

Effects of the Structural Components on Slow Crack Growth Process in Polyethylene Blends. Composition Intervals Prediction for Pipe Applications

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ABSTRACT: A linear low density polyethylene (LLDPE) obtained from a metallocene based catalyst, was blended in an extruder with a high density polyethylene (HDPE) homopolymer synthesized with an iron based catalyst. The bimodal polyethylenes, made with blends from 0 to 100 wt % of copolymer were characterized by SEC, DSC, ESEM, SEC-FTIR, and TREF, while their resistance to the slow crack growth (SCG) was evaluated through the PENT test. Results provide that polymer blends with co-

polymer contents between 47.5 and 72.5 wt % are suitable for pipe applications. Furthermore, a method based on the intercrystalline tie chains calculus is proposed as suitable and attractive, because of its simplicity and novelty, to forecast long term performance and to predict capabilities. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3269–3276, 2011

Key words: slow crack growth; polyethylene; pipe application; tie molecules; structure properties relations

INTRODUCTION

Since the first use of high density polyethylene (HDPE) for pipe manufacture, in the 60s decade, a gradual progression toward higher performance materials standards has been established.¹ This improvement has been driven by advances in catalysis and polymerization technology to get polymers with longer branches and broader or even bimodal molecular weight distribution (MWD), which are very suitable for pipe applications.² In this way, PE-80 and PE-100 are the most polyethylene resins used for pipe applications. They are named in this way because the pipe must withstand a minimum circumference (hoop) stress of 8 and 10 MPa respectively, for up to 50 years at 20°C.³ Additionally, the resins must present an adequate resistance to rapid crack propagation (RCP), where a craze is axially propagated by speeds greater than tens of meter per second in a brittle way along the whole length of a pipe.^{4,5} If the pressure is high enough such a crack may be able to propagate indefinitely. Last but not least, polyethylene can also

fail after a certain period of time, in a brittle way under a load well below its yield stress. This failure mechanism, named slow crack growth (SCG), involves the formation of a craze at a point of stress concentration and the subsequent growth and fracture of the material. This is the main long-term failure responsible in polyethylene pipelines, and hence the most convenient parameter for failure control.^{6–12}

Accordingly, several guarantees must be satisfied by the polyethylene resins to be employed in pipe manufacture.

For fulfilling all these requirements, mainly enhancing the SCG resistance, bimodal polyethylene was introduced at the beginning of the 90s. These resins are mainly composed of both, a low-molecular weight linear homopolymer with negligible comonomer content, and a high-molecular weight copolymer with large comonomer content and short chain branching (SCB).^{1,13} The former provides stiffness, because of its high density, together with a good processability, while the latter confers both, a satisfactory resistance to SCG, and a suitable tenacity. Regarding the comonomer distribution, it is really convenient to concentrate the SCB on the highest molecular weight chains to favor the occurrence of intercrystalline tie molecules and entangled chain loops, which affect the long-term mechanical properties, improving the SCG.¹⁴

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Unfortunately, the usual catalytic systems incorporate the comonomer mainly in the lower MW chains where SCB are not needed. To solve this drawback, bimodal resins can be synthesized by the use of cascade reactors operating under different polymerization conditions, or by the addition of two catalysts or one catalyst with two different active centers, in a single reactor.^{15,16}

Another different route, described and developed in the present study, deals with the extruder blend of two polymers obtained separately. On the one hand, a high molecular weight and low density ethylene-hexene copolymer known as linear low-density polyethylene (LLDPE) obtained from a metallocene based catalyst, and on the other hand a lower molecular weight and high density polyethylene (HDPE) homopolymer synthesized with an iron based catalyst.

Bimodal polyethylene obtained under the above-mentioned methodologies represents a promising challenge of enormous interest opened to next years, but the route proposed herein affords the control of the homopolymer/copolymer ratio in a simple way, and therefore to study the effect of modifying the ratio of the basic components.^{17–20}

Therefore, the main aim of this study is to provide a deeper characterization of these blends of polyethylene resins with bimodal MWD, investigating the effects of the structural components such as MW, SCB, SCB distribution, an tie molecules on the Slow Crack Growth process.

As standard to evaluate the SCG process, PENT test at 80°C according to ASTM F1473-01 was accomplished.²¹ In addition, for a better understanding of the SCG process micromechanisms, a fractographic analysis of the fracture surface was done by means of environmental scanning electron microscopy (ESEM).

Finally, polyethylene blends properties were compared with PE-80 and PE-100 resins, and the optimal composition interval, for these blends, was ascertained to be used as high performance pipe materials.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE) homopolymer, iron based catalyst, was blended with a lineal low-density polyethylene (LLDPE) copolymer synthesized with a zirconocene catalyst. Both materials were kindly supplied by Repsol Company. Polyethylene blends from 0 to 100 wt % of copolymer content were blended using a temperature profile from 190 to 240°C in a twin corotation intermeshing screw extruder, MP2000, specially designed to obtain bi-

modal polyethylene where an intimate mixture of the components is very important.

Molecular and physical characterization

High temperature Polymer Laboratories PL200 SEC (Size Exclusion Chromatography) was used to obtain molecular weight and molecular weight distribution with 1,2,4 trichlorobenzene (TCB) as solvent. A flow rate of 1 mL/min at a temperature of 145°C was employed. BHT (2,6-di-*tert*-butyl-4-methylphenol) at a concentration of 0.14 g/L was used as TCB stabilizer. The injection volume and the polymer concentration were 200 mL and 1.5 mg/mL, respectively. Dissolution of the sample was carried out by heating at 150°C for 3 h with occasional gentle stirring. The samples were cooled slowly and reheated to 150°C for 2 h prior to injection. The columns used were two PLGel Mixed A (7.8 × 300 mm²) and the system was calibrated with a broad linear polyethylene standard. Short chain branching distribution was obtained using a combination of a SEC system with a Fourier transform infrared (FTIR) detector on line.¹³

Temperature rising elution fractionation (TREF) tests were carried out in a Polymer Char equipment. Blends were previously dissolved at 160°C in 1,2,4 trichlorobenzene and then loaded onto a heated inert support (Chromosorb P.). Afterwards, the samples were slowly crystallized from 160 to 35°C at a rate of 0.5°C/min. Finally, the samples were eluted from the column at a constant flow rate of 0.5 mL/s with a heating rate of 1°C/min.

Densities were determined according to ISO 1183-2 in a gradient column with water and ethanol. The columns were previously calibrated with floating glass beads which have well-known densities at 23°C. To carry out the density determination the samples were previously compression molded and crystallized at 15°C/min. Melt flow index (MI) was measured in a Ceast Melt Flow Tester at 190°C under a 2.16 kg loading according to ISO 1133.

Thermodynamical measurements were carried out at a heat rate of 10°C/min with a DSC calorimeter Mettler-Toledo 822e, equipped with a liquid nitrogen subambient accessory. To assess the actual value of crystallinity of the tested materials, samples were cut from the core of the specimens used for the PENT test. The crystal thickness value, L_c , can be measured by DSC following the Gibbs-Thomson equation for a lamellar crystallite of large lateral dimensions and finite thickness:

$$L_c = \frac{2\sigma_e T_m^0}{\Delta H_m^0 \rho_c (T_m^0 - T_m)} \quad (1)$$

with the values proposed by Illers and Hendus²²

TABLE I
Properties of Polyethylene Blends

Material	LLDPE (wt %)	Density (g/cm ³)	M_w (kg/mol)	M_w/M_n (-)	MI (g/10 min)	T_m (°C)	L_c (nm)	Flexural modulus (MPa)
HDPE	0	0.9704	51.4	5.5	41	138.0	75.7	1805
PE-25	25	0.9610	128.8	12.4	5.4	137.7	68.8	1454
PE-35	35	0.9563	166.1	14.2	2.1	137.4	63.1	1330
PE-45	45	0.9519	190.5	15.2	0.68	136.7	52.8	1201
PE-50	50	0.9501	203.6	15.5	0.27	135.9	44.5	1170
PE-55	55	0.9479	218.8	15.4	0.20	135.2	39.1	1087
PE-58	57.5	0.9461	226.7	15.7	0.15	135.1	38.5	1068
PE-60	60	0.9451	229.6	14.5	0.12	134.4	34.4	1042
PE-63	62.5	0.9438	234.7	14.5	0.10	134.1	32.9	1020
PE-65	65	0.9431	241.1	14.9	0.07	133.9	32.0	976
PE-70	70	0.9404	265.0	13.7	0.05	133.4	29.9	898
PE-75	75	0.9393	277.0	12.6	0.03	132.9	28.0	855
LLDPE	100	0.9300	337.1	4.7	0.00	129.3	19.4	554

$T_m^0 = 414$ K is the equilibrium melting point of an infinite crystal

$\sigma_e = 79.5$ mJ/m² is the surface energy of the basal surface of the crystalline lamellae

$\Delta H_m^0 = 290$ J/g is the enthalpy of fusion for ideal polyethylene crystal

$\rho_c = 1.000$ g/cm³ is the density of the crystalline phase

T_m = Melting point measured by DSC

Flexural modulus was determined through the flexural test according to ISO 178. The test were conducted in a universal testing machine (MTS Alliance RT/5) at 23°C and 50% relative humidity at a rate of 2 mm/min.

Pent test

An Instron 3800 Series PENT Tester was used to evaluate the SCG resistance. The PENT test (Pennsylvania Edge-Notch Tensile test) described in ASTM F1473²¹ was performed by evaluating the time to failure of a single edge notched test specimen exposed to a constant load of 2.4 MPa at a temperature of 80°C. Measurements were carried out with compression molded plaques of 10 mm thick in a laboratory hydraulic press at 180°C, and a nominal pressure of 200 bars, and then slow cooled during more than 5 h at a rate of $\sim 0.5^\circ\text{C}/\text{min}$ up to room temperature. While cooling, the pressure was allowed to decrease naturally in accordance with ASTM F1473. Specimens of $50 \times 25 \times 10$ mm³ were machined from the plaques and then notched by slowly pressing with a razor blade into the specimen at a speed of about 200 $\mu\text{m}/\text{min}$. Side notches of 1 mm and front notch of 3.5 mm were made according to the cited international standard. In these conditions, fracture under plane strain conditions takes place, which contributes to the formation and evolution of the craze.^{6,23}

After the PENT test, the fracture surfaces were observed by environmental scanning electron microscopy (ESEM) (Philips XL-30) at 0.5 Torr and 15 kV. Since no need for extensive surface preparation in this type of microscopy is required, a more accurate observation of the fracture surface of the sample is allowed.

RESULTS AND DISCUSSION

HDPE and LLDPE blends were characterized by different techniques and results are summarized in Table I. As expected, density, melting temperature and lamellar thickness decrease with copolymer content while molecular weight increases. Figure 1 displays the results of SEC-FTIR analysis where the short chain branching distribution (SCB) profile is shown. Bimodal distributions for all the blends are observed, and additionally, respecting the two references, HDPE and LLDPE, a MWD broadening is

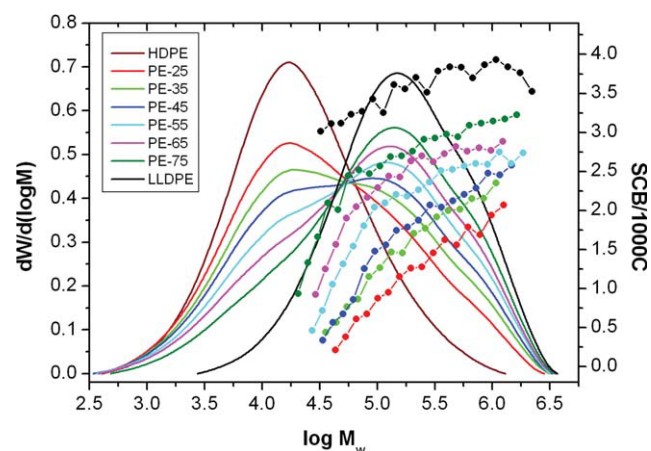


Figure 1 SEC-FTIR curves of polyethylene blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

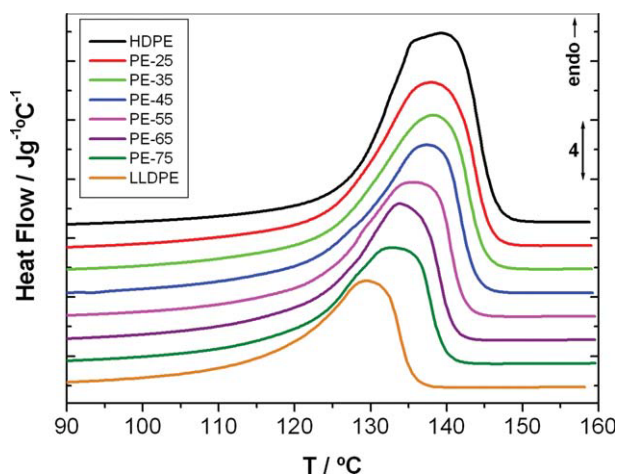


Figure 2 DSC curves of polyethylene blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exhibited in the whole range of blending, achieving values in the interval between 12.4 and 15.7. Both, molecular weight and SCB increase with copolymer content, and since the ramifications are mainly incorporated in the longest chains of ethylene copolymers, as previously recommended, the probability of formation of entangled chain loops and mainly inter-crystalline tie molecules are clearly favored.¹⁴ These tie molecules are the main responsible for joining together the different crystallites, distributing the stresses along the material and, in this way, improving the resin long-term resistance to the SCG.^{24,25}

Previously to the evaluation of the SCG resistance, the degree of compatibility of the different blends was studied by DSC analysis directly on the slow-cooled plaques, molded for measuring the PENT test (Fig. 2). The thermograms of the different blends do not show evidence of double peak, indicating a certain degree of compatibility during crystallization, and as consequence the cocrystallization of homopolymer and copolymer chains prevails against phase separation. Only the homopolymer shows a broad peak which could suggest a certain crystal sizes segregation.

An alternative approach to shed light on the degree of structural heterogeneity of these resins consists of analyzing the blends by means of TREF analysis of the different chains that compose these materials,^{26,27} as displayed in Figure 3. Previously, to favor the separation process of the blend components, a slow cooling process has been carried out. One interesting observation lies in the highest elution temperature displayed by the homopolymer because of its linear nature, while the LLDPE copolymer exhibits the lowest elution temperature as consequence of their ramifications. For the rest of blends, a principal peak, which is shifting down linearly as the copolymer content increases, is visual-

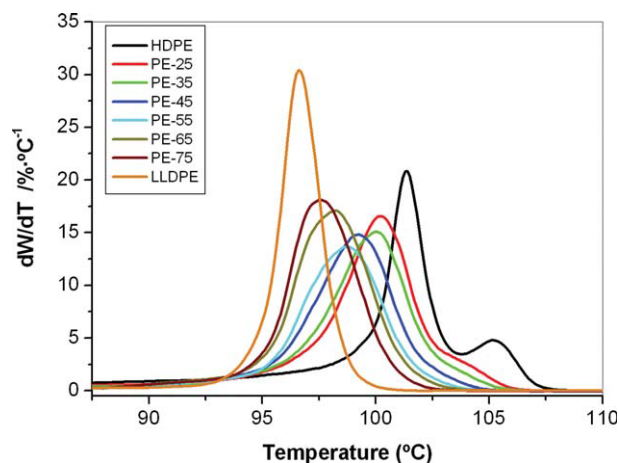


Figure 3 TREF curves of PE blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ized. This result may also suggest the previously stated cocrystallization process between both components is occurring. According to the literature this assumption is reasonable due to the similar nature of blended components and the low branching level of the copolymer with less than 4 SCB/1000C.^{28,29} Figure 3 also shows the homopolymer is composed of a double peak, which indicates the existence of different groups of chains with different length, and consequently with different crystallization capacity. This behavior is characteristic of homopolymers synthesized with an iron catalyst system.³⁰

Figure 4 shows the PENT test results of PE blends, in which each plaque was tested four times and the average value is displayed. In general, the SCG resistance increases exponentially with the copolymer content which means that better resistance to failure corresponds to an increase in the molecular weight

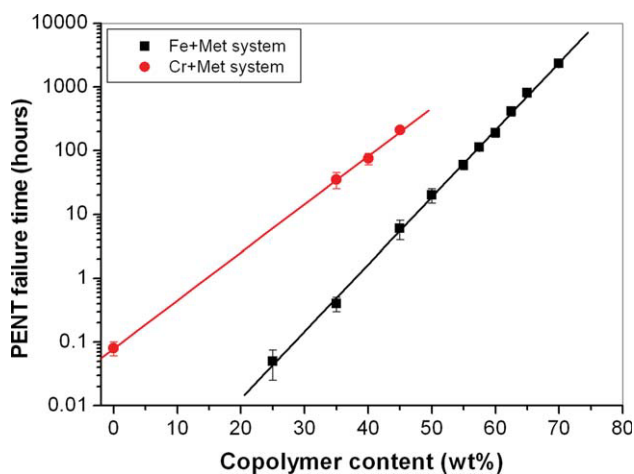


Figure 4 PENT test results for the different polyethylene blends as a function of copolymer content. Fe+Met and Cr+Met systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

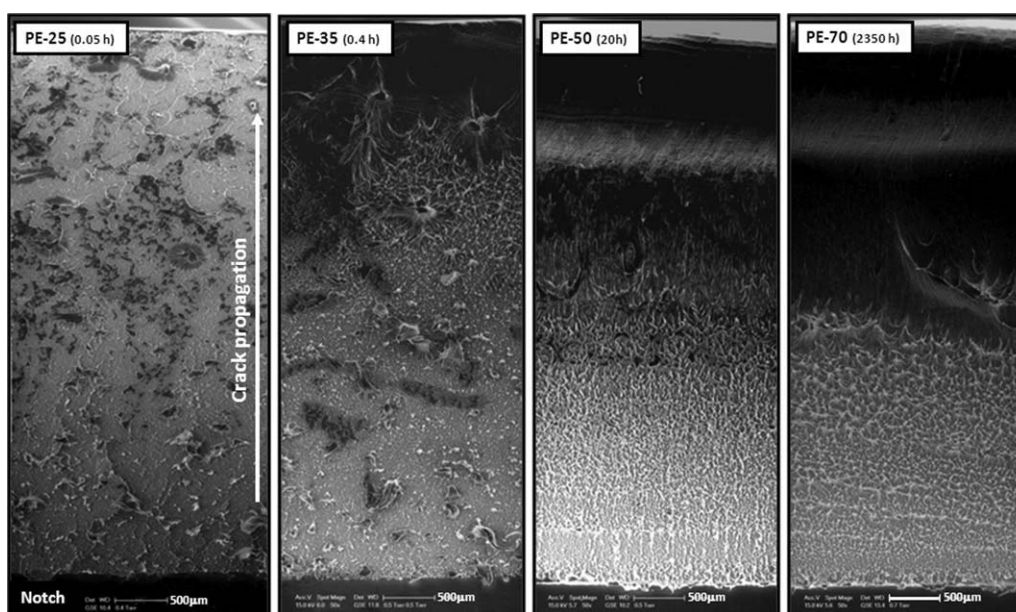


Figure 5 PENT fracture surfaces of different resins for the Fe+Met system.

and a decrease in the lamellar thickness (see Table I). Furthermore, when both blends are compared for the same copolymer content, samples from the Fe-Met set gives lower failure times than Cr-Met set. As reflected in Figure 1, and in the previous published work by our group,³¹ this fact is undoubtedly due to the effects of SCBD in each set of resin. Therefore, both parameters, MW and SCBD, are clearly involved in the different mechanisms that govern the SCG process, and their structural significance with regard to tie molecules formation will be addressed below.^{17,20}

PE-75 sample does not follow the same trend and presents failure times longer than 15,000 h. The low density value for this resin blend, which favors the formation of a sharp blunting process in the notch tip, seems to be the reason for the discrepancy with other samples. This blunting process inhibits the craze formation and hinders the subsequent SCG failure process inside the sample, giving rise to other different failure mechanisms.

Respecting the Fe+Met system, the growth of PENT failure time can be accurately expressed by the next semilogarithmic lineal relationship for polyethylene blends with less than 75 wt % of copolymer:

$$\log(t_{\text{PENT}}) = 0.106X_{\text{copo}} - 4.058 \quad (2)$$

where X_{copo} is the copolymer content in wt %.

Additionally, to confirm this exponential trend, the previously reported results by our research group for the SCG resistance of HDPE and LMDPE blends in a chromium-metallocene catalytic system³¹ are also represented in Figure 4. It follows from this result that the linear relationship between $\log(t_{\text{PENT}})$

and copolymer content allows a direct estimation of PENT failure time by SCG for PE blends, and accordingly it is possible to estimate the value of the failure time for any copolymer content, or inversely to reckon the copolymer content for a specific application.

Moreover, to study the crack propagation, the fracture surface morphology was studied after the PENT test using the ESEM. Figure 5 represents the sample fracture surfaces upon final failure. The fracture starts at the tip of notch and advances into the specimen as the arrow indicates. Clear differences are visualized among the blends, inferring that as the copolymer content increases the fracture surface changes to a high fibrillated morphology, which clearly improves the resistance to the SCG process.¹² Samples PE-50 y PE-70 show a structure typical of brittle fracture by SCG, in which the fibrillated first region of the sample extends up to the middle of the section. Second half displays a gradually fiber growth that changes to matted down fibrils stretched structure along the crack propagation direction, indicative of a ductile failure.³¹ Opposite, samples PE-25 and PE-35 exhibit a smooth surface, corresponding to a very brittle fracture process, which account for the short failure PENT time experimented by both samples.

According to our previous work³¹ one of the most critical parameter influencing the slow crack growth resistance resides on the tie molecules density, which can be estimated according to Huang and Brown Eq. (3).^{32,33}

$$\bar{P} = \frac{\int_0^{\infty} nPdM}{\int_0^{\infty} ndM} \quad (3)$$

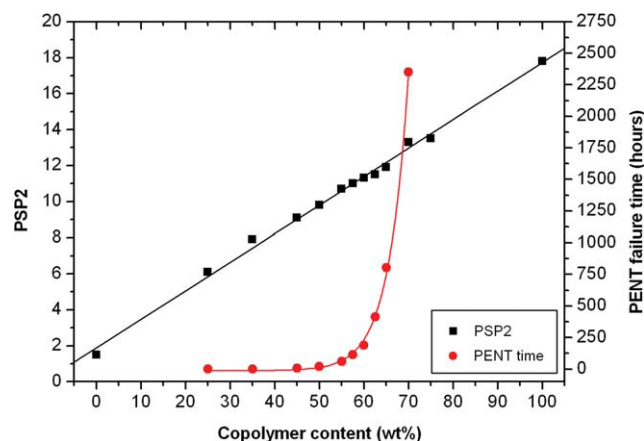


Figure 6 Plot of PSP2 values and PENT failure time for polyethylene blends as function of different copolymer content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Different authors have tried to solve the former probability equation, for example Pedraza et al.,³⁴ developed a program that calculates the tie molecules probability for a polydisperse system, estimating the probability value of each molecular species contained in the sample. The problem of this method resides in the omission of the SCB distribution influence over the tie molecules estimation. A more precise method, developed by DesLauriers and Rohlfiing^{35,36} is based on a primary structural parameter (PSP2) which takes into account not only the influence of the molecular weight distribution

(MWD) on the tie molecule probability value, but also the density value of every MWD slice according to the SCB distribution, previously measured through the SEC-FTIR data over the whole MWD.

Figure 6 shows the probability of tie molecules formation, using the PSP2 parameter, and PENT failure time versus copolymer content. Both parameters increase with copolymer content but, while PSP2 grows linearly, the SCG resistance does it exponentially. As displayed, from 60% copolymer content, the PENT time increases dramatically, while the PSP2 parameter continues growing linearly with the copolymer content. At this point, the main question that arises is why the resistance grows so faster from the 60 wt % copolymer content. The reason may be explained by the introduction of a new concept previously discussed by Brown, the network efficiency concept.^{18,19} This concept describes how once the network composed by crystal and tie molecules turn into continuous, the resistance to SCG rapidly increases. Initially, at low copolymer contents, the polymer structure consist of isolated groups of crystals weakly connected between them. As the amount of copolymer content increases, the crystals are joined together until a continuous network is formed and the SCG resistance dramatically grows.

To explain the network efficiency concept better, in Figure 7 the crystal-tie molecules network at different copolymer contents are schematically represented. Around 60% of copolymer content a

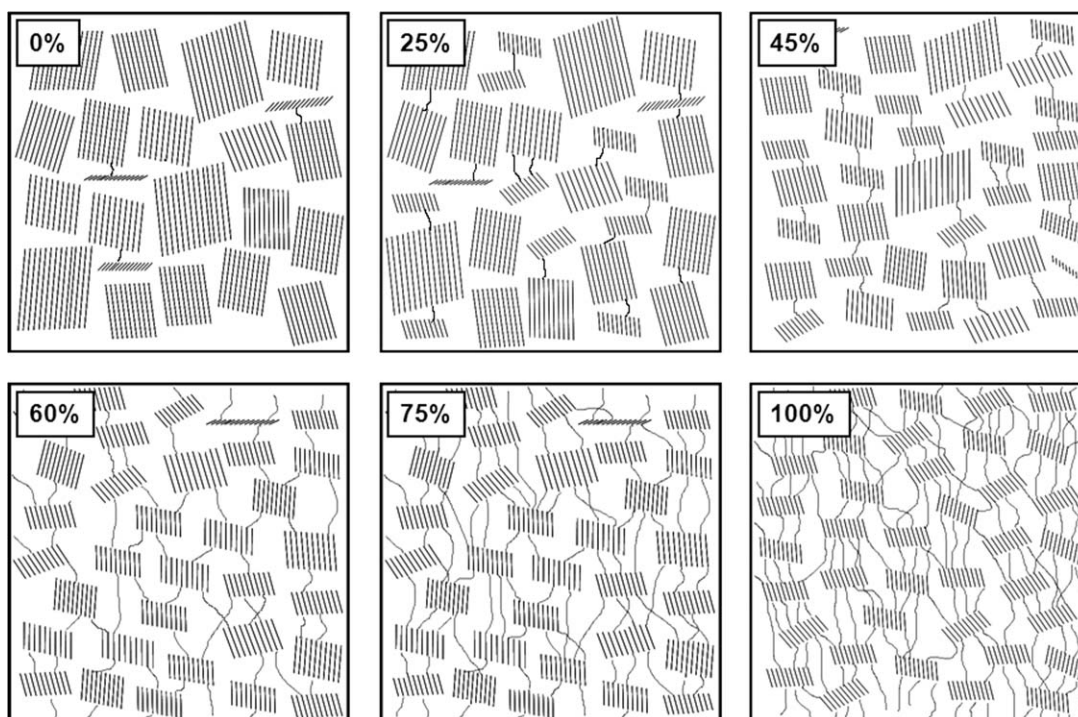


Figure 7 Qualitative interpretation of the crystal-tie molecules network concept. Parallel lines represent crystalline lamellae. Remaining area is the amorphous region.

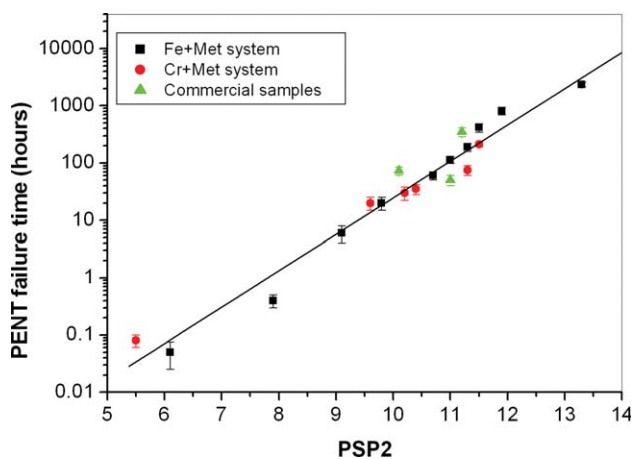


Figure 8 Representation of the PENT failure time as function of the PSP2 value. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

continuous network consisting of crystal and tie molecules is formed, and the strength and effectiveness of this continuous network seems to be the main responsible for the high increment in the PENT failure time above 60% copolymer content. Although basically this is a qualitatively interpretation, in Figure 6 the crystal size distribution and the heterogeneous nature of the iron catalyst based homopolymer has been taken into account from the DSC and TREF results. In addition, the tie molecules concentration depicted in the different graphs is related to the obtained PSP2 data.

To measure the capacity of the PSP2 method for predicting the PENT failure time, we have extended the range of application to other different blends from distinct catalytic systems, which would allow the achievement of an absolute method to calculate either the resin failure time or the final resin application by means of an easy and nontime dependent method. In Figure 8, the PENT time versus the PSP2 value for the Fe+Met blend system, and the Cr+Met system previously published, are represented.³¹ Additionally, three commercial PE-80 and PE-100 degrees have been added to the figure, and as displayed, the samples are clearly fitted to the same curve than the analyzed blends. As consequence, the simplicity of the method could be suitable and attractive to forecast long-term performance and to predict capabilities.

TABLE II
Polyethylene Characteristics for Pipe Applications

Properties	Units	PE2406-PE80	PE3408-PE100
PENT time	hours	>10	>100
Density	g/cm ³	>0.925	>0.940
Flexural modulus	MPa	>552	>758
Melt Index	g/10 min	1.0–0.15	<0.15

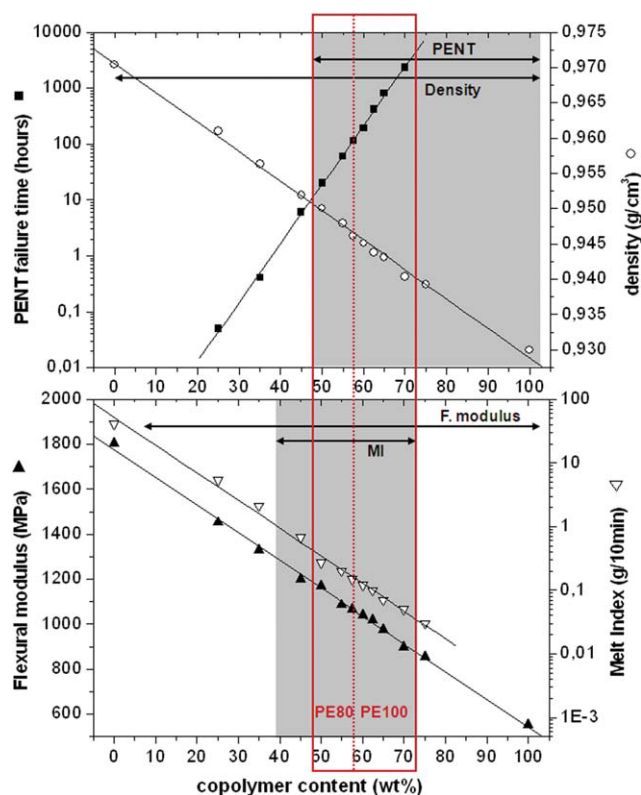


Figure 9 Properties of the polyethylene blends required for pipe applications. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Along this work the iron-metallocene based catalysts resin blends have been completely characterized, including the evaluation of mechanical properties, to explore its feasibility to be used as water or gas pipe. On the one hand the determination of the failure time, by PENT test, and flexural modulus, and on the other hand the evaluation of the density beside the melt flow index (Table I), to determine the processability, are key properties, between others, that necessarily need to be under control to satisfy the adequate features required by resin to be employed on pipe applications.³⁷

The specifications of polyethylene resins to be used in water and gas pipes manufacture are described in the ASTM D3350-06.³⁸ Depending on the final application, polyethylene materials must have several characteristics collected in Table II for water pipes (American PE 2408 or European PE80 grades) or gas pipes (American PE3408 or European PE 100 grades).

Figure 9 displays a representation of these properties (PENT time, density, flexural modulus and melt flow index) as a function of copolymer content in PE blends. The balance between them determines the final resin application. As shown, density and flexural modulus decrease linearly with copolymer content while melt index decreases in an exponential way. From the observations of the values specified

in Table II, it was concluded that PE resin blends with copolymer contents between 47.5 and 72.5 wt % are suitable for pipe applications.

It is clearly distinguished that the PENT resistance will determine the minimum copolymer percentage, while the maximum one will depend on the polyethylene melt flow index. Polymer blends with copolymer contents between 47.5 and 57.5 wt % overlap in properties and applications with PE80 or PE2406 grade, whereas higher copolymer contents (57.5 and 72.5 wt %) are needed to get PE100 or PE3408 grades. In this case, the minimum melt index value considered for pipe applications was 0.04 g/10 min although it can be modified according to the final resin application.

CONCLUSIONS

A high density polyethylene homopolymer (HDPE) was blended with a linear low-density polyethylene (LLDPE). The SCG resistance of polyethylene blends increases exponentially with the copolymer content which means that better resistance to failure corresponds to an increase in the molecular weight and a decrease in the lamellar thickness. Therefore, both parameters are clearly involved in the mechanisms that govern the SCG process. For every polyethylene blend system the SCG resistance may be predicted from an empirical equation. In the same way with this equation, the amount of copolymer needed for getting a certain SCG resistance can be also predicted.

The increment in the tie molecules density and short chain branching (SCB) with the copolymer improves the SCG resistance of the resin. From a certain copolymer content, the SCG resistance drastically grows, as a consequence of the development of a continuous crystal-tie molecules network. For the Fe+Met system, this value is above 60 wt % in copolymer content.

From the blend systems and the commercial resins analyzed, a good agreement between the Primary Structural Parameter (PSP2), which takes into account the effect of a particular SCBD across the MWD to estimate the tie molecules, and the PENT failure time, has been found. This important result allows the possibility of estimating the SCG resistance of a resin in a simple way without the need to perform the PENT test.

Regarding resin properties needed for pipe applications, it has been deduced that for the Fe+Met system with polymer blends with copolymer contents between 47.5 and 57.5 wt % overlap in properties and applications with PE80 or PE2406 grades, whereas higher copolymer contents (57.5–72.5 wt %) are needed to get PE100 or PE3408 grades.

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