlation is provided by the Kramer-Brown model for craze propagation and craze-crack transition where the most important intrinsic material parameter that is governing propagation and failure of crazes is the density of the network of effective entanglements which can in a straightforward way be assessed by measuring the amount of strain hardening

This technique offers a relatively easy way of predicting slow crack growth resistance in materials without using surfactants. The presented test method shows very low standard deviation and furthermore, measuring times are dramatically reduced in comparison to traditional methods from thousands of hours to only a few. This accelerated test method is suitable for small sample sizes for R&D purposes and also is suitable as a batch release test for both resin suppliers and pipe converters.

INTRODUCTION

Polyethylene (PE) has been used successfully in pipe applications for about 50 years. Typically, a service life of 50 years is required although 100 years have been proposed more recently. Traditionally, the long-term properties of PE pipes are determined using internal pressure tests. It is well known that slow crack growth (SCG), so called Stage II failure in the stress rupture curve

of a plastic pipe ($\log(\text{hoop stress})$ versus $\log(\text{failure time})$), is the critical parameter that determines the lifetime of a PE pipe.

Therefore a number of different accelerated testing procedures have been developed (e.g. FNCT, PENT, NPT) and are widely used in PE pipe industry. However, the newest HDPE pipe grade materials show more than excellent slow crack growth resistance. The failure times of such materials are un-practically long even when the above mentioned accelerated test methods are employed. Therefore, there is a need for a faster, reliable and robust test method to predict slow crack growth behaviour. In this paper we present such a method.

THE PHENOMENOLOGY OF SLOW CRACK GROWTH RESISTANCE

Slow crack growth resistance in polyethylene has been reported extensively in the literature.^{1,2,3,4,5,6,7,8,9,10} Resistance to slow crack growth is considered when the applied stress on a specimen (product) is much lower than the yield stress and in the presence of bulk inhomogeneities (scratches, pigments, catalyst residues). The overall failure habit is brittle and it proceeds via a so-called craze crack mechanism that commences with a deformation zone or plastic zone formed at the tip of an advancing crack. Such a deformation zone consists of microscopic cavities (voids) that will grow and join up to form a cross-tied network of essentially fibrillar entities usually referred to as a craze.^{11,12,13} The craze-crack mechanism, from the development of the deformation zone up to the fracture of the fibrils, within a craze is usually considered to proceed through three main stages, i.e. initiation, propagation and the craze crack transition. The initiation step includes the formation of the deformation zone, which is strongly associated with the yield stress and stiffness of a material^{14,4}. Once the deformation zone is formed it will start to propagate which is usually associated with the formation of a surface tension driven meniscus instability void formation at the crack tip. The oncoming of this voided material is dominated by yield stress and surface tension¹⁵. Consequently the material between voids stretches into a network of strain hardened cross tied fibrils. This network will eventually fail due to the stress concentration in the critically loaded fibril at the craze crack transition point as shown in Figure 1. The failure of this critically loaded fibril is governed by the network of effective entanglements in the strain hardened fibril^{16,17}. This basically means that the resistance to craze initiation and failure in such a slow crack growth mechanism is primarily determined by the intrinsic strain hardening response of fibrils and hence of the material in a pure plane stress uniaxial load as is schematically represented in Figure 2. This is why a simple tensile test to assess the strain hardening behaviour of a material will be predictive for the slow crack growth resistance.

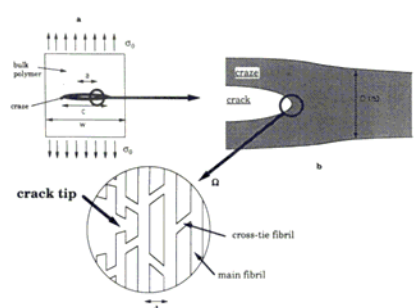


Figure 1: Craze crack transition with cross-tie fibrils (taken from Brown¹⁶)

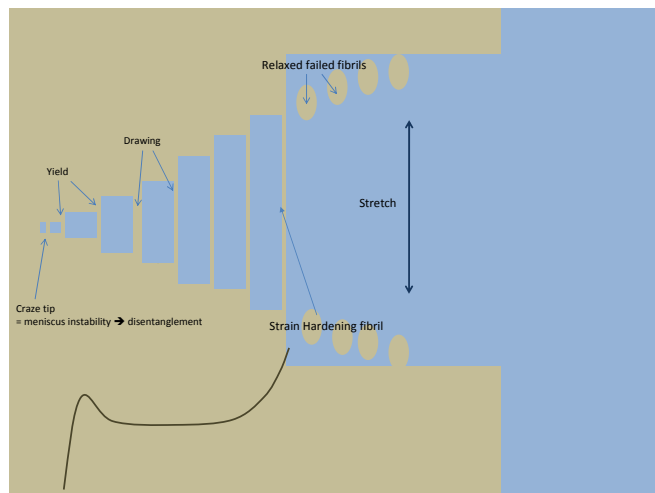


Figure 2: Schematic representation of fibril strain hardening in a craze and its relation to uniaxial tensile drawing

Because slow crack growth is a very slow process, testing of such long-term properties is commonly accelerated by usage of a non-ionic surfactant environment and/or the use of elevated temperature. Such tests are claimed to be designed in such a way that the failure mechanism is the same one as encounters during slow crack growth.¹⁸ The role of surfactants in the acceleration of slow crack growth failure has been studied and it has been shown that surfactants facilitate craze growth by plasticizing the amorphous phase¹⁹ and promote fracture by interacting with the crystalline region of the fibrils at the base of the craze where it might act as a lubricant for chain sliding^{7,20}. Aging of the surface-active environment has also been studied by a number of authors. One author claims that new and old solutions lead to irreproducible results²¹ whereas another states that the aging of nonylphenol polyglycol ether solutions do not affect failure times.²² It is clear that the use of surfactants to accelerate slow crack growth is complex and is not completely understood.

Acceleration of slow crack growth can also be achieved by using elevated temperatures. This provides enhanced chain mobility within a crystal (α -relaxation process²³) facilitating solid-state chain diffusion through the crystalline phase and subsequently crystal shear.²⁴ In the above mentioned conceptual Kramer-Brown framework on craze propagation the ease of formation of internal surface in a polymer is determined by surface tension. This surface tension is determined by the sum of secondary interactions and the contribution of load bearing chains that need to be fractured or to slip to form a surface. This elegant model explains the effect of a detergent and temperature as a decrease in the stress needed to propagate the craze, the so called craze stress. However, the possibility to shorten testing times by increasing temperature is limited because it is clear that brittle fracture has to be attained in order to make a reliable prediction of long term properties. If, at the selected temperature the stress level is chosen too close to the yield stress of the material, ductile behaviour will predominate and obtained results will not be a measure of brittle failure.¹⁹

Based on the above described principle of using surfactants and increased temperatures a number of different testing procedures have been developed and are widely used in PE pipe industry. Examples are the Full Notch Creep Test (FNCT),¹⁸ The Pennsylvania Notch Test (PENT), the Notched Pipe Test (NPT),²⁵ Environmental Stress Crack Resistance (ESCR), cone test, bent strip

test.²⁶ The problem often encountered with such testing methods is their poor long term reproducibility, high sensitivity to surfactant quality and rather critical specimen preparation (namely notching procedure).²¹

In the mid nineties, O'Connell et al.^{27,28} approached the slow crack growth step via the creep rate deceleration of drawn polyethylene samples. In their approach they simulated the fibrillar structure within a craze by a tensile bar drawn to its natural draw ratio. They found a uniform relation between the creep rate deceleration of the drawn material and the growth as well as the failure of the craze. Cawood et al. showed that there is a direct relationship between the creep rate deceleration and a standard (accelerated) ESCR measurement.^{29,30} These results clearly showed that the creep of the fibrils within a craze is a determining factor determining slow crack growth in polyethylene. We have previously shown³¹, following the Kramer-Brown framework, that it is equivalent and experimentally more simple to use stress-strain curves at the identical deformation rates to assess long term performance (SCG) of HDPE products, see Figure 3. The parameter which we linked to SCG performance is the measure of resistance against further deformation above the natural draw ratio i.e., the slope of the strain hardening part of a stress-strain curve, notably at elevated temperature (~80 °C). The higher temperature is necessary to assess the response of the effective molecular entanglements within the material at creep rate (i.e. long relaxation times) when the molecular chains become mobile with respect to the crystals within the fibrils. To that end the α -relaxation temperature of polyethylene was adopted to ascertain this condition.

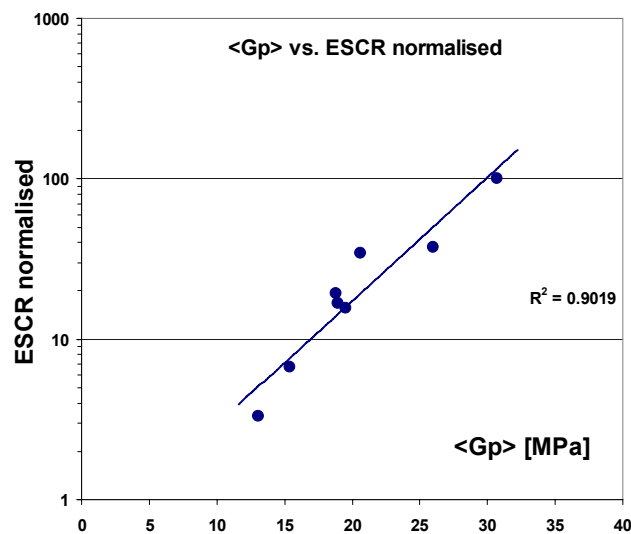


Figure 3: Correlation of ESCR (normalised) with $\langle G_p \rangle$ measured at 80 °C.³¹

In the present paper, the potential of this strain hardening method is further developed for PE pipe materials and it is shown to be a relatively easy way of predicting slow crack growth resistance in materials without using surfactants.

EXPERIMENTAL

Materials

For this study a range of commercially available bimodal HDPE pipe grades (both PE80 and PE100) have been selected.

Sample preparation for tensile testing

The materials are pressed at 160 °C to a sheet with a thickness of about 0.3 or 1mm. The procedure for pressing the materials is: 5 min heating up at 0 kN load, 3 min at 10 kN load, 3 min at 50 kN load and cooling down to room temperature at a load of 180 kN. After pressing, the samples are annealed for 1 h at 120 °C and then slowly cooled down to room temperature by switching off the temperature chamber. Finally the test specimens (ISO37 type 3) are punched from the pressed sheets.

Tensile measurements

The measurement is in principle a standard tensile test. The test specimen is extended along its major axis at constant speed (10 mm/min) until the strain reaches 1200%. The maximum strain value is limited by the length of the climate hood. During the test the load sustained by the specimen and the elongation are measured. A 200N load cell is used for the load measurement. The elongation is determined with an optical extensometer. Therefore two reflecting and self-adhesive gauge marks are attached to the test specimens. The initial distance l_0 between these marks (gauge length) is determined after reaching the pre-load before each test. Prior to testing the test specimen are kept for about 30 min in the temperature chamber at the envisaged test temperature so as to allow thermal equilibrium. The traverse speed was kept constant during the measurements and as a consequence the true strain rate was not constant. This may not be unimportant because in the course of a measurement the true strain rate drops with a factor λ . Hence the strain rate drops an order of magnitude towards the end of the measurement. This means that the strain intrinsic hardening moduli obtained at true constant strain rate may be larger than the reported ones.

Data treatment

The instantaneous force load $F(t)$ in N is calculated to a true stress σ_T in MPa by dividing it by the initial cross section A_0 in mm^2 and multiplying it by the instantaneous extension ratio $\lambda(t)$:

$\sigma_T = \lambda(t)F(t)/A_0$ with $\lambda(t) = l(t)/l_0$. The true strain is usually represented as a Hencky strain $\ln(\lambda(t))$ but for the present paper we adopt $\lambda(t)$ as measure of true strain. The values of true stress and true strain obtained in this way are only valid assuming homogeneous deformation. This means that only the values before yield stress and beyond the natural draw ratio are valid true stress true strain data. The average strain hardening slope $\langle G_p \rangle$ in MPa is defined in our previous paper is defined as:

$$\langle G_p \rangle = \frac{1}{N} \sum_{i=1}^N \frac{\sigma_{i+1} - \sigma_i}{\lambda_{i+1} - \lambda_i}$$

where the average is calculated between $\lambda=8$ and $\lambda=12$ and N represents the number of measuring points between $\lambda=8$ and $\lambda=12$. There should be no confusion with the strain hardening modulus G_p as defined by Haward³² although using the above expression for $\langle G_p \rangle$ and assuming a valid constitutive model both can be related to each other.

Whereas for Cr HDPE's it is never a problem to reach $\lambda=12$ this may become troublesome for pipe grade bimodal PE's where the strain hardening values are generally much higher. This experimental condition leads to problems with clamp slip when the tensile force becomes too large for the available clamping stress which is determined by the sample shape. To circumvent this difficulty we adopted a Neo-Hookean constitutive model to obtain G_p .

$$\sigma_T = C + G_p \left(\lambda^2 - \frac{1}{\lambda} \right)$$

and calculate $\langle G_p \rangle$ from this Neo-Hookean fit to our data. C is a mathematical parameter of the constitutive model describing the yield stress extrapolated to $\lambda=0$ which is of no consequence for our calculation because it is vanishing in the derivative or the difference quotient to calculate $\langle G_p \rangle$ anyway. This approach is found to reproduce all former measurements of $\langle G_p \rangle$.

Slow crack growth resistance measurement: traditional methods

Two different slow crack growth resistance measurement test methods were used in this study. Both methods differ in sample preparation, shape, temperature and surfactant. They will henceforth be referred to as method 1 and method 2. The time to failure (hours) of each test sample is registered and normalised to 100 arbitrary units. Each test was carried out in triplicate.

RESULTS AND DISCUSSION

Tensile response

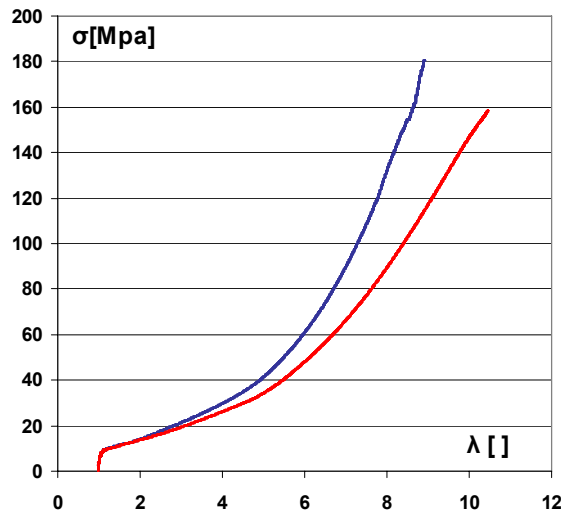


Figure 4: True stress True strain response for two arbitrary bimodal grades at 80°C. The red one has $\langle G_p \rangle = 31$ and the blue one has $\langle G_p \rangle = 57$

In Figure 4, two examples of true stress true strain tensile curves at 80°C are shown, one must keep in mind that the strain hardening data are only valid from the natural draw ratio, defined as

the second tangent from the Considère construction³³. It is clearly seen that significant variation is present even within the set of bimodal grades.

Figures 5 and 6 show the average slope of strain hardening measured at 80 °C, defined as $\langle G_p \rangle$ plotted against the normalised slow crack growth resistance values obtained by the use of the two different accelerated SCG resistance tests used in this study. These results elegantly demonstrate that the accelerated slow crack growth resistance test data correlate well with $\langle G_p \rangle$. This supports our working hypothesis that the intrinsic strain hardening of a tensile sample in plane stress conditions mimics the resistance to creep loaded craze fibril failure. This correlation makes it plausible to state that the strain hardening response is determined by the same molecular differences that govern SCG resistance in HDPE, measured by a traditional SCG resistance test.

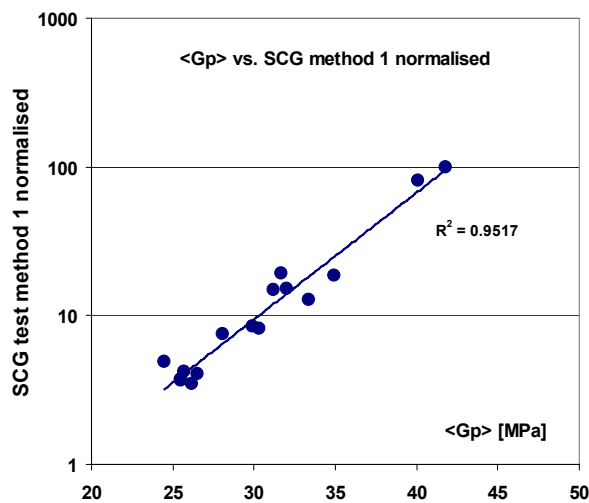


Figure 5: Strain Hardening modulus $\langle G_p \rangle$ versus SCG test method 1(normalised)

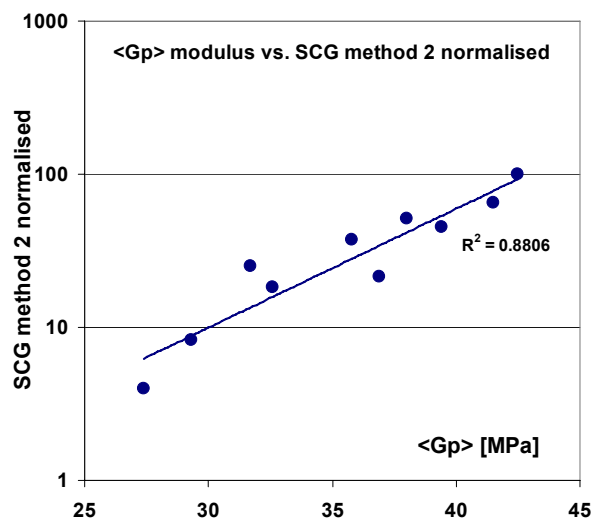


Figure 6: Strain Hardening modulus $\langle G_p \rangle$ versus SCG test method 2(normalised)

The mechanical resistance of craze fibrils against further deformation and failure can be explained and understood in terms of the Kramer-Brown model as it is briefly outlined above. As already stated this model also explains the importance of the effective entanglement network for the propagation of a craze in a material. The higher the number of effective entanglements, the higher the craze stress and the more likely that the material will actually follow a shear like deformation habit without the formation of crazes. This means that materials that feature a high strain hardening may be expected to give more resistance to craze initiation. It is henceforth not amazing that strain hardening provides such good predictive measures for slow crack growth processes. At this point it is worthwhile to mention some independent observations that support our approach. In mid nineties O'Connell et al.^{34,35} approached the slow crack propagation step via the creep rate deceleration of drawn polyethylene samples. In their approach they simulated the fibrillar structure within a craze by a tensile bar drawn to its natural draw ratio. They found a uniform relation between the creep rate deceleration of the drawn material and the growth as well as the failure of the craze. Cawood et al. showed that there is a direct relationship between the creep rate deceleration with a standard (accelerated) ESCR measurement.^{36,37} Because creep rate deceleration is directly related with strain hardening via the unique true stress - true strain - true strain rate hypersurface of a material the observations of O'Connell and Cawood are equivalent.

Also Laurent³⁸ observed a very good correlation of SCG with the natural draw ratio NDR, which is directly related, via the Considère construction, to the initial strain hardening modulus.

	<Gp>	SD	SCG method 1	SD
	MPa	MPa	normalised	
HDPE 1	30.3	1.6	8.3	1.5
HDPE 2	33.4	0.9	12.8	1.3
HDPE 3	31.2	0.6	15.0	2.4
HDPE 4	29.9	0.5	8.5	2.1

Table 1: <Gp> moduli and normalised SCG failure times according to test method 1 of different HDPE materials

Finally table 1 also reveals that the experimental scatter on the SCG measurements are much larger than the experimental scatter on <Gp> . Actually most of the experimental scatter seen in fig 3, and fig 5 and fig 6 arises from the scatter on the SCG data.

CONCLUSIONS

It has been shown in this paper that the average strain hardening slope <Gp> correlates with the data obtained by traditional slow crack growth test methods.

The underlying mechanism of slow crack growth can be understood in terms of the Kramer-Brown framework describing the propagation and failure of crazes. In this framework the central parameter that determines craze stress and the resistance to failure is the network of effective entanglements. This implies that all molecular changes aimed at improving slow crack growth should aim at increasing the number of effective entanglements.

The strain hardening measurement offers a relatively easy way of predicting slow crack growth resistance in materials without using surfactants. The presented test method shows very low standard deviation and furthermore, measuring times are dramatically reduced in comparison to traditional methods from thousands of hours to only a few.

This accelerated test method is suitable for small sample sizes for R&D purposes and also is suitable as a batch release test for both resin suppliers and pipe converters. It should also be mentioned that this new way of assessing slow crack growth data can be applied in any mechanical laboratory equipped with a tensile machine featuring a temperature chamber and an optical extensometer.

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