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A Tensile Strain Hardening Test Indicator of Environmental Stress Cracking Resistance

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Environmental stress cracking resistance (ESCR) is an important indicator of performance for high density polyethylene (HDPE) in structural and polymer pipe applications. The commonly used test for determining ESCR of HDPE can be time consuming and rather imprecise. A tensile strain hardening test was recently proposed to offer a faster way to characterize ESCR of polyethylene. In this paper, a practical approach is adopted whereby the test is extended to room temperature and shown to relate reliably to the ESCR of HDPE. Several HDPE resins (including pipe-grade resins) are analyzed at strain rates of 0.5 mm/min and 7 mm/min to compare the effect of strain rate. Comparisons between the conventional ESCR test method and the strain hardening test show that strain hardening can be used to rank ESCR of HDPE in a reliable fashion. In our study the more direct measure of "hardening stiffness" is used to compare resins instead of strain hardening modulus. Because no true stress-strain measurement is needed, this is a much simpler test method than other methods previously suggested. In addition, the use of the natural drawing ratio (NDR) as ESCR ranking indicator is examined. Results show that NDR can also be employed as a strain rate-independent indicator of ESCR of HDPE. The test proposed herein is practical, simple and precise, and hence a more reliable indicator of ESCR performance of HDPE.

Keywords: environmental stress cracking resistance; strain hardening test; high density polyethylene; natural drawing ratio; tensile test; polyethylene resin comparison

1 Introduction

Polyethylene materials do not show any signs of brittle fracture until the materials have failed completely. This poses a serious problem for polyethylene used in structural and pipe applications. Environmental stress cracking (ESC) is a type of brittle fracture failure often observed in polyethylene. Polyethylene pipe that should have a service life of fifty years or more is often known to crack within a year due to ESC (1). Therefore, study and testing of environmental stress cracking resistance (ESCR) of polyethylene are of great interest. The notched constant load test (NCLT), ASTM D5397, is commonly used to measure ESCR of polymers. This is a time consuming test method, as high density polyethylene is known to have NCLT values in the range of thousands of hours (2).

Environmental stress cracking is the stress failure of a polymer when subjected to an aggressive environment, such as "soapy" water (water and emulsifier). In most cases, the type of fracture associated with ESC is characterized by clean cracks, which indicate a brittle fracture mechanism (3). Any cracking of polymer due to an aggressive environment can be referred to as environmental stress cracking (for example, the degradation of polymer due to exposure to UV light that may lead to mechanical failure of the material). However, most of the time ESC refers to the stress cracking of polymer due to an active environmental effect without any chemical alteration of the material (therefore, a purely physical process). Polar solvents such as alcohols, detergents (soaps, emulsifiers) and silicone oils represent aggressive environments for polyethylene.

Stress cracking of polyethylene can take a long time. An active environment, such as a surfactant in water, is believed to reduce the surface free energy of the fibrils in a craze and prevent the fibrils from packing into a dense structure, thus leading to craze stabilization. Ultimately, this leads to the formation of cracks and the failure of the polymer (4). The exact mechanism of how commonly employed surfactants, such as Igepal, facilitate SCG (slow crack growth) is not clear. Ward et al. (5) proposed that the long Igepal molecules align themselves with tie-molecules (see below) in the fibrils, thus

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reducing the frictional stress as tie-molecules disentangle from crystals. As tie-molecules become untangled more easily, the ESCR of the polymer decreases. It is generally accepted that an active environment can act as 'lubrication' for chain disentanglement (6), thus resulting in accelerated SCG of polyethylene. Research has shown that the initial rate of SCG for polyethylene samples in Igepal solution is the same as for samples in air. It is only after a sufficient time period has elapsed, allowing Igepal to diffuse into the crystalline region of the polymer, that the cracking process is accelerated (5). This indicates that the initial rate of ESC is controlled by diffusional limitations of the active ingredient. The ESCR of polyethylene can thus be increased if diffusion of the aggressive agent is limited.

Environmental stress cracking occurs by a brittle fracture mechanism. Brittle fracture is believed to be caused by disentanglement of inter-lamellar links (3). The number and type of these inter-lamellar connections play an important role on ESCR of polyethylene. There are two types of these connections. The first kind is called bridging tie-molecules, or tie-molecules for short. The two ends of these molecules crystallize in two different lamellae, thus connecting them. Tie-molecules have strength due to covalent bonds. The other type of inter-lamellar links is made of entanglements of loose loops and cilias, which are believed to be held together by van der Waals forces (3) and chain coupling (7). From this point on, only bridging tie-molecules will be referred to as tie-molecules. All other types will be lumped together in what we refer to below as entanglements.

Physical chain entanglements in a polymer are the second type of inter-lamellar linkage that holds crystalline lamellae together. The importance of tie-molecules on environmental stress cracking of polyethylene has been studied extensively; however, physical chain entanglements have not. Since brittle fracture occurs through a mechanism of chain disentanglements (3), the time it takes for physical chain entanglements to separate from one another will also contribute to the ESCR of polyethylene. Research has certainly shown that physical chain entanglements influence tensile behavior of polyethylene (8–10). Physical entanglements may not be as strong as tie-molecules (11), but probability calculations showed that the chance of occurrence of entanglements in the amorphous phase is much higher than the occurrence of tie-molecules (12). Therefore, both tie-molecules and chain entanglements are important for ESCR of polyethylene.

Environmental stress cracking resistance of a polymer is known to increase with increasing tie-molecules concentration (11, 13). Molecular weight (12, 14, 15) and short chain branching (SCB) play critical roles in tie-molecule formation (13, 16, 17). The higher the molecular weight of the material the more likely to have chains long enough to be embedded in two or more crystalline lamellae and hence form tie-molecules. On the other hand, SCB interrupts the chain folding process of lamella formation (18), therefore long polyethylene chains with SCB are more likely to have more tie-molecules and entanglements. Polyethylene resins for pipes developed over the years have incorporated many of the features that lead to better ESCR. The latest, PE100 resins (2), are made with both high molecular weight and high SCB content in mind. These resins are known to have desirable ESCR properties.

Strain hardening occurs when the amorphous phase of polyethylene is stretched to its maximum extension during tensile deformation. It is a phenomenon observed in fully drawn (and cold-drawing of) polymers. The cause of increase in stress at strain hardening is reported as due to molecular alignment resulting in increased drawing stress (19). As the material is drawn, strain-induced crystallization occurs and drawing stress increases. In semi-crystalline polymers, such as polyethylene, both crystalline and amorphous phases play important roles in ductile deformation (20–22). In a uniaxial tension test, before yield, the stiffer crystalline phase of polyethylene undergoes little deformation whereas the amorphous phase deforms substantially to accommodate the overall deformation of the material sample. After the yield point but before strain hardening, the slipping of lamellae occurs, and both crystalline and amorphous phases play a part in load bearing and straining. When the amorphous phase is fully stretched, the onset of strain hardening begins. In the strain hardening phase, the fully extended amorphous phase becomes the rigid load-bearing element, while crystalline lamellae break apart and unfold to accommodate the change in strain (23). The load-bearing elements in the amorphous phase of polyethylene are comprised of both tie-molecules and entanglements. Since these are very important elements for the ESCR of polyethylene, it follows that strain hardening and ESCR behavior of polyethylene can be correlated.

Finally, the strain at onset of strain hardening is a function of the extensibility of the polymer network. The measurement used to characterize the extensibility of a polymer network is the natural drawing ratio (NDR). In crosslinked polymers, extensibility of the material is controlled by the number of crosslinks. For polymer without crosslinks, chain entanglements control the extensibility of the material. Evidence supporting this relationship between network extensibility (and hence, NDR) and physical chain entanglements has been observed in the behavior of melt-spun fibers (24).

In the strain hardening state, physical chain entanglements and tie-molecules are the molecular structural entities that hold the bulk of the material together. This is the basis of the recent suggestion by Kurelec et al. (25) and the practical extension proposed in the current paper. In order to carry out their tests at a high strain rate (10 mm/min), Kurelec et al. (25) conducted their experiments at an elevated temperature of 80°C, with the aid of an optical extensiometer, an instrument not commonly found in most laboratories. In our work we propose a practical extension towards a much simpler tensile strain hardening test carried out at ambient conditions as a tool for screening ESCR values of high density polyethylene. Comparisons between the proposed strain hardening test method and the time consuming and rather imprecise, commonly used NCLT method suggest that strain hardening at ambient temperatures can successfully rank ESCR of HDPE, and hence, has the potential of replacing the more tedious and noisy conventional test.

2 Experimental

2.1 *Polymer Characterization*

Resin molecular weights were determined via high-temperature size exclusion chromatography (SEC). A Waters GPCV 150+ instrument equipped with a Viscotek 150R viscometer was used (at 140°C, with 1,2,4 trichlorobenzene (TCB) as solvent). Short chain branch (SCB) content of resins was investigated using an AVANCE 500 Bruker NMR. ^{13}C-NMR analysis was run at 120°C. Each sample consisted of 5 mg of polymer dissolved in trichlorobenzene, with trichloroethylene (TCE) used as tracer. Crystallinity levels of resins were determined using DSC (differential scanning calorimetry) on a DSC 2920 module. The method employed a 10°C/min ramp from 40°C to 240°C. The theoretical value for a 100% crystalline polyethylene used in the calculations of percent crystallinity of samples was 293.6 J/g (26). Sample size used per DSC run was approximately 5 mg.

2.2 *Tensile Test*

Tensile tests were carried out on an Instron 4465 machine at room temperature, using strain rates of 0.5 mm/min and 7 mm/min. The dogbone sample was pulled at a constant deformation rate until ultimate break to study the strain hardening behavior of HDPE. Load versus displacement was measured and the strain hardening stiffness calculated. Dogbone samples were punched from compression molded resin plates (Fig. 1). Each resin plate was compression molded at 190°C ± 5°C and 10000 lbf; the plate was allowed to cool down in the mold at room temperature over a period of 24 h before dogbones were cut out from it. The tensile test follows the guidelines of ASTM 638 standard. Independent replicates and repeats were carried out. NDR is defined as the ratio of sample strain at onset of strain hardening and its initial length (19). Due to limitations of the available equipment setup, true strain measurements were not possible. Therefore, we defined a nominal/engineering NDR to be used with our results without any change of or effect on the conclusions. All further references to NDR in the "Results and Discussion" section will hence be based on the following modified definition:

$$\mathrm{NDR} = \frac{\text{Sample displacement at onset of strain hardening}}{\text{Inital sample length}} \tag{1}$$

2.3 *Notched Constant Load Test (NCLT)*

NCLT is used to measure creep response of polyethylene under an aggressive environment, a well accepted and commonly employed method both in academia and industry. Results of NCLT are used as an indication of the ESCR of a polymer. Experiments were run at 50°C in a temperature bath containing 10% Igepal (nonyl phenyl ether glycol, $C_{19}H_{19}$-C_6H_4-O-$(CH_2CH_2O)_8$-CH_2CH_2OH) solution. A load equal to 15% of the yield stress of the material was used to ensure fracture occurs in the brittle failure region (1). Dogbone shaped samples were cut out from plates of polymer made from compression molding at 190°C ± 5°C. Specimen dimensions are shown in Fig. 2. The thickness of the sample was 1.8 ± 0.1 mm. A notch was introduced into the samples at the middle of the dogbone using a sharp razor blade. For our test we used a notch that was 40% of the thickness of the sample instead of 20% (as indicated by ASTM D5397). The effect of this change is discussed in section 3.1.1. Independent replicate tests were carried out to investigate the repeatability of the method. This important independent replication is often overlooked in the literature, thus making the appreciation of a method and validity of conclusions more difficult and less reliable, respectively.

2.3.1 *Experimental Design for NCLT*

A randomized central composite design (with blocking) was used to investigate the effects of different levels of tensile stress and notch depth on the outcome of NCLT tests. The resin used in this investigation was PE1. (Table 2 summarizes

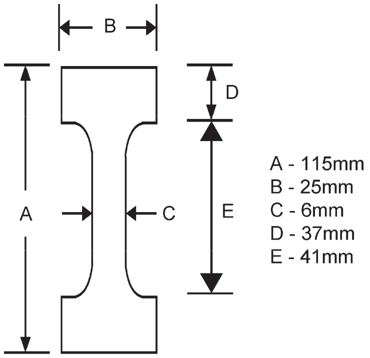

Fig. 1. Dogbone dimensions for tensile test.

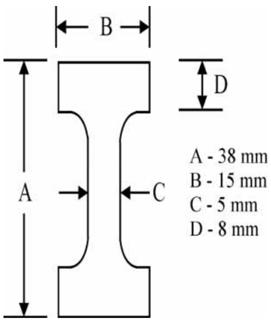

Fig. 2. Dogbone dimensions for NCLT.

Table 1. Experimental design[1] for NCLT of PE1

	Block	(%) Notch depth	(%) Yield strength	(%) Notch depth	(%) Yield strength
1	1	−1	−1	20.0	10.0
2	1	−1	1	20.0	25.0
3	1	1	−1	50.0	10.0
4	1	1	1	50.0	25.0
5	1	−1.41	0	18.8	15.0
6	1	1.41	0	61.2	15.0
7	1	0	−1.41	40.0	4.4
8	1	0	1.41	40.0	25.6
9 (C)[a]	1	0	0	40.0	15.0
10 (C)[a]	1	0	0	40.0	15.0
11	2	−1.41	0	60.0	22.9
12	2	1.41	0	60.0	37.1
13	2	0	−1.41	45.9	30.0
14	2	0	1.41	74.1	30.0
15 (C)[a]	2	0	0	60.0	30.0

[1] Conventional test settings: 15% yield strength, 40% notch depth.

[a] C: Center point.

the resins and some of their characteristics pertinent to this paper). The test levels for the full design are listed in Table 1. A total of 15 tests were completed. For block-1 tests, the center point of the design is shifted to 40% notch depth and 15% yield strength in order to compare to conditions of previous tests (see beginning of section 2.3). In block-2, a partial central composite design was used to clarify the behavior at higher notch depth and percentage yield strength. Overall, the notch depth used ranged from 18.8%–74.1%, whereas the percentage yield strength (stress level) applied ranged from 4.4%–37.1%.

3 Results and Discussion

3.1 *ESCR Results from NCLT Test*

Ten industrial high density polyethylene resins were studied in this paper (see Table 2). The resins included three blow molding resins (PE1–3), three injection molding resins (PE4–6), and four pipe resins (PE7–10). PE8 is a PE80 grade pipe resin, while PE7, PE9 and PE10 are PE100 grade pipe resins. In Table 2, Mn, Mw and Mz stand for number-, weight- and z-average molecular weights, respectively, whereas PDI denotes polydispersity.

Results from NCLT on polyethylene resins in our study are listed in Table 3. Out of the ten resins in this study, PE5 and PE6 could not be tested using the NCLT method because the material was very brittle and could not survive the notching process. Pipe grade polyethylene resins (PE7–10) have dramatically longer time to failure than non-pipe grade resins (PE1–4). The ESCR time of pipe resins essentially follows the grading; PE100 resins are more resistant than PE80 resin. It is especially worth noting that the PE10 samples did not fail even after 3000 h. Blow molding resins (PE1–3) and injection molding resins (PE4–6) cannot be compared to pipe resins in terms of the magnitude of NCLT failure time. Of the six non-pipe resins, PE1 and PE4 have the longest NCLT failure time.

Table 2. Characteristics of resins

Resin	Density	Mn (kg/mol)	Mw (kg/mol)	Mz (kg/mol)	PDI Mw/Mn	Percent crystallinity (%)	SCB (/1000C)
PE1	0.95	16.3	127.5	814.0	7.8	55	2.8
PE2	0.96	15.7	118.5	837.1	7.6	59	1.1
PE3	0.96	17.9	140.1	889.8	7.8	58	0.9
PE4	0.95	19.7	79.4	239.3	4.0	55	3.8
PE5	0.95	11.4	49.7	157.8	4.4	54	7.0
PE6	0.95	14.0	62.0	195.0	4.4	57	4.7
PE7	0.95	11.8	222.8	1593.5	18.9	53	4.3
PE8	0.96	14.0	202.1	1398.4	14.4	56	4.5
PE9	0.96	10.4	217.9	1244.2	20.9	62	7.0
PE10	0.96	5.9	315.4	2129.3	53.3	51	11.8

Table 3. NCLT results

	NCLT (h)	Standard deviation (h)	Coefficient of variation
PE1	4.8	0.92	0.19
PE2	1.2	0.17	0.14
PE3	2.8	0.25	0.09
PE4	3.6	0.53	0.15
PE5	N/A	N/A	N/A
PE6	N/A	N/A	N/A
PE7	1395.8	338.74	0.24
PE8	198.3	44.74	0.23
PE9	872.1	338.90	0.39
PE10	>3000	—	—

Values in Table 3 are means (averages) over several independent replicates (usually, three dogbones from the same plate, and often two or three independent plates with two to five dogbones per plate). A detailed analysis of the variability of NCLT is presented later in section 3.1.1. The standard deviation of NCLT results is higher for higher molecular weight (MW) resins, as expected. Hence, the coefficient of variation (standard deviation over mean) for each resin is presented to clarify the masking effect of the differences in magnitude of ESCR values. The coefficient of variation values for all resins range from 0.09–0.39. The average coefficient of variation is 0.20. The lack of precision of test results is a known problem associated with NCLT. In industry, some NCLT results have been reported with coefficients of variation as high as 0.50 (27).

As mentioned earlier, ESCR of polyethylene is known to increase with increasing molecular weight. Pipe resins have much higher MW values (note the much higher weight- and z-average MW values) as compared to other types of resins, as can be seen in Table 2. Therefore, they exhibit larger ("better") ESCR values. The importance of MW on ESCR can be further demonstrated by looking, for example, at resins PE4–6. PE4 has an average ESCR value of 3.6 h, while PE5 and PE6 have negligible ESCR values. The molecular weight distribution (MWD) curves of these three resins have a similar shape, with the only difference being that the curve for PE4 is shifted to higher MW values (Fig. 3). The higher Mz average molecular weight is especially significant, since it is an indication of a longer and/or larger tail in the high molecular weight end of the molecular weight distribution. Large chains are more likely to form tie-molecules and entanglements that are critical to ESCR of HDPE.

The MWD of polyethylene also influences its ESCR. Resins with larger polydispersity index (PDI) values have higher ESCR values (see Tables 2 and 3). This suggests that resins with broad MWD exhibit higher ESCR. GPC analysis of all resins showed that PE4–6 have the narrowest MWD (Fig. 3), followed by PE1–3 (Fig. 4), whereas the pipe resins PE7–10 have the broadest MWD (Fig. 5). Of the four pipe resins, PE9 and PE10 have bimodal and much broader MWD than all other resins. It is especially worth noting that PE10 shows a much larger fraction of polymer at the high MW tail of the distribution compared to all other resins. Higher content of high MW chains leads to the formation of more inter-lamellar connections, which explains the improved ESCR for the resin.

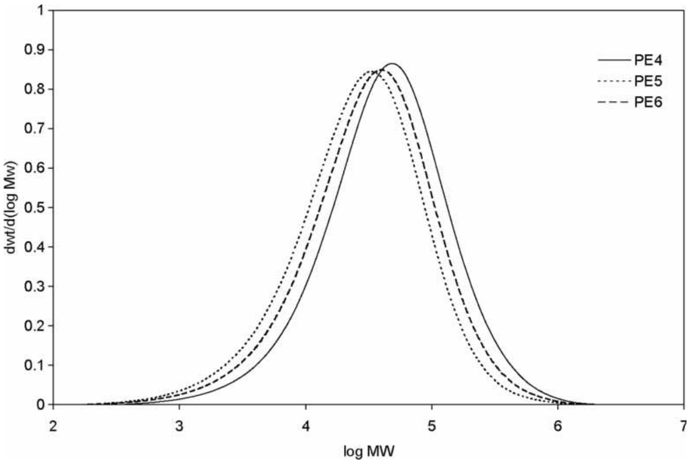

Fig. 3. MWD curves of PE4–6.

Molecular weight and molecular weight distribution differences alone cannot explain the different ESCR behavior of the resins. PE 1–3 have similar MW values and MWD shapes (Fig. 4), yet PE1 has a higher ESCR value than PE2 or PE3. This difference can be attributed to the different SCB content of these resins. All of the resins in this study have butyl branches as the side chain group. PE9 also has a small amount of methyl branches. Table 2 lists the number of short branches per 1000 carbon atoms for all resins as measured via ^{13}C-NMR. Comparing PE1–3, PE1 has almost three times as much SCB compared to PE2 or PE3. As mentioned earlier, an increase in resin SCB content is known to improve ESCR of polyethylene. However, a

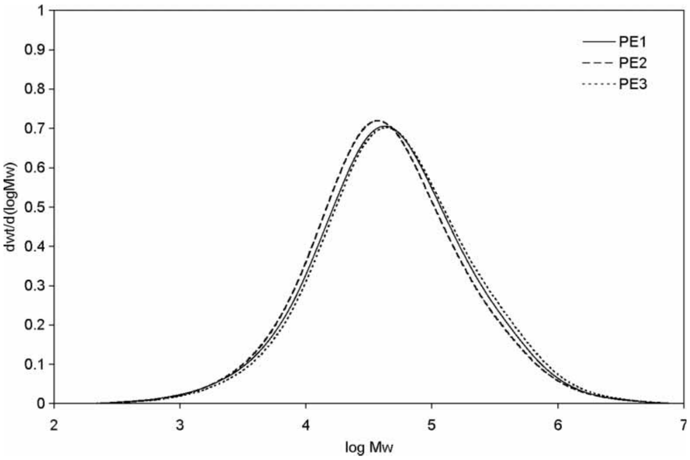

Fig. 4. MWD curves of PE1–3.

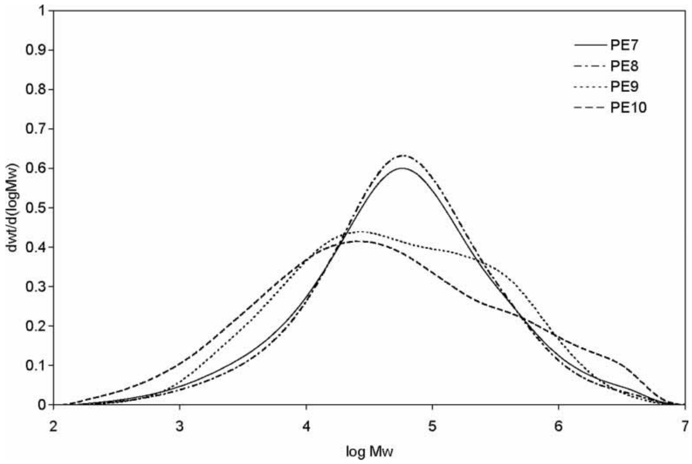

Fig. 5. MWD curves of PE7–10.

higher SCB content alone, as in the case of PE5–6, did not result in good ESCR behavior. Based on the analysis results so far, it is important to point out (and re-emphasize the point from the literature) that high SCB content must be combined with sufficiently high MW values (and appropriate breadth of the MWD) in order to improve ESCR of a resin.

For linear polyethylene, crystallinity increases in a way directly proportional to MW. The presence of SCB interrupts the chain folding process of crystallization and reduces the overall crystallinity of the material. Long chains that are not incorporated into the crystalline lamellae, form chain entanglements and tie-molecules that increase ESCR of polyethylene (28). For polymers of similar MW, resins containing higher SCB content would possess lower crystallinity. Comparing PE1–3, PE1 has higher SCB content, lower crystallinity (Table 2) and higher ESCR value (Table 3). The same trend is also observed for the pipe resins. PE10 has the highest ESCR value with the lowest percent crystallinity. In summary, pipe grade resins take longer to fail in NCLT than non-pipe resins. The differences in measured ESCR values can be explained by current theory and understanding of ESC of polymers.

3.1.1 *Effect of Notch Depth and Stress Level on NCLT*

The notched constant load test is a standard ASTM method that is widely used by both academia and industry (2, 25) to determine ESCR of a polymer. To investigate whether the test procedure used for NCLT contributes any significant variability to the results, independently replicated tests were conducted.

Tests were replicated starting from step one, sample plate molding. Comparisons were made between samples from different molded plates. Results of the tests were then analyzed using statistical methods to investigate sources of variability. Table 4 shows the ANOVA (ANalysis Of VAriance) for replicated tests using PE1. The F-observed value of Table 4 is smaller than the F-critical value of 224.58 (based on a 5% significance level and (1, 4) degrees of freedom). This means that there is no statistically significant difference in variability between the results of the independently replicated tests. Therefore, the test procedure used does not contribute significantly to the variability of the measurements. Independent replicated tests on other resins also demonstrated that the test procedure does not contribute significant variability to the results. Therefore, the main source of variability in NCLT is from the material itself.

Table 4. ANOVA of independent replicated test results for PE1

	df	SS	MS	F
Same molded plate	4	2.527	0.632	94.33
Different molded plates	1	0.0067	0.0067	
Total	5	2.5337		

In the ASTM method (ASTM D5397) for NCLT, the notch depth is recommended to be at 20% of the thickness of the sample, but there is no recommendation for the applied level of stress. In the literature, various applied stresses are reported. Some take the approach of applying stress as a percentage of the yield strength of the material, while others use a constant stress level for different polymers. In order to clarify the effect that yield stress and notch depth have on the results of NCLT, experiments using a central composite design (29) were carried out. The design matrix of the experiment was given earlier in the Experimental section (Table 1).

PE1 was again the resin selected for this experiment because it has a reasonable NCLT failure time. The tensile strength at yield for PE1 is 27 MPa. Results from the experiments are presented in Table 5. Figure 6 is a contour plot of ESCR (in h) as a function of stress applied (percentage yield strength) and notch depth (percentage notch depth). The change in ESCR is larger with changes in stress level

Table 5. NCLT results for PE1 at different levels of notch depth and yield stress

(%) Notch depth	(%) Yield strength	ESCR (h)
20	10	167.8
20	25	1.9
50	10	87.9
50	25	1.3
19	15	32.0
61	15	7.0
40	4	300.0
40	26	1.6
40	15	6.0
40	15	6.1
60	23	2.2
60	37	0.4
46	30	0.4
74	30	1.8
60	30	1.4

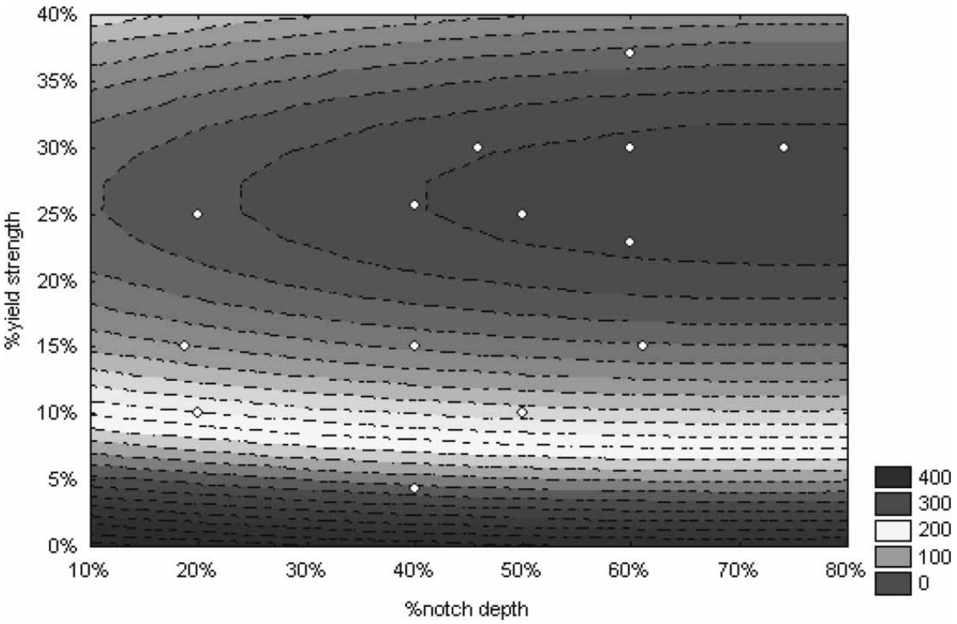

Fig. 6. Effect of % yield strength and % notch depth on NCLT results (h).

than with changes in notch depth. Observe the more closely packed contour lines in the decreasing yield strength (stress level) direction, an indication of steeper increase of ESCR values. This shows that NCLT results are more sensitive to changes in stress level than changes in notch depth. When the stress level is low, the effect of notch depth is rather small.

The contour plot of Fig. 6 is generated using an equation of the following form,

$$z = \beta_0 + \beta_1 x + \beta_2 y + \beta_3 x^2 + \beta_4 y^2 + \beta_5 xy + \varepsilon \qquad (2)$$

z - NCLT result, x - % notch depth, y - % yield stress, ε - error.

Analysis of variance carried out on Equation (2) above gives indications of the influence that each term has on the NCLT results. In Table 6, the linear and quadratic terms of % yield strength have the largest F values, which indicate that yield stress used has the greatest influence on NCLT results. The notch depth terms do not have an F value larger than the corresponding F-critical value of 5.32 (with (1, 8) degrees of freedom at 5% significance level), hence, they do not have a significant influence on NCLT results. There is also no significant interaction from the combined effect of percentage notch depth and percentage yield stress applied (xy term in Equation (2), 1L by 2L in Table 6). The ANOVA results indicate that the change from 20% notch depth to 40% notch depth has no significant effect on the NCLT results. At a stress level of 15% of the yield strength, Fig. 6 also shows that there is no significant change in NCLT values of samples with different notch depth. Therefore, the use of 40% notch depth does not alter the conclusions drawn on ESCR behavior of polyethylene. Hence, it was decided to adopt 15% of yield stress as the common test stress level (as a compromise), since this level gave consistent results for the wide range of different resins in this study. Since NCLT results are sensitive to the level of stress used, caution should be exercised when comparing test results from different sources.

Table 6. ANOVA of effect of yield strength and notch depth on NCLT results (h)

	SS	Df	MS	F
Test date (blocks)	742.0	1	742.0	0.422
Notch depth(1L[a])	1063.5	1	1063.5	0.605
Notch depth(Q[a])	124.9	1	124.9	0.071
%Yield strength (2L)	22172.0	1	22172.0	12.617
%Yield strength (Q)	20527.3	1	20527.3	11.681
1L by 2L	2.2	1	2.2	0.001
Error	14059.0	8	1757.4	
Total SS	101602.6	14		

[a] L-linear term, Q-quadratic term.

3.2 *Strain Hardening and ESCR of Resins*

NCLT is a time-consuming test method. As seen in the previous section, sample test times range from a few hours (h) to several thousands of hours. There is a great interest in the development of a faster test for classifying ESCR behavior of polymers (of course, in a reliable way). Tensile tests performed on "pre-strain-hardened" samples of polymer have shown promise in correlating ESCR to tensile properties of polyethylene (30, 31). Raman spectroscopy studies of polyethylene at the strain hardening stage have shown that the structures of cold drawn material just before failing and slow crack growth fibrils are very similar (4). Hence, strain hardening behavior can be related to ESCR of polyethylene. Recently, Kurelec et al. (25) proposed the use of strain hardening modulus obtained at 80°C as a possible correlation to ESCR values of polyethylene.

Since most PE applications are under ambient conditions, a method to test the ESCR of resins at room temperature would be practical. With this aim in mind, tensile constant strain rate tests were carried out at room temperature following the general guidelines of the standard tensile test (ASTM D638). Displacement of crosshead and the sample load were measured at constant strain rate. As compared to approaches where true stress and true strain measurements are needed (25, 32), this method does not require any special equipment and can be readily carried out on any tensile tester.

The elongation of sample was observed to follow the typical deformation behavior of a semi-crystalline polymer (Fig. 7). Load increases with increasing displacement until the yield point; then the load drops and the test sample undergoes ductile deformation at a relatively constant load value until strain hardening occurs and the load increases again with increasing displacement; finally, the sample breaks.

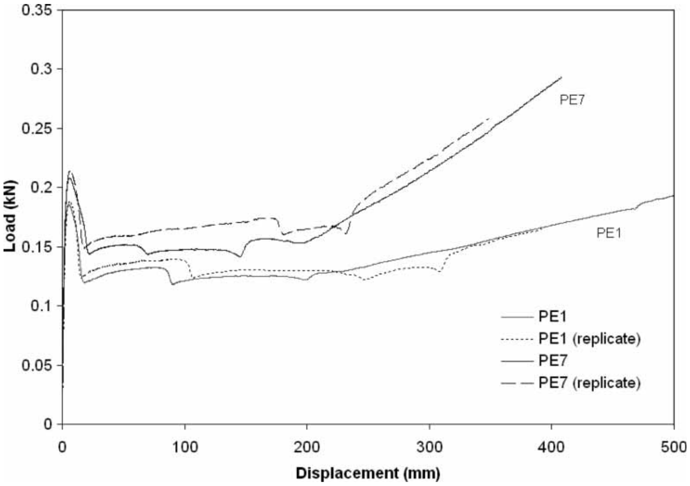

Fig. 7. Tensile elongation at constant strain rate of 0.5 mm/min.

Independent replicated tests were carried out for selected resins to investigate the reproducibility of the strain hardening test. In Fig. 7 replicates of PE1 and PE7 are shown. The load value for the strain hardening section of the graph for PE1 is the same for both samples. For PE7 there is a small difference in the load value of 4.3%. The results are well within the acceptable range, demonstrating good reproducibility of the strain hardening test. Detailed statistical analysis of the strain hardening test is presented later in section 3.5. Several resins (PE2, PE3, PE5 and PE6) could not be tested using the strain hardening test method. PE5 and 6 are brittle and break before full elongation can be achieved. PE2 and 3 did not achieve strain hardening even at maximum extension of the test apparatus. These resins are excluded from the subsequent discussion.

The rate of load increase in the strain hardening stage is faster for high MW material than for low MW material. This can be seen in the behavior of PE7 and PE1 in Fig. 7. The strain hardening section of the elongation curve is linear and well-defined. Therefore, a characteristic slope can be determined for each resin. This characteristic slope is a function of applied load over total sample displacement, which could be considered as a definition of "material stiffness" (19). This measurement is related to strain hardening modulus (25), thus, in order to distinguish it from the conventional definition of "stiffness" for a material (related to Young's modulus in the pre-yield section of the graph), we will call this characteristic slope the "hardening stiffness" (HS). The values of HS and ESCR for each resin tested are listed in Table 7.

In Fig. 8 the strain hardening section of the load-displacement graph (Fig. 7) for all resins is plotted and shifted to the same origin, in order to illustrate more clearly the differences between their slopes. The curves of resins with lower ESCR value have less of a steep slope in Fig. 8. PE80 grade resin (PE8) has lower ESCR/NCLT value than the PE100 resins (PE7, PE9 and PE10). The differences can be clearly seen in the slopes of the curves. For resins with similar ESCR values, such as PE7 and PE9, the strain hardening behavior is similar, which is well reflected by the overlap of the two curves in Fig. 8. The same trend is observed for PE1 and PE4, which also have similar ESCR values.

Table 7. Hardening stiffness (HS) and NDR of polyethylene

	Strain rate - 0.5 mm/min			Strain rate - 7 mm/min			
	Hardening stiffness (N/mm)	Coefficient of variation of HS	NDR	Hardening stiffness (N/mm)	Coefficient of variation of HS	NDR	ESCR (h)
PE4	0.183	0.08	9.3	0.287	0.13	10.5	3.6
PE1	0.250	0.08	7.2	0.527	0.003	8.6	4.8
PE8	0.578	0.02	7.0	0.730	0.11	6.3	198
PE9	0.609	N/A	6.4	0.895	0.03	7.1	872
PE7	0.657	N/A	6.1	0.940	0.02	7.1	1396
PE10	0.663	0.02	6.6	1.008	0.01	6.9	>3000

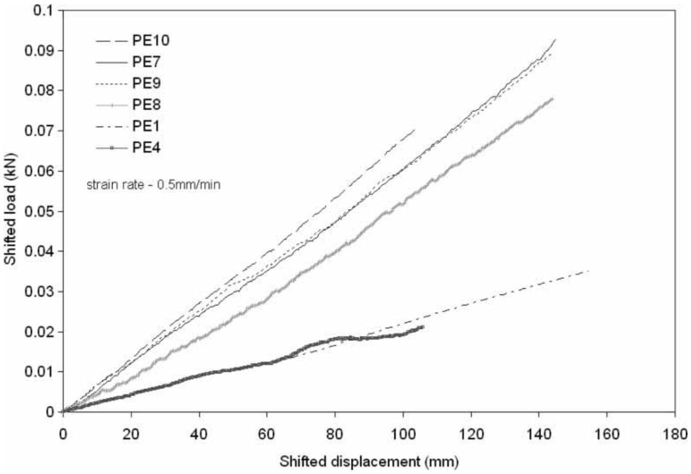

Fig. 8. Shifted load-displacement curves of the strain hardening stage; 0.5 mm/min strain rate.

The characteristic slope of curves in Fig. 8 gives the HS value for each resin. These values are cited in Table 7. In Fig. 9 the ESCR value of each resin (as log(ESCR)) is plotted against its hardening stiffness. The plot shows that the stiffer the material during strain hardening the higher its ESCR, and therefore, establishes that the hardening stiffness can be used as a measure of the ESCR of polyethylene. Although ESCR and strain hardening behavior are well correlated, the same can not be said for the correlation between ESCR and the yield point of a resin. For a discussion on this aside, see Appendix A.

3.3 *Natural Drawing Ratio (NDR) and ESCR*

An alternative tensile test measurement that has recently gained attention as a possible property to correlate to ESCR values of polymers is the natural drawing ratio (33, 34). NDR has been defined in Equation (1). The NDR values of resins in this study are listed in Table 7. ESCR of resins is plotted against NDR in Fig. 10. NDR appears to be inversely proportional to ESCR, which is in agreement with observations reported in the literature. Our test results show that resins with higher ESCR values, such as PE10, have smaller NDR. NDR is a function of the extensibility of the polymer network. As established earlier, resins with higher ESCR have more inter-lamellar linkages. A more entangled polymer network would have lower extensibility and hence, smaller NDR. Therefore, it should be possible to correlate low NDR to high ESCR.

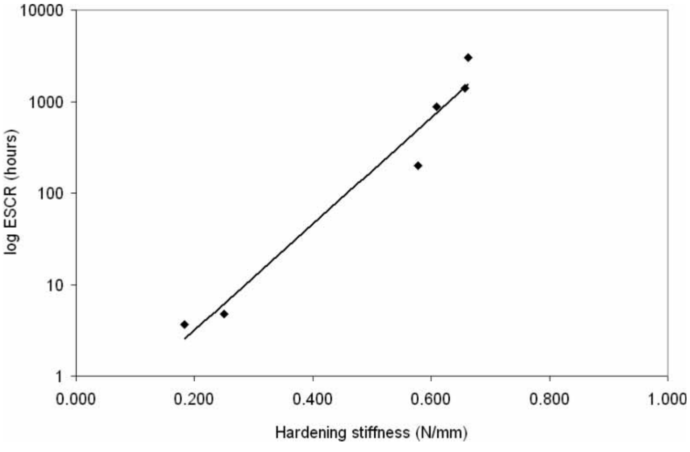

Fig. 9. Relation between ESCR and strain hardening stiffness of polyethylene at 0.5 mm/min strain rate.

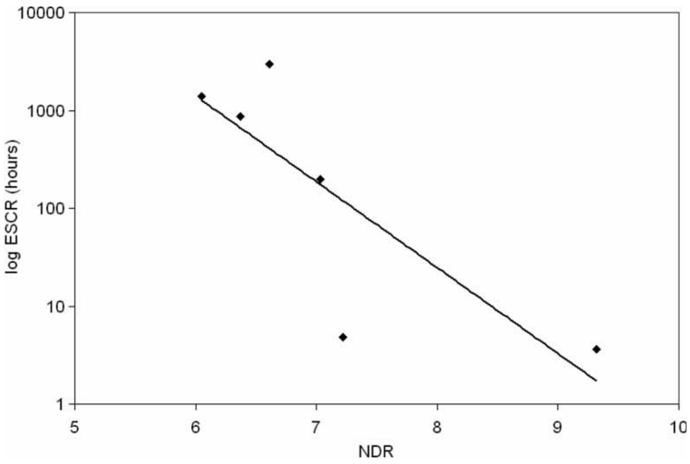

Fig. 10. Relationship between ESCR and NDR of polyethylene at 0.5 mm/min strain rate.

In Fig. 10, it can be seen that the data points are relatively scattered (compared to the points of Fig. 9). As shown in Fig. 7, the load-displacement curves of resins are not smooth in the necking section (for example, observe curves in the displacement range of 50 mm to 150 mm). This is because the deformation is not uniform during the necking stage. Once full extension of the dogbone is realized, at the onset of strain hardening, the material deformation becomes uniform and the load-displacement curve is relatively smooth. The fluctuations in the steady elongation section of the load-displacement curve make the determination of the onset of strain hardening difficult (in agreement again with observations of Appendix A), thus effectively resulting in the increased scatter of NDR data.

3.4 *Effect of Strain Rate*

The reason for developing a tensile test as an indicator of ESCR of polyethylene is because NCLT can be time consuming (and rather imprecise). Therefore, it is worth considering a tensile test at a high strain rate. Previous work done by Kurelec et al. was carried out at a 10 mm/min strain rate at 80°C (25). The reason for conducting the test at an elevated temperature was because of the lack of sensitivity in detecting differences in materials at high strain rate and lower temperature. In their opinion, testing at room temperature might be possible (i.e., reliable) if the strain rate is lowered to 0.25 mm/min.

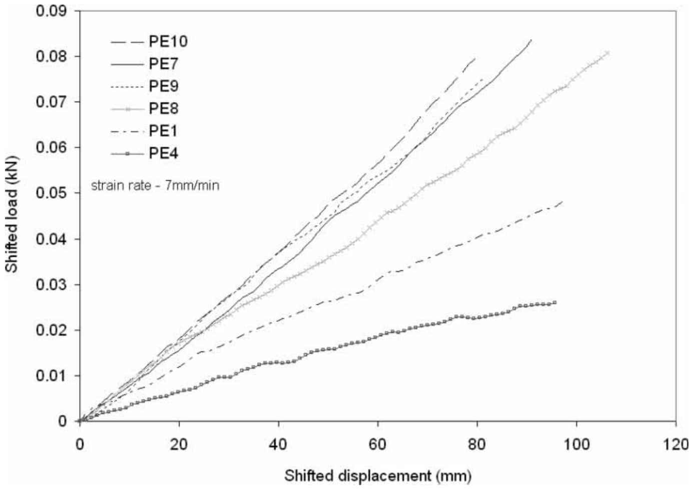

Fig. 11. Shifted load-displacement curves of polyethylene; 7 mm/min strain rate.

Since increasing the speed of testing is one of the motivations for exploring tensile testing as a method for determination of ESCR of polyethylene, we subsequently investigated the use of higher strain rates at room temperature. The highest strain rate tried was 7 mm/min. In Fig. 11, the shifted load-displacement curves for samples tested at 7 mm/min are shown. At 7 mm/min, resins exhibit curves with larger slopes compared to the tests done at 0.5 mm/min (compare Figures 8 and 11, and entries of Table 7). The difference between PE100-grade resins, PE80-grade resin and other types of HDPE was more pronounced at the higher strain rate. Within the PE100 resins, PE7 and PE9 curves showed similar slopes, as before.

Let's consider again the values of strain hardening stiffness (HS) and NDR for 7 mm/min strain rate as listed in Table 7. The differences in HS values of the resins can be clearly seen. In Fig. 12, ESCR values are plotted versus hardening stiffness values at 7 mm/min and 0.5 mm/min. The trend in hardening stiffness at 7 mm/min strain rate is the same as tests done at 0.5 mm/min. Higher hardening stiffness values are associated with higher ESCR values. At the higher strain rate, resins show higher hardening stiffness values (the curve for 7 mm/min is shifted to the right of the 0.5 mm/min curve). The difference between ESCR of resins is able to be detected equally well using both strain rates at room temperature. The 7 mm/min strain rate is comparable in magnitude to the 10 mm/min strain rate used by Kurelec et al. at 80°C (25). Therefore, this demonstrates that it is possible to carry out reliable strain hardening tests using a relatively high strain rate (in order to minimize the duration of the test) even at room temperature conditions.

The NDR values do not seem to be affected by the difference in strain rates as much as the strain hardening stiffness. In Fig. 13 the NDR values at 0.5 mm/min and 7 mm/min strain rate overlap with each other (with slightly more scatter than the hardening stiffness data). The same issue related to the determination of the onset of strain hardening point persists in tests run at 7 mm/min strain rate as well. NDR is related to the extensibility of the polymer network, and hence the speed of the extension should not have much effect. The results show that NDR can be used as a strain rate-independent indicator of the ESCR trends of a polymer, albeit with some caution due to the noisier nature of the NDR correlation with ESCR data.

3.5 *Reproducibility of Strain Hardening Test*

One of the main issues of the NCLT method is the large variability associated with its test results. As mentioned in section 3.1, the coefficient of variation for NCLT can be as high as 0.5. Therefore, before the strain hardening test can be proposed as a good indicator of ESCR, better reproducibility than NCLT must be demonstrated. If the test method has large variability, then the difference between materials would become hard to detect. Repeats and independent replicate

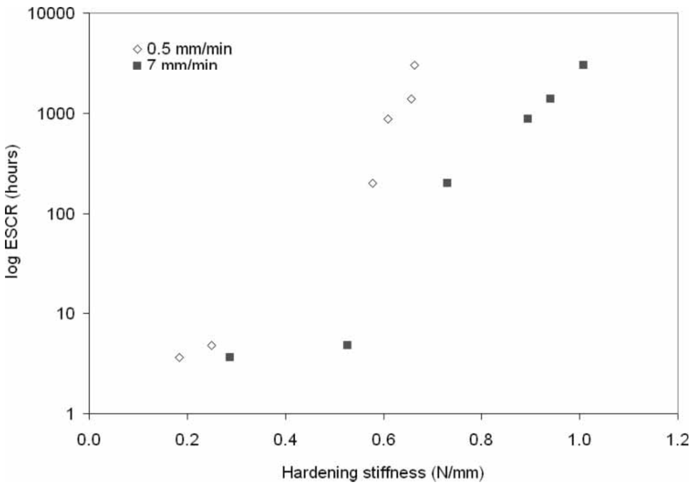

Fig. 12. ESCR vs. hardening stiffness at different strain rates.

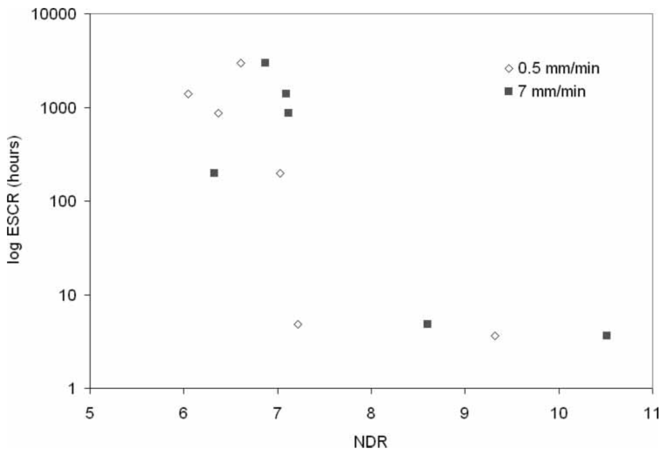

Fig. 13. ESCR vs. NDR at different strain rates.

tests were carried out to investigate the variability (and sensitivity) of the strain hardening test.

The coefficient of variation for hardening stiffness measurements listed in Table 7 ranged from 0.003–0.13. The average coefficient of variation for both 0.5 mm/min and 7 mm/min strain rates is 0.05. HS values have smaller coefficient of variation than NCLT results, for which the smallest value is 0.09 and the average value is 0.20 (Table 3). The smaller coefficients of variation show that the strain hardening test is more precise than the NCLT.

Once again, independently replicated tests were carried out to determine the contribution of variability by the test procedure, for the strain hardening test. In Table 8, results from ANOVA analysis of PE8 are presented. The F-observed value is smaller than the F-critical value of 10.13 (5% significance level and (1, 3) degrees of freedom), which indicates that the test procedure does not contribute significant variability to the measurements.

It has been shown above that the variability of the hardening stiffness measurement is relatively small. To verify that there are true differences between the HS measurements (and hence, to demonstrate that the HS measurements can truly detect differences in ESCR between resins), we employ again the analysis of variance technique. In Table 9, ten samples tested at 0.5 mm/min were analyzed. The results show that the F-observed value (187.57) is larger than the F-critical value (6.26) at 5% significance level and (5, 4) degrees of freedom. This means that there are true differences between the measurements for the resins and these can be detected by (are reflected in the values of) H. The same analysis is repeated for the 7 mm/min strain rate results with 19 samples (Table 10). The F-observed value (86.54) is larger than the F-critical value of 3.03 at 5% significance level and (5, 13) degrees of freedom, which indicates again true differences exist between resins. Based on these analyses we conclude that the strain hardening test is indeed sensitive to material differences at both 0.5 mm/min and 7 mm/min strain rates at room temperature.

Table 8. ANOVA of PE8 at 7 mm/min strain rate

	df	SS	MS	F
Samples from different plates	1	0.0131	0.0131	2.259
Samples from same plate	3	0.0174	0.0058	
Total	4	0.0305		

Table 9. ANOVA of hardening stiffness values at 0.5 mm/min strain rate

	df	SS	MS	F
Different resins	5	0.4126	0.08253	187.57
Same resin	4	0.0018	0.00044	
Total	9	0.4144		

Table 10. ANOVA of hardening stiffness values at 7 mm/min strain rate

	df	SS	MS	F
Different resins	5	1.3198	0.26395	86.54
Same resin	13	0.0396	0.00305	
Total	18	1.3594		

4 Conclusions

In this work, it is shown that strain hardening stiffness can be reliably correlated to ESCR of resins. The strain hardening test method proposed in this paper is an improvement on work presented by Kurelec et al. (25), because hardening stiffness values can be calculated from simpler load-displacement measurements made under ambient conditions, which eliminates the need for the specialized equipment required to measure true stress and true strain and maintain sample temperature. Kurelec et al. (25) suggested that to conduct strain hardening tests at room temperature is only possible at low strain rates of 0.25 mm/min. We showed that the strain hardening test can be extended to detect differences in ESCR of resins even at high strain rates of up to at least 7 mm/min (thus reducing the duration of the test). Strain rate of 7 mm/min is comparable in magnitude to the 10 mm/min strain rate (at 80°C) used by Kurelec et al. (25). This provides for much faster and reliable and reproducible results at room temperature than previously reported.

The measurements of ESCR of high density polyethylene resins via NCLT and strain hardening methods were compared in our work (Table 11) using statistical analysis of several independent replicates. In the entries of Table 11, a "No" means failure to record a measurement. This is due to the nature of the resin/specimen tested and in no way a limitation of the test. Of the two methods, the strain hardening method was preferred as it was demonstrated to be a faster technique, which could potentially decrease analysis time by up to hundred-fold. In addition, the strain hardening test is much simpler to perform than NCLT as there is no need for sample notching, or a temperature-controlled and concentration-controlled bath. For any good analytical method, efficiency is not the only requirement; good precision and reproducibility are also needed. Statistical analysis of the test results showed that the strain hardening test is more precise than NCLT. For the strain hardening test the average coefficient of variation is 0.05, which is a significant improvement compared to that of NCLT, which has an average coefficient of variation of 0.20. Therefore, it has been demonstrated that the strain hardening method proposed herein is a simple, precise, reproducible and hence a more practical way to classify ESCR of high density polyethylene.

Table 11. Resins tested with NCLT and strain hardening test (summary)

Resin	NCLT	Strain hardening test	Comments
PE1	Yes	Yes	
PE2	Yes	No	Could not reach strain hardening at low strain rate. At high strain rate, specimen failed before fully elongated.
PE3	Yes	No	Could not reach strain hardening at low strain rate. At high strain rate, specimen failed before fully elongated.
PE4	Yes	Yes	
PE5	No	No	Material brittle and can not be "notched" for NCLT. Strain hardening test failure occurs before specimen being fully extended at all strain rates.
PE6	No	No	Material brittle and can not be "notched" for NCLT. Strain hardening test failure occurs before specimen being fully extended at all strain rates.
PE7	Yes	Yes	
PE8	Yes	Yes	
PE9	Yes	Yes	
PE10	Yes	Yes	

5 Appendix A: Yield point and ESCR

In contrast to the good correlation between ESCR values and strain hardening behavior (see Figures 8 and 9), the behavior at the yield point during tensile tests did not show any correlation to the ESCR of resins. In Fig. A1 the load-displacement curves of the initial stages of ductile deformation are shown (see Fig. 7, magnification of area below 50 mm displacement). Neither the yield load nor the point of onset of steady elongation offers any correlation to the resin ESCR value. During the strain hardening stage, the roles of inter-lamellar linkages are emphasized. Since chain entanglements and tie-molecules do not play a major role in the initial stage of ductile deformation, no correlation between ESCR and tensile yield behavior of polyethylene can be made.

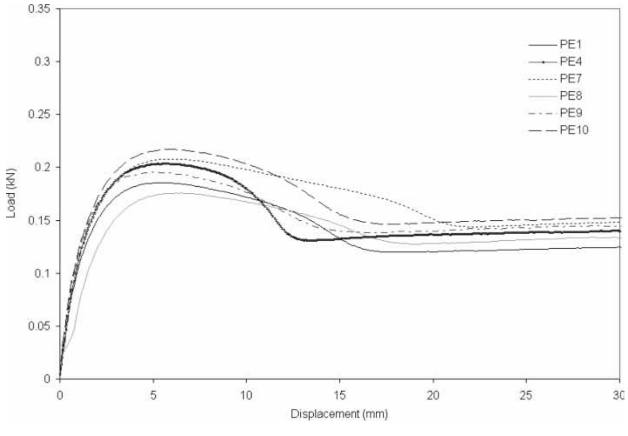

Fig. A1. Tensile elongation curves at yield point, 0.5 mm/min strain rate.

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