

Strain hardening test on the limits of Slow Crack Growth evaluation in high resistance polyethylene resins: Effect of comonomer type

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ABSTRACT

Long term performance assessment of polyethylene pipes is an issue that has greatly increased in importance in recent years due to the incorporation in the market of high resistance to crack polyethylene grades (PE100RC), where established Slow Crack Growth (SCG) evaluation using traditional tests such as Full Notch Creep Test (FNCT) or Pennsylvania Notch Tensile (PENT) Test is insufficient. The development in recent years of fast evaluation techniques such as Strain Hardening (SH) modulus has opened an important alternative for quick SCG evaluation since it correlates well with other conventional tests such as FNCT and PENT. In this work, a large number of commercial and experimental polyethylene pipe resins with different comonomer types were evaluated in order to define their SH values to rank the resins as PE100 or PE100RC. A relationship is proposed that utilizes SH test results to estimate the SCG resistance of PE pipes. 1-Butene copolymer resins display threshold SH values of 38 and 53 MPa that have been assigned to PE100 and 100RC grades, respectively. Moreover, dependence of the SH values on comonomer type used has been demonstrated. The experimental results show that 1-hexene copolymer resins exhibit higher SH values than 1-butene comonomer based resins.

1. Introduction

Slow Crack Growth (SCG) is one of the most critical mechanical properties that must be controlled and evaluated to assess the long-term performance of polyethylene resins. After a time at a point of stress concentration, polyethylene pipes suffer specific brittle failure that starts with craze formation that progressively propagates to lead finally to material failure [1,2]. With the introduction during the nineties of bimodal polyethylene resins with a comonomer distribution located in the high molecular weight region and, in particular, during recent years with the inclusion of the fourth generation polyethylene resins with high resistance to cracking, designated PE100RC, the prediction of SCG performance of PE resins has gained considerable interest [3,4]. Moreover, SCG determination using traditional tests such as Full Notch Creep Tests (FNCT) [5] or Pennsylvania Notched Tensile Test (PENT) [6–8] is very time-consuming, typically requiring one year or more [9].

In order to reduce the long failure times, different accelerated test methods have been developed in recent decades. Some are based on the search for more constraining physical settings, in particular, loading, temperature and environmental conditions that significantly accelerate

the failure process and reduce the test time by between six and twenty times [10–13]. The main drawback of these accelerated methodologies lies in whether or not real crazing and stress cracking control the failure process, i.e. if SCG is the main failure mechanism that is taking place in the PE resin.

Other accelerated tests, based on alternative methods, have gained extraordinary importance in recent years [14–17]. Thus, tests on plaques such as Strain Hardening (SH) modulus (ISO 18488) [18] or the Cracked Round Bar (CRB) test, a fatigue test that has been standardized by ISO 18489 [19], are really good alternatives that correlate well with conventional direct tests like FNCT or PENT. The advantages claimed for SH tests are the small amount of plastic consumed and the outstandingly short test time required, together with the nonalignment with any intrinsic material property, such as the molecular structure, molecular weight, comonomer type or polymerization process [20]. However, a few works have reported that the SH measurements are influenced by the comonomer type present in the PE resin [9,21,22].

The main aim of this work, apart from evaluating and confirming the SH test as a good alternative to traditional tests, is to analyse the possible comonomer type effect on the SH performance. At a crucial time when

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the threshold values (for PE100 and PE100RC resins) for the different accelerated tests are under discussion, this work attempts to shed more light on the subject.

2. Experimental

2.1. Materials

This work studied a large number of commercial and experimental polyethylene grades from blow moulding to high resistance pipe grades. There were three different sets of resins: (i) commercial ethylene-1-butene copolymers based on a Ziegler–Natta catalyst, (ii) commercial ethylene-1-hexene copolymers based on a chromium catalyst, and (iii) experimental homopolymers, ethylene-1-butene and ethylene-1-hexene copolymers synthesized with a Ziegler–Natta catalyst, as well as bimodal blends of both types. The experimental polymerizations were carried out at 85 °C with stirring in a 2.0-L glass reactor filled with 1 L of n-heptane (99%, Scharlab) as diluent and 0.5 mL of triethylaluminum (TEA, 93%, Sigma-Aldrich) as scavenger. Ethylene (99.99%, Air Liquide) was deoxygenated and dried through columns containing R-3/15 BASF catalyst, and alumina and 3 Å molecular sieves. Comonomers, 1-butene and 1-hexene were added in amounts varying from 10 to 100 mL at the beginning of the polymerization, as well as hydrogen when necessary. The flow rate needed to keep a constant pressure of 8.5 bar during the polymerization was measured with a mass-flow indicator (Bronkhorst Hi-Tec). After 60 min, the polymerization was stopped by depressurization and quenching with acidified (HCl) methanol. Finally, the polymer obtained was separated by filtration and dried under atmospheric pressure at 70 °C.

2.2. Pennsylvania edge-notch tensile (PENT) tests

An Instron 3800 Series PENT tester was used to perform tests according to ASTM F1473. 10 mm thick plaques were compression moulded in a hydraulic press at 180 °C and a nominal pressure of 200 bar. Afterwards, they were cooled slowly for 5 h at a rate of approximately 0.5 °C/min until reaching room temperature. During the cooling stage, the pressure was decreased naturally. Subsequently, 50 × 25 × 10 mm specimens were machined from the plaques, followed by notches slowly pressed into the specimen by a razor blade at a speed of about 200 µm/min. Side notches of 1.0 mm and a front notch of 3.5 mm were made according to the ASTM F1473 requirements. Under the standard PENT conditions, specimens were exposed to a constant load of 2.4 MPa at a temperature of 80 °C.

2.3. Full Notch Creep Test (FNCT)

FNCT was carried out with an IPT tensile creep tester following the standard conditions defined in ISO16770 using a 2% Arkopal N100 solution at 80 °C and 4 MPa. 10 mm plaques were compression moulded at 180 °C and 100 bar, and then slowly cooled at 2 °C/min to room temperature. 100 × 10 × 10 mm specimens were machined from the plaques and 1.0 mm coplanar notches were introduced at the centre of each face using a notching machine. After the tests, the fracture surfaces of the specimens were examined using optical microscopy and Environmental Scanning Electron Microscopy (ESEM) to ensure that brittle failure governed the SCG process.

2.4. Strain hardening modulus determination

The strain hardening modulus is easily determined from a simple uniaxial tensile test at 80 °C, and was performed according to ISO 18488 using a universal test machine (INSTRON 5565) with a 500 N load cell and a video extensometer (INSTRON 2663-822) to measure the elongation. The samples were compression moulded to a form a sheet with a hydraulic press at 180 °C, nominal pressure of 200 bar and cooling rate

of 15 °C/min, as per ISO 1872-2. After pressing, the samples were annealed for 1 h at 120 °C and then slowly cooled to room temperature. Dumbbell shaped specimens were punched from the pressed sheets. In accordance with ISO 18488, the strain rate was 20 mm/min, the initial distance between the gauge marks on the centre of the test specimen was 12.5 ± 0.1 mm, and the thickness was 0.30 + 0.05/-0.03 mm. The laboratory device used to measure the thickness had the required accuracy (0.005 mm).

2.5. Molecular weight and short chain branching characterization

Molecular weight distribution (MWD) and short chain branching distribution (SCBD) were characterized using a high temperature gel permeation chromatograph, GPC-IR5 (Polymer Char). This equipment has a special set of columns and an infrared detector to determine on-line concentration and composition which is capable of distinguishing differences of 1 branch per 1000 atoms of carbon. Sample solutions at a concentration of 0.75 mg/mL in 1,2,4 trichlorobenzene (TCB), stabilized with BHT (2,6-di-tert-butyl-4-methylphenol), were obtained by gentle stirring at 150 °C for 2 h. Analyses were performed at a flow rate of 1 mL/min and a temperature of 160 °C.

A Chemical Composition Distribution curve (CCD) was determined using a Temperature Rising Elution Fractionation (TREF) instrument, model 200+ (Polymer Char), equipped with an infrared concentration detector. Samples were dissolved in 1,2,4 TCB at a concentration of 4 mg/mL at 150 °C for 60 min. Then, solutions were cooled and stabilized at 130 °C for 45 min. Afterwards, temperature was decreased from 130 to 35 °C at a rate of 5 °C/min. Polymer elution was carried out from 35 to 140 °C at a rate of 1 °C/min with TCB flowing through the column at a constant flow rate of 0.5 ml/min.

3. Results and discussion

3.1. Limits to the SCG evaluation by direct methods

The traditional tests can have some limits when measuring the performance of high resistant to crack resins that could mask correct analysis and give misleading resin classifications. In previous work, an extruder blend system composed of a metallocene catalyst-based linear low-density ethylene-1-hexene copolymer (LLDPE) and an iron catalyst-based high-density polyethylene (HDPE) homopolymer was analyzed, concluding that PENT failure resistance grows exponentially with the copolymer content up to 70% [4]. Using such an empirical model and predictions based on the PSP2 parameter [23], 8000 h of PENT resistance is expected for resins with 75% LLDPE content. Contrary to expectations, the experimental results show that the SCG resistance for such resins is 21,000 h (around three times over the expected result), which would correspond to a PE100RC grade resin.

Fig. 1 shows the fracture surface and Crack Opening Displacement (COD) evaluation when the PENT test was conducted for resins with 70 and 75% copolymer content (samples A and B, respectively) [4]. The analysis of the fracture surface determined by ESEM measurements and COD curves shows several differences between samples. The ESEM micrograph of sample A shows fibrillated morphology, which indicates a clear brittle regime SCG process. Correspondingly, the COD curve clearly displays an initial craze formation region, and the point where a crack develops matches with the first plateau of the COD curve, with subsequent growth to the final failure. The ESEM micrograph of sample B shows a similar fibrillar morphology, but a region with a very smooth morphology is also observed at the beginning of the micrograph. This indicates the occurrence of yielding and, therefore, a well-defined initial blunting process that makes the subsequent craze nucleation difficult, hence delaying the SCG process. This blunting process is well correlated with the COD curve, where sample B (red curve) is significantly above sample A (black curve), which indicates a higher creep mechanism for this resin. This phenomenon inevitably delays or arrests the normal

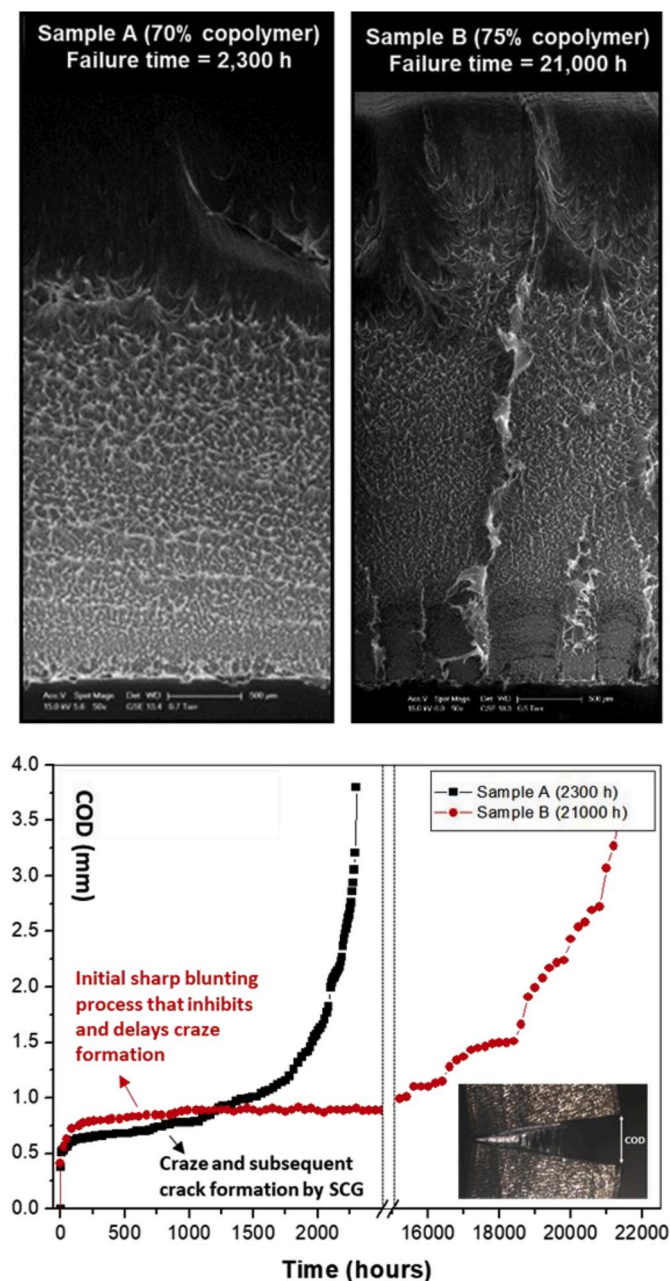


Fig. 1. ESEM micrographs showing the fracture surfaces and COD curves after PENT tests (ASTM F1473).

craze formation and later crack growth, leading to longer failure times and over-estimated SCG resistance and misleading conclusions. This failure time deviation demonstrates that thermal ageing of the resin becomes critical and even partially controls the mode of failure.

Table 1 summarizes the characterization of a series of high resistance polyethylene pipe materials, two bimodal 1-butene Ziegler-Natta and two multimodal 1-hexene Chromium resins [3]. Such specimens all

Table 1
Physico-chemical characterization of a series of high SCG resistance commercial PE pipe resins.

Material	Catalyst	Comonomer	Density (kg/m ³)	M _w (kg/mol)	M _w /M _n (-)	SCB/1000C	PENT (hours)	FNCT (hours)	SH <G _p > (MPa)
PEAD1	Z-Natta	1-butene	955.3	260	30	2.7	>12,000	>8760	52.0
PEAD2	Z-Natta	1-butene	957.0	290	26	3.4	>12,000	>8760	53.5
PEAD3	Chromium	1-hexene	957.4	430	68	2.1	>12,000	7500	57.6
PEAD4	Chromium	1-hexene	955.0	462	79	1.9	>12,000	>8760	64.0

show PENT failure times higher than 12,000 h, i.e. typical values for high crack resistance resins. At these high failure times, the thermal degradation process can lead to erroneous determination of the SCG resistance. To overcome this drawback, another established test, FNCT, was performed to evaluate the SCG performance of these resins. Excepting PEAD3 resin, all samples show values higher than 8760 h, typical of PE100RC grades. These values are lower than those of the PENT test, but again too high to avoid the inconvenience of long performance tests. Moreover, as previously mentioned, the yielding phenomenon can also appear and, therefore, other more reliable tests to predict the SCG performance are necessary to correctly classify the resins.

Among alternative tests, SH has gained great attention in recent years due to the claim that it is a good short-term predictor of SCG performance. Table 1 also shows the SH values for these resins where significant differences can be observed. High resistance Chromium 1-hexene resins have higher SH values than the Ziegler-Natta 1-butene ones. Up to now, SH modulus was considered an intrinsic material property with wide application areas, showing good correlation with ESCR tests independent of molecular weight distribution, comonomer type or polymerization process [20]. However, in recent years, several authors have reported data supporting the conclusion that the comonomer nature can influence the SH values [9,21,22]. In this sense, it is interesting to note how PEAD3 resin, with a higher SH value than PEAD1 and PEAD2, has a FNCT value significantly lower than those resins. This result suggests a possible influence of the type of comonomer on the SH value.

3.2. Comonomer influence on strain hardening modulus determination

To confirm the previous results, and in order to analyse possible different trends of SH values as a function of comonomer type and molecular architecture, in this section, an important number of commercial bimodal Ziegler-Natta 1-butene and monomodal Chromium 1-hexene resins from blow moulding to PE100 and PE100RC grades were tested using SH, PENT and FNCT tests. The main aim of this study is to find a calibration curve that allows accurate prediction of the PENT and FNCT failure times based on SH determination and, likewise, a threshold value that identifies PE100 or PE100RC resins, allowing resins to be ranked based on the SH measurements.

As is well-known, the PENT (ASTM F1473 – ISO 16241), and FNCT (ISO 16770) tests are the most common direct methodologies for evaluating SCG resistance on compression moulded resins. Thus, first of all, PENT and FNCT values were correlated for all the resins, and the results are shown in Fig. 2. It can be seen from Fig. 2 that the PENT time correlates well with the FNCT. The minimum value of failure time for a PE100RC material is well defined in PAS 1075 [24] and implies a FNCT failure time higher than 8760 h. In the case of the PENT test, this failure time is not defined, but it is easily estimated with the fitted equation to be around 22,000 h. As mentioned above, this long-term test performance could favor thermal aging becoming the driving force and producing misleading results.

Figs. 3 and 4 show the FNCT and PENT failure times expressed as a function of the SH values for the commercial Ziegler-Natta and Chromium resins. Both, the FNCT and PENT results correlate very well with the SH. However, some important differences are seen. The first is that, at low SCG resistance and low SH values, the FNCT and PENT values are

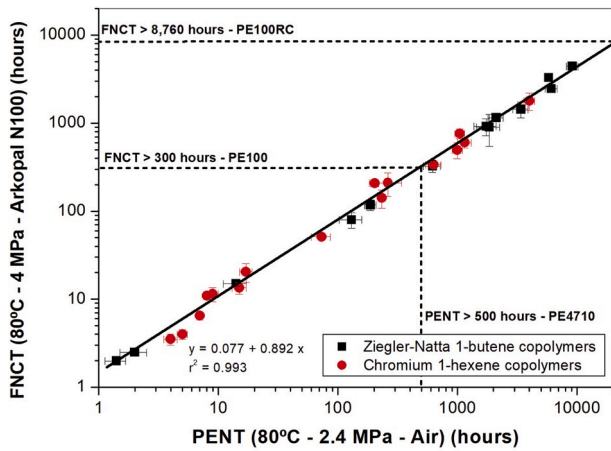


Fig. 2. Standard FNCT (80 °C, 4 MPa, 2% Arkopal N100) versus PENT test (80 °C, 2.4 MPa, Air).

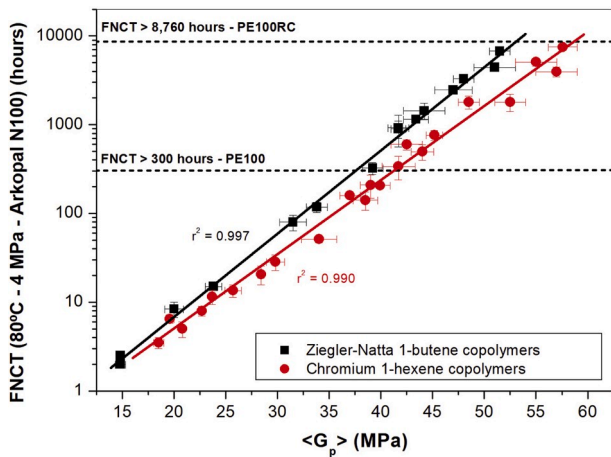


Fig. 3. FNCT failure time vs SH value. Ziegler-Natta (1-butene resins) and Chromium (1-hexene resins).

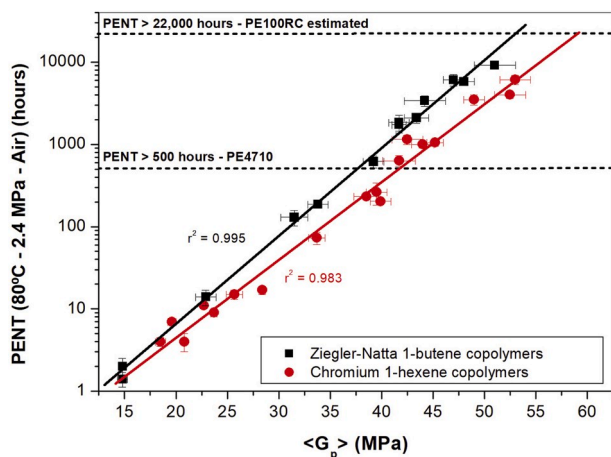


Fig. 4. PENT failure time vs SH value. Ziegler-Natta (1-butene resins) and Chromium (1-hexene resins).

almost coincident, independently of the comonomer type used. Nevertheless, at higher SCG resistance (FNCT and PENT tests), more deviation of the SH values is seen. This means that, if two resins with the same FNCT or PENT resistance but different comonomer types are analyzed,

the SH value is higher for the 1-hexene compared to the 1-butene copolymer resin. Therefore, the obvious question is to ask what is the reason for this different slope.

Fig. 5 shows the molecular weight distribution (MWD) and short chain branching distribution (SCBD), determined by GPC, and the chemical composition distribution (CCD), ascertained by TREF, for the Ziegler-Natta 1-butene and the Chromium 1-hexene commercial copolymers. It is noted that the Ziegler-Natta based resins display clear bimodality, as expected, in comparison with the unimodality for Chromium-based resins. This result indicates that the short chain branching (SCB) content for the Ziegler-Natta system was preferentially located in the highest molecular chains, opposite to the Chromium system. It is well known that SCG resistance can be greatly enhanced if the SCBs are preferentially placed in the higher molecular weight chains [25–27]. The CCD distribution shows clear differences between branching and linear segments in the 1-hexene resin in comparison to 1-butene comonomer-based resins. These results indicate that methyl branches of 1-butene comonomer could be partially incorporated into the crystalline phase, while butyl branches of 1-hexene are preferentially excluded from crystalline regions [28]. Thus, the higher occurrence of co-crystallization mechanisms in 1-butene compared with 1-hexene comonomers leads to a more homogeneous and efficient crystal-tie molecules network, with the subsequent increment of the SCG resistance (PENT and FNCT tests). Likewise, the SH test also depends on the total amount of tie molecules and entanglements, but it is less sensitive than traditional SCG tests to how these bridge molecules are distributed in the network, as further explained. SCG resistance,

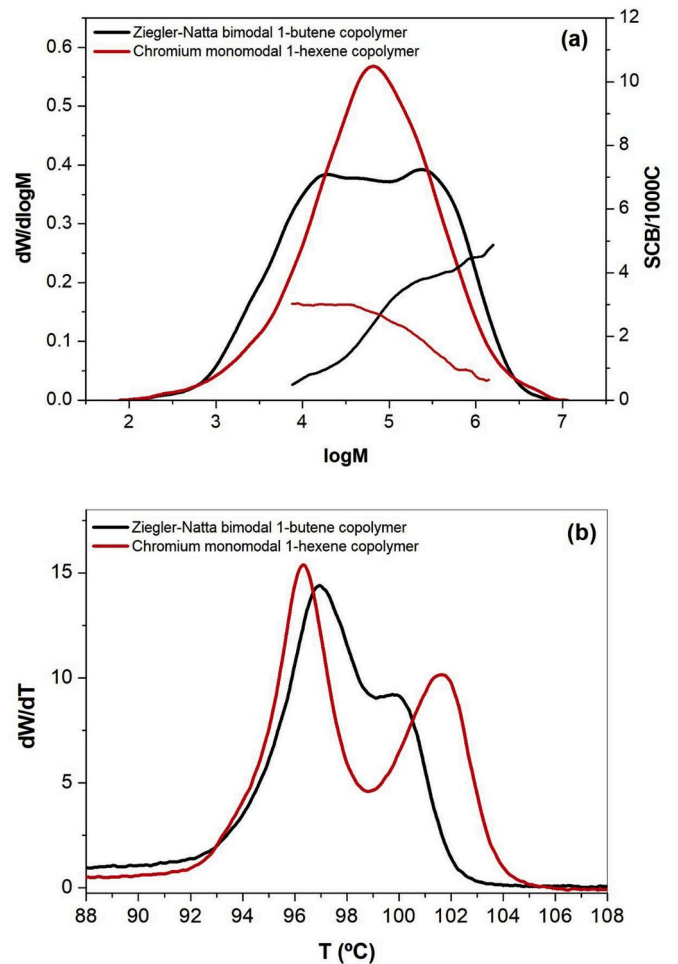


Fig. 5. MWD and SCB distribution determined by GPC (a) and CCD distribution determined by TREF (b) for a Ziegler-Natta and Chromium-based resins.

measured by traditional tests (PENT or FNCT), is a process directly controlled by loops and tie molecules disentanglement. Based on our and other previous studies [4,26,29,30], it is proved that a homogeneous distribution of these tie molecules improves the SCG resistance, inhibiting or delaying the craze formation and subsequent crack growth, suggesting that the influence of the tie molecules and molecular entanglements comes from a microscopic level; its density and distribution throughout the network both being important. In the case of the SH test, the SCG measurement also depends on both tie molecules and molecular entanglements, but this test is not as sensitive to where they are distributed in the network as direct traditional SCG tests, in which the SCG resistance is determined under very little deformation of the sample. In contrast, SH values are obtained from the modulus calculated from the last part of the stress-strain curve where the specimen is highly deformed and oriented. Therefore, the number of links and molecular entanglements represent key variables to calculate the SH values, and their effect is remarkably higher than the homogeneity of the distribution of these unions and bridges that rule out the SCG resistance determined by traditional tests. Both effects are the responsible for the different slopes found in Figs. 3 and 4.

To verify and evaluate the influence of the comonomer type on the SH value, a series of homopolymer and copolymer resins were synthesized following the procedure described in the experimental section. Resins with molecular weight values between 100,000 g/mol to 1,000,000 g/mol were explored and, in the case of 1-butene and 1-hexene comonomer, resins with 3.0–4.0 SCB/1000C were used in order to eliminate the comonomer content as a variable. Fig. 6 shows the SH values as a function of molecular weight for each system. Materials with SH value above 80 MPa have draw ratios below 9. In these cases, the SH value was evaluated as the slope measured in the last part of the curve in the interval of one unit of lambda. Although ISO 18488 specifies that test pieces that break below 8.5 must be rejected, the SH value was estimated following the above procedure. In general, the increment in molecular weight values promotes enhancement of the SH result according to a non-linear fit. Fig. 6 also shows that the different resin systems exhibit distinct critical molecular weights, from which the SH values start to grow. These values are significantly lower for copolymer than for homopolymer resins. These critical molecular weight values are directly related to the molecular entanglements, which are responsible for the enhancement of the SCG resistance and SH values [31]. It is reported and accepted that, for ethylene-hexene copolymer resins, the SCG resistance significantly increases when the critical molecular weight reaches 150,000 g/mol [32]. This value matches well with the experimentally observed results. Based on the data shown in Fig. 6 for the

synthesized ethylene-hexene copolymers, the critical molecular weight value from which the SH values grow is around 150,000 g/mol, and hence the same as predicted by the PENT test.

Moreover, and confirming the comonomer influence on SH modulus determination, it is clear from Fig. 6 that, for the same molecular weight, the SH values are significantly higher when 1-hexene instead of 1-butene is used as comonomer. Deveci et al. also recently noted this different trend for a series of experimental ethylene 1-butene and 1-hexene bimodal copolymer resins [21]. The reason of this difference could be the higher amount of entanglements and tie molecule density that 1-hexene comonomer produces [33]. In comparison to 1-butene, 1-hexene comonomer reduces the formation of a crystalline region and lowers the crystal thickness, which implies a lower lamellar thickness and critical distance L . Therefore, the amount of bridge or tie molecules that are able to attach the different lamellae is larger in comparison to 1-butene copolymers [4,30,34]. Furthermore, 1-hexene copolymer promotes an increment in the number of entanglements due to the reduction of the molecular weight between entanglements [35,36]. This analysis suggests that the higher amount of entanglements in 1-hexene compared with 1-butene copolymers affects the SH values much more than SCG values obtained from PENT or FNCT. As previously commented, a likely explanation lies in the fact that SH is measured once the polymer specimen is totally strained and highly oriented, and an increment of the molecular entanglements and tie molecules yields to higher SH values. These entanglements are obviously relevant in the SCG resistance measured by traditional FNCT or PENT tests, but their influence is much lower than that of the homogeneous and efficient crystal-tie molecules network.

It was not possible to perform the SCG test on the copolymer resins shown in Fig. 6 because the low density of the copolymers could produce an initial blunting process at the tip of the notch, with consequent inhibition of craze formation. According to previous experience of our research group, polyethylene resins with density values below 939 kg/m³ cannot be correctly evaluated through the PENT test.

In order to shed more light on the previous results and to study the influence of comonomer type, not only on the SH value but also on SCG performance of the resin, 12 bimodal blends were prepared using the low molecular weight homopolymers and different high molecular weight (400,000–800,000 g/mol) copolymers shown in Fig. 6. Blends were prepared using a rheometer mixer Haake Rheocord 9000 at 160 °C and 40 rpm for 10 min in order to ensure intimate mixing of the blend components. Table 2 shows the resin properties from the experimental blends. As expected, as the molecular weight or short chain branching content increases, the PENT failure time and SH values also increase due to the higher amount of tie chains and molecular entanglements in the resin. However, as previously indicated and Fig. 7 confirms, the increment in SH values is different depending on the comonomer type used. This behavior, previously observed in the commercial resins, continues to occur in the case of the experimental blends, with the conclusion that the SH differences exclusively depend on the copolymer type used, since the catalysts, synthesis process and blend preparation were the same. Therefore, it is concluded that the SCG evaluation through the SH test leads to different threshold values that must be taken into account depending on the comonomer type present in the polymer. When different resins or pipes are compared, and there is uncertainty as to the comonomer used, a 10% difference in SH modulus does not mean a better or worse SCG resistance and, therefore, to claim better SCG resistance for a given material, an increase in SH modulus of more than 10% should be found. It is believed that this is quite an important consideration for polymer's investigation, particularly for the industry. Considering the results depicted in Figs. 3 and 4, Table 3 lists the threshold values for each type of commercial polyethylene pipe resin.

4. Conclusions

High resistance polyethylene resins currently in use are difficult to

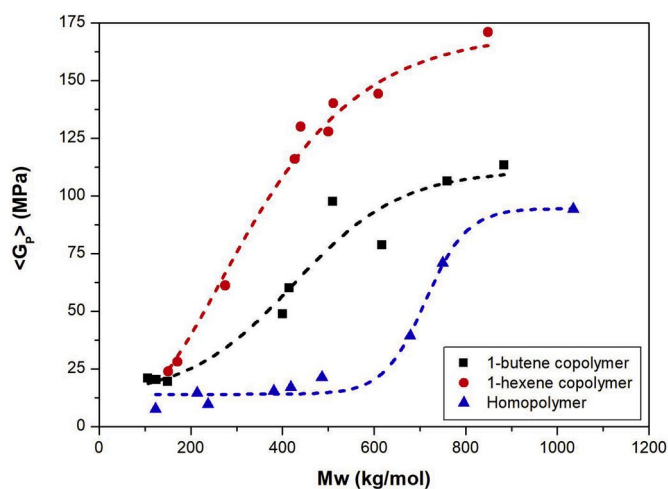


Fig. 6. SH value as function of molecular weight for homopolymer, 1-hexene copolymer and 1-butene copolymer resins.

Table 2
Physico-chemical characterization of bimodal Ziegler-Natta polyethylene blend resins.

Material	Comonomer	Density (kg/m ³)	M _w (kg/mol)	M _w /M _n (-)	SCB/1000C	PENT (hours)	SH <G _p > (MPa)
bPEbut1	1-butene	951.8	268	10.2	0.51	14	23.3
bPEbut2	1-butene	958.6	302	25.8	0.79	37	23.9
bPEbut3	1-butene	959.4	308	34.1	0.75	73	27.1
bPEbut4	1-butene	957.7	337	32.2	1.3	656	35.4
bPEbut5	1-butene	960.4	347	39.8	2.0	891	37.1
bPEbut6	1-butene	958.0	357	32.1	2.1	3050	41.9
bPEhex1	1-hexene	951.9	270	10.4	0.30	10	22.5
bPEhex2	1-hexene	949.7	408	26.2	0.20	20	25.9
bPEhex3	1-hexene	955.1	298	19.4	0.53	37	29.5
bPEhex4	1-hexene	951.0	361	21.9	0.82	930	42.5
bPEhex5	1-hexene	954.4	226	19.2	1.1	1200	45.2
bPEhex6	1-hexene	957.3	260	27.7	1.5	1593	45.5

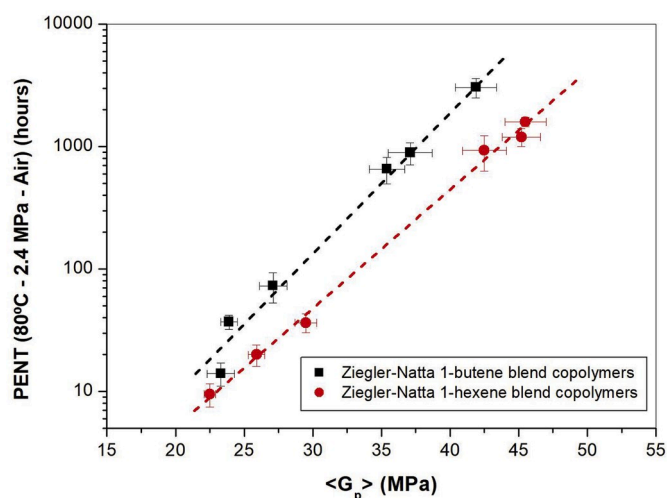


Fig. 7. PENT failure time vs SH value. Experimental blend resins.

Table 3
Proposed SH value as function of copolymer type used.

Grade	Strain Hardening value (MPa)	
	1-butene copolymer	1-hexene copolymer
PE100 – PE4710	38	41
PE100RC	53	59

evaluate according to the established SCG methodologies such as FNCT or PENT tests. Due to the limits of the SCG evaluation with the test methods now in use, SH determination has been established as a good short-term alternative for SCG performance of PE resins. The experimental data also showed that the SH test correlates well with other established SCG tests such as standard FNCT and PENT tests. However, the comonomer type effect on the SH performance is an important issue that must be considered. It was demonstrated that polyethylene resins with 1-hexene as comonomer have higher SH values, especially in high resistance to failure resins. Evaluation of PE100 or PE100RC using SH methodology shows that different threshold values are achieved. For most recent high resistance PE100RC resins, SH values of 53 MPa are achieved in the case of 1-butene, while values of 59 MPa are obtained in the case of 1-hexene comonomer-based resins. At a crucial time when the threshold values (for PE100 and PE100RC resins) for the different accelerated tests are under discussion, the results of this work establishing noteworthy differences in the SH values when different comonomer types are used are expected to be of great help for the correct characterization of the long-term mechanical properties of pipe grades.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymeresting.2019.106155>.

References

- [1] N. Brown, S.K. Bhattacharya, The initiation of slow crack-growth in linear polyethylene under single edge notch tension and plane-strain, *J. Mater. Sci.* 20 (1985) 4553–4560. <https://link.springer.com/article/10.1007%2FBF00559346>.
- [2] A. Lustiger, R.D. Corneliusen, The role of crazes in the crack-growth of polyethylene, *J. Mater. Sci.* 22 (1987) 2470–2476. <https://link.springer.com/article/10.1007%2FBF01082132>.
- [3] P.J. DesLauriers, M.P. McDaniel, D.C. Rohlffing, R.K. Krishnaswamy, S.J. Secora, E. A. Benham, P.L. Maeger, A.R. Wolfe, A.M. Sukhadia, B.B. Beaulieu, A comparative study of multimodal vs. bimodal polyethylene pipe resins for PE-100 applications, *Polym. Eng. Sci.* 45 (2005) 1203–1213. <https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.20390>.
- [4] R.A. Garcia, A. Carrero, C. Martin, C. Dominguez, Effects of the structural components on slow crack growth process in polyethylene blends. Composition intervals prediction for pipe applications, *J. Appl. Polym. Sci.* 121 (2011) 3269–3276. <https://onlinelibrary.wiley.com/doi/abs/10.1002/app.33911>.
- [5] ISO 16770, Plastics - determination of environmental stress cracking (ESC) of polyethylene - Full-notch creep test (FNCT). <https://www.iso.org/standard/31061.html>, 2004.
- [6] ASTM F1473, Standard test method for notch tensile test to measure the resistance to slow crack growth of polyethylene pipes and resins. <https://www.astm.org/Standards/F1473.htm>, 2018.
- [7] ISO 16241, Notch tensile test to measure the resistance to slow crack growth of polyethylene materials for pipe and fitting products (PENT). <https://www.iso.org/standard/32163.html>, 2005.
- [8] X.C. Lu, Z.Q. Zhou, N. Brown, A sensitive mechanical test for slow crack growth in polyethylene, *Polym. Eng. Sci.* 37 (1997) 1896–1900. <https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.11839>.
- [9] C. Domínguez, A. Perez, N. Robledo, C. Gonzalez, B. Paredes, R.A. Garcia, Evaluation and Comparison of Standard and Accelerated Slow Crack Growth Determination Methodologies: Effect of the Comonomer Type Influence, *Plastic Pipes XIX*, Las Vegas, Nevada, 2018.
- [10] B. Gerets, M. Wenzel, K. Engelsing, M. Bastian, Slow crack growth of polyethylene—accelerated and alternative test methods, in: W. Grellmann, B. Langer (Eds.), *Deformation and Fracture Behaviour of Polymer Materials*, Springer International Publishing, 2017, pp. 177–187.
- [11] C. Domínguez, R.A. Garcia, M. Aroca, A. Carrero, Study of the PENT test conditions for reducing failure times in high-resistance polyethylene resins for pipe applications, *Mech. Time-Dependent Mater.* 16 (2012) 105–115. <https://link.springer.com/article/10.1007%2Fs11043-011-9151-z>.
- [12] N. Robledo, C. Domínguez, R.A. García-Muñoz, Alternative accelerated and short-term methods for evaluating slow crack growth in polyethylene resins with high crack resistance, *Polym. Test.* 62 (2017) 366–372. <https://www.sciencedirect.com/science/article/pii/S0142941817307936?via%3Dihub>.
- [13] J. Hessel, H. Warnecke, 3R International Vulkan Verlag, 2013.
- [14] L. Kurelec, M. Teeuwen, H. Schoffeleers, R. Deblieck, Strain hardening modulus as a measure of environmental stress crack resistance of high density polyethylene, *Polymer* 46 (2005) 6369–6379. <https://www.sciencedirect.com/science/article/pii/S0032386105006555?via%3Dihub>.

- [15] A. Frank, G. Pinter, Evaluation of the applicability of the cracked round bar test as standardized PE-pipe ranking tool, *Polym. Test.* 33 (2014) 161–171. <https://www.sciencedirect.com/science/article/pii/S0142941813002419?via%3Dihub>.
- [16] A.M. Sukhadia, M.J. Lamborn, P.J. desLauriers, R.A. Garcia, C. Dominguez, *Assessing the Slow Crack Growth Resistance of Polyethylene Resins and Pipe Service Lifetimes Predictions, Plastic Pipes XV* Vancouver, Canada, 2010.
- [17] J. Cazenave, R. Seguela, B. Sixou, Y. Germain, Short-term mechanical and structural approaches for the evaluation of polyethylene stress crack resistance, *Polymer* 47 (2006) 3904–3914. <https://www.sciencedirect.com/science/article/pii/S0032386106004058?via%3Dihub>.
- [18] ISO 18488, Polyethylene (PE) materials for piping systems - determination of Strain Hardening Modulus in relation to slow crack growth - test method. <https://www.iso.org/standard/62593.html>, 2015.
- [19] ISO 18489, Polyethylene (PE) materials for piping systems - determination of resistance to slow crack growth under cyclic loading - cracked Round Bar test method. <https://www.iso.org/standard/62593.html>, 2015.
- [20] L. Havermans, R. Kloth, R. Deblieck, *Strain Hardening Modulus: an Accurate Measure for Slow Crack Growth Behavior of HDPE Pipe Materials, Plastic Pipes XVII* Barcelona, Spain, 2012.
- [21] S. Deveci, S.K. Kaliappan, J. Fawaz, U. Gadgoli, B. Das, Sensitivity of post yield axial deformation properties of high-density ethylene/alpha-olefin copolymers in relation to molecular structure and slow crack growth resistance, *Polym. Test.* 72 (2018) 285–297. <https://www.sciencedirect.com/science/article/pii/S0142941818308699?via%3Dihub>.
- [22] P.J. DesLauriers, M.J. Lamborn, J.S. Fodor, Correlating polyethylene microstructure to stress cracking: correlations to post yield tensile tests, *Polymer* 153 (2018) 422–429. <https://www.sciencedirect.com/science/article/pii/S0032386118307274?via%3Dihub>.
- [23] P.J. DesLauriers, D.C. Rohlfing, Estimating slow crack growth performance of polyethylene resins from primary structures such as molecular weight and short chain branching, *Macromol. Symp.* 282 (2009) 136–149. <https://onlinelibrary.wiley.com/doi/abs/10.1002/masy.200950814>.
- [24] PAS 1075, Pipes made from Polyethylene for alternative installation techniques –Dimensions, technical requirements and testing. <https://www.thenbs.com/PublicationIndex/documents/details?Pub=DIN&DocID=321171>, 2009.
- [25] R.K. Krishnaswamy, Q. Yang, L. Fernandez-Ballester, J.A. Kornfield, Effect of the distribution of short-chain branches on crystallization kinetics and mechanical properties of high-density polyethylene, *Macromolecules* 41 (2008) 1693–1704. <https://pubs.acs.org/doi/10.1021/ma070454h>.
- [26] R.A. Garcia, A. Carrero, M. Aroca, O. Prieto, C. Dominguez, Slow crack growth resistance in resin blends of chromium and metallocene catalyzed ethylene-hexene copolymers for pipe applications, *Polym. Eng. Sci.* 48 (2008) 925–933. <https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.21038>.
- [27] X.L. He, X.J. Zha, X. Zhu, X. Qi, B.P. Liu, Effect of short chain branches distribution on fracture behavior of polyethylene pipe resins, *Polym. Test.* 68 (2018) 219–228. <https://www.sciencedirect.com/science/article/pii/S0142941818300138?via%3Dihub>.
- [28] S. Sanmartín, J. Ramos, J. Martínez-Salazar, Following the crystallization process of polyethylene single chain by molecular dynamics: the role of lateral chain defects, *Macromol. Symp.* 312 (2012) 97–107. <https://onlinelibrary.wiley.com/doi/abs/10.1002/masy.201100006>.
- [29] Z. Zhou, N. Brown, Slow crack growth of blends of high density and linear low density polyethylenes as influenced by morphology, *Polymer* 35 (1994) 3619–3623. <https://www.sciencedirect.com/science/article/pii/0032386194905371>.
- [30] R. Seguela, Critical review of the molecular topology of semicrystalline polymers: the origin and assessment of intercrystalline tie molecules and chain entanglements, *J. Polym. Sci. B Polym. Phys.* 43 (2005) 1729–1748. <https://onlinelibrary.wiley.com/doi/abs/10.1002/%28SICI%291099-0488%2819960730%2934%3A10%3C1809%3A%3AAID-POLB12%3E3.0.CO%3B2-F>.
- [31] A. Adib, C. Dominguez, J. Rodriguez, C. Martin, R.A. Garcia, The effect of microstructure on the slow crack growth resistance in polyethylene resins, *Polym. Eng. Sci.* 55 (2015) 1018–1023. <https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.23970>.
- [32] X.C. Lu, N. Ishikawa, N. Brown, The critical molecular weight for resisting slow crack growth in a polyethylene, *J. Polym. Sci. B Polym. Phys.* 34 (1996) 1809–1813. <https://onlinelibrary.wiley.com/doi/abs/10.1002/%28SICI%291099-0488%2819960730%2934%3A10%3C1809%3A%3AAID-POLB12%3E3.0.CO%3B2-F>.
- [33] J. Fawaz, S. Deveci, V. Mittal, Molecular and morphological studies to understand slow crack growth (SCG) of polyethylene, *Colloid Polym. Sci.* 294 (2016) 1269–1280. <https://link.springer.com/article/10.1007%2Fs00396-016-3888-5>.
- [34] Y.L. Huang, N. Brown, Dependence of slow crack-growth in polyethylene on butyl branch density - morphology and theory, *J. Polym. Sci. B Polym. Phys.* 29 (1991) 129–137. <https://onlinelibrary.wiley.com/doi/abs/10.1002/polb.1991.090290116>.
- [35] J.J. Cheng, J.A. Alvarado-Contreras, M.A. Polak, A. Penlidis, Chain entanglements and mechanical behavior of high density polyethylene, *J. Eng. Mater. Technol.* 132 (2010) 7. <http://materialstechnology.asmedigitalcollection.asme.org/article.aspx?articleid=1428602>.
- [36] J.D. Ferry, *Viscoelastic Properties of Polymers*, 3RD ed., 1980.