Full Paper

Evaluation of bimodal polyethylene from chromium oxide/metallocene hybrid catalysts for high resistance applications

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An interesting alternative to the industrial two-stage cascade process for the production of bimodal polyethylene, used for high resistance applications such as pressure pipes, has been developed. The key point is a binary catalytic system with chromium and metallocene sites incorporated together on AlSBA-15 mesostructured material. This hybrid catalyst is able to produce bimodal polyethylene in a single reactor. In the present work, we show that, in the presence of hydrogen and comonomer (1-butene or 1-hexene) in the reaction medium, the obtained polyethylenes exhibit appropriate mechanical properties for pipes manufacture, such as resistance to rapid crack propagation (RCP) and Slow Crack Growth (SCG), reaching standards for PE100 and even for PE100RC grades.

Metallocene & Chromium
supported on AlSBA-15

Ethylene
+
Comonomer & H$_2$

NEW BIMODAL
POLYETHYLENE
FOR PIPES

X

TESTING
MECHANICAL
PROPERTIES
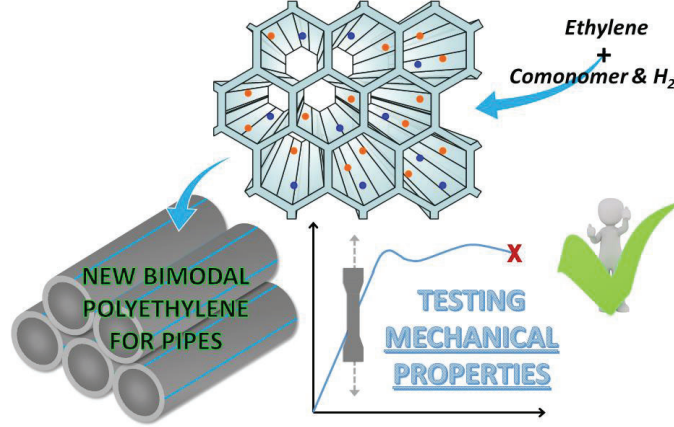
1. Introduction

The combination of different kinds of active sites on the same catalyst has been a strategy commonly used in the chemical industry for overcoming the limitations of more conventional catalytic systems. In the polyolefins field, this way has been explored for both, widening polymer properties and designing more versatile production processes[1–4]. As we have previously reported[5–7], the mixture of chromium and MAO/metallocene sites on the mesostructured AlSBA-15 material leads to a binary catalyst (denoted Met-Cr-AlSBA-15) that, under appropriate conditions such as hydrogen pressure and comonomer amount, can produce bimodal polyethylene in a one-step polymerization process. As known, some grades of bimodal polyethylene, such as PE100, are especially interesting for several commercial applications because they combine the strength and stiffness of high-density polyethylene (HDPE) with the high-stress crack resistance and processability of unimodal medium density grades[8]. One of the most employed technology for the production of bimodal polyethylene at industrial scale is a two-stage cascade polymerization process by using a Ziegler-Natta catalyst[9]. The possibility of designing an alternative based on a single reactor pathway is undoubtedly attractive because of numerous reasons: lower investment costs, simpler process control, and greater mixture of chains with low and high molecular weight (they would be simultaneously generated on the same catalyst), among others[7,10]. In this context, previous results obtained with the binary Met-Cr-AlSBA-15 catalyst showed that it is a promising production route that should be more deeply explored. According to aforementioned data, the use of hydrogen is necessary to get a bimodal molecular weight distribution because it has a strong influence on metallocene sites, leading to a considerable reduction of their chains length[11,12] in comparison with those coming from chromium, which maintain their contribution to the high molecular weight fraction[6,13]. Likewise, adding a comonomer during the polymerization carried out on the binary mesostructured catalyst leads to interesting short chain branching (SCB) distribution across the molecular weight curves of the polymers, providing in some cases flat or even growing

comonomer distributions[7]. This is a very interesting fact since numerous branches located into de shortest polymer chains are not desirable for most polyethylene properties, especially for mechanical ones[14,15]. So, these growing profiles could involve significant enhancements of some mechanical properties of the polymers such as stress crack resistance or impact strength, leading to novel and improved polyethylene grades. However, investigations focused on evaluating the mechanical properties of these new bimodal resins coming from the Met-Cr-AlSBA-15 catalyst have not been developed yet.

This work aims to study in deep the mechanical features of polyethylenes produced by the binary Met-Cr-AlSBA-15 catalyst in only-one step polymerization process, as well as their relationship with some operational variables like using hydrogen as chain transfer agent and comonomers (1-butene and 1-hexene) as SCB sources. Commercial PE-100 resin is included in the study as the reference material, expecting that its mechanical properties will be reached or improved by those corresponding to the new bimodal polymers.

2.   Experimental Section

2.1. Catalyst synthesis and polymerization tests

Hybrid metallocene-chromium catalytic system Met-Cr-AlSBA-15 was prepared according to works previously published[5-7], as well as ethylene polymerizations[7] carried out at 70 ºC and 12 bars of ethylene pressure. In reactions with comonomer, 20 mL of 1-butene or 1-hexene were added at the beginning of the polymerization. When using hydrogen as chain transfer agent, two experimental procedures were employed: discontinuous and continuous addition. In the discontinuous method, the hydrogen volume (1 Nl) was added at the beginning of the reaction, while in the continuous one the same hydrogen volume was uniformly fed during the reaction, leading to an average molar ratio H_2/Ethylene for feeding the reactor around 0.015. The polymerization reaction time was set at 60 min employing 100 mg of catalyst, yielding an amount of 80 grams of polyethylene as an average. All the experiments were run at least twice

in order to have enough amount of polyethylene to carry out mechanical characterization of the samples. Accordingly, 8 polyethylene samples were synthesized to evaluate their mechanical properties:

- 2 samples using hydrogen but without comonomer, denoted H2-CONT (continuous feeding), and H2-DISC (discontinuous method).

- 2 samples using comonomer but without hydrogen, denoted C4 (comonomer = 1-butene), and C6 (comonomer = 1-hexene).

- 4 samples using hydrogen and comonomer, denoted C4-H2-CONT (comonomer = 1-butene, continuous feeding), C4-H2-DISC (comonomer = 1-butene, discontinuous method), C6-H2-CONT (comonomer = 1-hexene, continuous feeding), and C6-H2-DISC (comonomer = 1-hexene, discontinuous method).

2.2. Polymers 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 online concentration and composition, providing differences of 1 branch per 1000 atoms of carbon. Sample solutions at a concentration of 0.75 mg·mL^{-1} in 1,2,4- trichlorobenzene (TCB), stabilized with BHT (2,6-di-tert-butyl-4-methylphenol) were obtained by gentle stirring at 150 ºC for 2 hours. Analyses were performed at a flow rate of 1 mL·min^{-1} and a temperature of 160 ºC.

Thermal measurements were performed at a heat rate of 10 ºC·min^{-1} with a DSC Mettler-Toledo 822e. The degree of crystallinity was calculated from the melting enthalpy values of the samples, using as reference a value of 290 J·g^{-1} for the enthalpy of fusion for an ideal PE crystal. High load melt flow index (HLMI) was measured in a Melt Flow Tester 2000 at 190 ºC under a load of 21.6 kg, according to the ISO 1133 standard. Polymers density was determined by

means of density gradient columns where a linear density gradient is created by ethanol and water mixtures (density range is from 0.7900 to 1.0000 $g \cdot cm^{-3}$). Measurements were carried out at 23 ºC according to the ISO 1183 standard.

Tensile and flexural tests were developed in a universal testing machine (MTS Alliance RT/5) at 23 ºC and 50 % relative humidity. Tensile tests were carried out on the dumbbell shaped specimens 1BA at a crosshead speed of 50 $mm \cdot min^{-1}$, according to UNE-EN ISO 527-2:2012. The yield stress was determined as the first maximum in the stress-strain curves. Flexural tests were accomplished on the rectangular bars samples with a three-point bending geometry according to the ISO 178:2010 standard at a crosshead speed of 2 $mm \cdot min^{-1}$.

Charpy impact test was carried out following the UNE-EN ISO 179-1:2010 standard from a rectangular test piece measuring 80x10x4 mm, extracted from a plate previously molded by compression.

An Instron 3800 Series PENT tester was used to perform tests, according to ASTM F1473, to evaluate the SCG resistance. 10-mm-thick plaques were compression-molded in a hydraulic press at 180 ºC and at a nominal pressure of 200 bars. Afterwards, they were cooled slowly for 5 hours at a rate of approximately 0.5 $ºC \cdot min^{-1}$ until reaching room temperature. During the cooling stage, the pressure was decreased naturally. Subsequently, specimens of $50 \times 25 \times 10$ mm were machined from the plaques, followed by notches slowly pressed into the specimen by a razor blade at a speed of about 200 $\mu m \cdot min^{-1}$. Side notches of 1.0 mm and a front notch of 3.5 mm were made according to the ASTM F1473 standard. Under the standard PENT conditions, specimens were exposed to a constant load of 2.4 MPa at a temperature of 80 °C.

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 molded to a form a sheet with a hydraulic press at 180 ºC, nominal pressure of 200 bars and cooling rate of 15 $ºC \cdot min^{-1}$, as per ISO 1872-2. After

pressing, the samples were annealed for 1 h at 120 ºC and then slowly cooled to room temperature. Dumbbells shaped specimens were punched from the pressed sheets. In accordance with ISO 18488, the strain rate was 20 mm·min^{-1}, the initial distance between the gauge marks on the center 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).

3. Results and Discussion

3.1. Bimodal polyethylene produced by chromium-metallocene binary catalytic system (Met-Cr-AlSBA-15)

Table 1 summarizes the main physic-chemical properties of the polymers produced by using chromium-metallocene binary catalysts under the different reaction conditions previously described in the experimental section. Also, Figures 1-3 depict the molecular weight distributions (MWDs) and short-chain branching (SCB) distributions of these samples. As observed, most of the synthesized polyethylenes present bimodal MWDs. As we have previously reported[5–7] an adequate combination of chromium and metallocene sites on mesostructured AlSBA-15 material leads to a binary catalytic system (catalyst Met-Cr-AlSBA-15, used in this work), which is able to produce bimodal polyethylene in only one-step reaction pathway. According to the results of Table 1 and Figures 1-3, the properties of this bimodal polyethylene can be tuned by the two tested ways: changing the method used for adding hydrogen during the reaction (continuous and discontinuous) and using or not comonomer (1-butene and 1-hexene). Due to the highly broad molecular weight distributions of the obtained polymers (with polydispersity values in the range 20 to 246), it is complex connecting changes of these distributions with those observed in other basic properties such as the melting point, density or crystallinity. Likewise, SCB amount and location across the molecular weight distributions also show important variations by adding hydrogen due to the different responses

of chromium and metallocene sites to the presence of both, hydrogen and comonomer. The different response of each kind of active center towards hydrogen and comonomer could be addressed for adjusting polymer's features. For instance, working with low hydrogen concentration in the reactor affects more strongly to the activity of metallocene sites and the corresponding polymer properties than what happens to the chromium sites[6]. So, under these conditions, the activity of both kinds of catalytic centers is quite similar, and the molecular weight of the metallocene chains are shifted to lower values, resulting in bimodal molecular weight distribution, in which chromium mainly provides the longer chains and metallocene the shorter ones. This can be clearly observed in Figure 1, where the bimodality of MWD appears when using hydrogen (samples H2-CONT and H2-DISC) compared to the reference sample (polyethylene produced on Met-Cr-AlSBA-15 without hydrogen neither comonomer).

Table 1. Basic properties of the polymers obtained by Met-Cr-AlSBA-15 under different reaction conditions.

Sample	Hydrogen	Comonom[c]	M_w/M_n	CH$_3$/ 1000C	T_m (ºC)	α (%)	HLMI (g/10 min)	ρ (g/ml)
H2-CONT	Cont.[a]	---	246	---	135	76.9	1.80	0.9636
H2-DISC	Discont.[b]	---	172	---	133	77.1	6.52	0.9637
C4	--	1-butene	16	5.0	129	56.8	8.17	0.9354
C4-H2-CONT	Cont.	1-butene	65	1.0	130	65.4	52.86	0.9479
C4-H2-DISC	Discont.	1-butene	36	3.5	131	66.3	1.32	0.9469
C6	--	1-hexene	40	0.7	132	62.6	0.70	0.9432
C6-H2-CONT	Cont.	1-hexene	104	2.1	131	64.5	81.8	0.9545
C6-H2-DISC	Discont.	1-hexene	20	2.9	132	72.0	2.32	0.9574
PE100			31	3.8	129	65.1	11.1	0.9501

[a]Continuous method: 1 Nl of H$_2$ was uniformly fed during the reaction time; [b]discontinuous method: 1 Nl of H$_2$ was added at the beginning of the reaction; [c]amount of comonomer =20 ml.

Regarding the method used for adding hydrogen, results show that the position and contribution of the high and low molecular weight fractions to the whole distribution are noticeably influenced by the selected procedure. This fact is in agreement with previous work[7] and it can be observed by comparing H2-CONT with H2-DISC (Figure 1), C4-H2-CONT with C4-H2-DISC (Figure 2), and C6-H2-CONT with C6-H2-DISC (Figure 3). The higher hydrogen concentration existing in the reactor at the beginning of the polymerization in the discontinuous

method affects more markedly to metallocene sites, which decrease their contribution to the MWD. Thus, by using the discontinuous procedure the fraction of low molecular weight (metallocene contribution) is commonly smaller, leading to an increase of the number of polymer chains coming from chromium centers (i.e., rising the contribution of the high molecular weight fraction). This fact usually involves that polyethylenes obtained by adding all the hydrogen at the beginning of the reaction present lower polydispersity, as can be seen in data of Table 1. Another polymer property affected by the hydrogen addition method is the melt index (HLMI), which is directly connected to the polyethylene processability. As a general rule, the lower the contribution of the metallocene sites (discontinuous process), the lower values of HLMI. This has been also reported in our aforementioned work[7] for samples produced with Met-Cr-AlSBA-15 in presence of both, hydrogen and comonomer. However, it seems to be different for homopolymers (see data of Table 1) although, in this case, differences between MWDs obtained by changing the procedure for adding hydrogen are much lower than those observed for copolymers (see Figure 1), leading to lower variations of the product's properties.
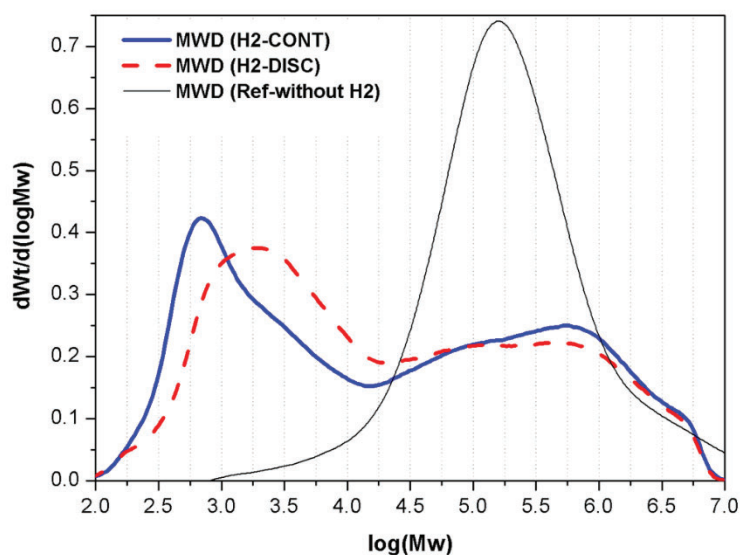
Figure 1. Molecular weight distributions and short chain branching (SCB) distributions of the polymers obtained without comonomer.
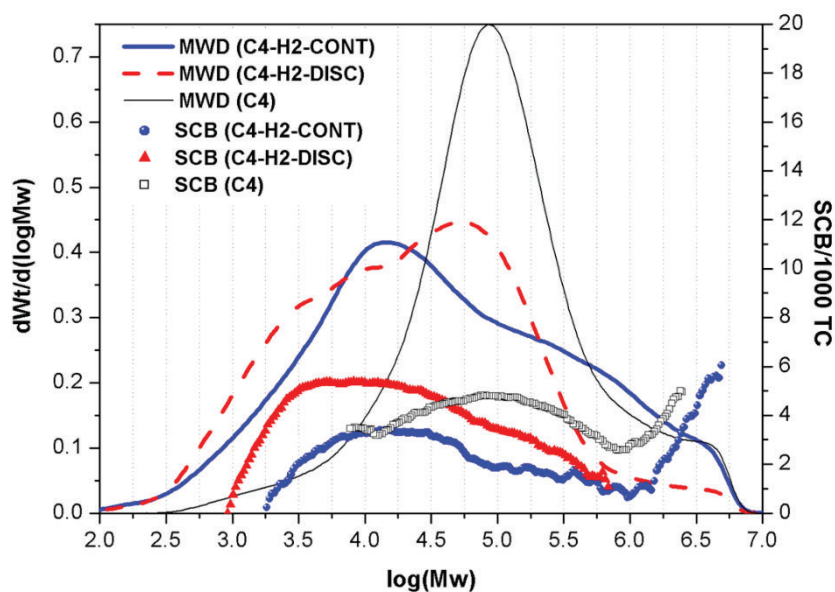
Figure 2. Molecular weight distributions and short chain branching (SCB) distributions of the polymers obtained using 1-butene.
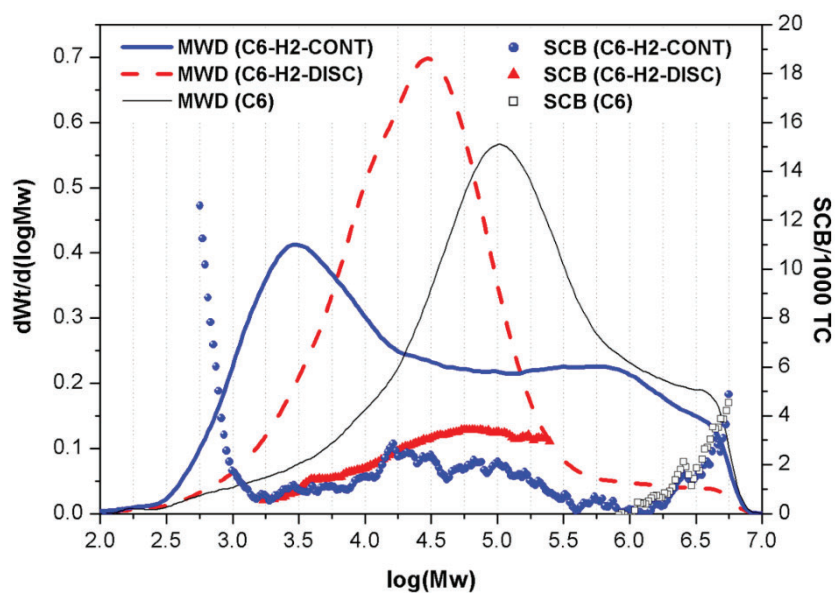

Figure 3. Molecular weight distributions and short chain branching (SCB) distributions of the polymers obtained using 1-hexene.

Concerning the influence of using comonomers during the reaction, it produces a clear reduction of melting point, crystallinity, and density of the polymers, as expected when SCBs are incorporated into the polyethylene chains. The different behavior reported for the individual catalysts when using comonomers under similar conditions (positive comonomer effect for Cr-AlSBA-15 and negative one for Met-AlSBA-15), probably modifies the relative contribution of the two kinds of centers to the polymer growth when using the binary catalytic system[7]. So, the positive comonomer effect associated with chromium sites could involve a higher amount of the longer chains in polymers (coming from chromium sites). This fact can be deduced by comparing the MWD of H2-DISC sample (Figure 1) with MWDs of C4-H2-DISC (Figure 2) and C6-H2-DISC (Figure 3) (copolymers with highest comonomer contents), in which the contribution of chromium sites (longer chains) seems to be similar or even larger than the corresponding to metallocene centers. Thus, positions of the key mode of the distributions are clearly shifted to higher molecular weight fraction by using comonomers. Finally, it must be pointed out that copolymerization seems not to be enough to generate bimodal polyethylene with the Met-Cr-AlSBA-15 catalyst, being more effective the use of hydrogen. It is needed to modulate the activity of metallocene sites (much more active than chromium ones) and, at the same time, it is able to reduce the average molecular weight of their polymer chains, achieving MWDs with two comparable and distinguishable fractions.

3.2. Mechanical properties of bimodal polyethylenes produced by Met-Cr-AlSBA-15 catalyst

To assess the strength of the synthesized polyethylenes and their potential use in the manufacture of polyethylene pressure pipes, as a high resistance application, the short- and long-term mechanical properties were studied.

Tensile stress-strain curves and flexural modulus were determined for all the samples at room temperature. According to bibliography[16–18], for PE100 pipe grades, tensile strength yield and

elongation at break should be above 23 MPa and 500 % respectively, while the flexural modulus must be above 900 MPa.

Yield strength value for all polyethylenes synthesized with both hydrogen and comonomer is above 23 MPa, which perfectly fits with the requirements for PE100 grades, as well as elongation at break, which is around the limit value. Flexural modulus values are also above the minimum required for PE100 grades. Hence, these factors do not represent any limitation related to the potential application of the synthesized PE materials in pipe manufacture.

Polyethylenes obtained with hydrogen, H2-CONT and H2-DISC, present a slight different behavior in comparison with the other synthesized samples, as the yield strength and flexural modulus are higher, which is due to the higher density of this materials[19,20]. In general, for all the samples studied, elongation at break seems to be more responsive to molecular weight distribution and more markedly to crystallinity and SCB level.

Additionally, an important limitation in the short-term mechanical properties is the resistance to rapid crack propagation (RCP), which is related with how a fast-moving brittle crack could propagate across the material, and is one of the main design criteria for limiting the operational pressures of polyethylene pipes. There are several factors that affect the resin RCP resistance, such as pipe geometry and test conditions[21,22]. Several investigations have indicated that the absorbed energy measured in a Charpy test is related to the resistance to fast fracture in a pressurized pipe[23]. Although there is some controversy with the association between the Charpy energies at room temperature and the small scale steady state S4 critical temperature (Tc)[24], this technique can be used as an indicator of the toughness of the materials. According to this, Table 2 shows the results of Charpy impact energy for all the samples, indicating that just polyethylenes synthesized with hydrogen present impact energy below than that corresponding to PE-100, which can be related with the important contribution of the quite low molecular weight chains for both samples, H2-CONT and H2-DISC.

- 12 -

Table 2. Short-term mechanical properties of the polymers obtained by Met-Cr-AlSBA-15 under different reaction conditions.

Sample	Hydrogen	Comonom[c]	Yield strength (MPa)	Elongation at break (%)	Flexural modulus (MPa)	Charpy impact energy (kJ/m^2)
H2-CONT	Cont.[a]	---	29.2	307	1664	16
H2-DISC	Discont.[b]	---	28.9	259	1639	19
C4	--	1-butene	17.9	512	937	30
C4-H2-CONT	Cont.	1-butene	23.6	497	1018	32
C4-H2-DISC	Discont.	1-butene	23.4	511	1026	38
C6	--	1-hexene	22.2	482	919	36
C6-H2-CONT	Cont.	1-hexene	25	526	1081	35
C6-H2-DISC	Discont.	1-hexene	26.8	467	1394	32
PE-100			23.5	531	981	20

[a]Continuous method: 1 Nl of H$_2$ was uniformly fed during the reaction time; [b]discontinuous method: 1 Nl of H$_2$ was added at the beginning of the reaction; [c]amount of comonomer =20 ml.

Regarding long-term mechanical properties, Slow Crack Growth (SCG) is the key long-term failure in polyethylene pipes and, hence the most critical parameter to control[25]. Under low stress upon an extended period of time, PE fails in a brittle mode[26,27]. This type of failure is typically considered in the design of pipelines, as a craze could be formed, during transport and installation, in the pipe, and can grow gradually until the brittle failure happens[28].

The long-term performance for synthesized polyethylenes has been studied through the PENT test that allows evaluating the SCG resistance. Accepted failure times for PE80 and PE100 pipe grades are above 30 and 500 hours[17,18], respectively. Therefore, as it can be observed in Table 3, polyethylenes obtained with both hydrogen and comonomers achieve the requirements for PE100 grade. It is remarkable that those polymers, C4-H2-DISC and C6-H2-DISC, in which hydrogen has been added just at the beginning of the polymerization, almost reach a PE100RC grade, that is, the fourth generation of polyethylene resins recently incorporated to the market with high resistance to crack (RC)[29]. Even though the resistance to SCG is dependent on molecular architecture, particularly molecular weight, branching, crystallinity and tie molecules[30,31] both polymers, C4-H2-DISC and C6-H2-DISC, present similar long-term characteristics presenting just the differences related to the comonomer employed in each case, as can be easily observed by the Strain Hardening (SH) modulus. SH is an accelerated test for

SCG resistance determination[32]. Polyethylene resins with 1-hexene as comonomer have higher SH values, especially in high resistance to failure resins. According to Dominguez et al.[29], for PE100RC grade, 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.

Therefore, the results obtained reveal that Met-Cr-AlSBA-15 catalytic system, under specific reaction conditions (hydrogen and comonomer), not only is it capable of producing bimodal polyethylene, but this polyethylene has very suitable characteristics for the manufacture of pipes.

Table 3. Long-term mechanical properties of the polymers obtained by Met-Cr-AlSBA-15 catalyst under different reaction conditions.

Sample	Hydrogen	Comonom[c]	PENT failure time (hours)	SH, Gp (MPa)
H2-CONT	Cont.[a]	---	19	27.5
H2-DISC	Discont.[b]	---	21	29
C4	--	1-butene	8	16.7
C4-H2-CONT	Cont.	1-butene	854	45.9
C4-H2-DISC	Discont.	1-butene	9331	50.4
C6	--	1-hexene	6	14.3
C6-H2-CONT	Cont.	1-hexene	491	42
C6-H2-DISC	Discont.	1-hexene	8541	59
PE-100			2185	37.2

[a]Continuous method: 1 Nl of H_2 was uniformly fed during the reaction time; [b]discontinuous method: 1 Nl of H_2 was added at the beginning of the reaction; [c]amount of comonomer =20 ml.

4. Conclusions

Properties of bimodal polyethylene synthesized in one-step reaction pathway, using previously developed Met-Cr-AlSBA-15 binary catalytic system, can be adjusted by changing the method employed for hydrogen feeding (continuous or at once) and using or not comonomer (1-butene and 1-hexene), due to the different response of each catalytic center, metallocene and chromium, to hydrogen and comonomer.

For both type of comonomers, 1-butene or 1-hexene, when using the discontinuous method for hydrogen supply, as there is a high concentration of chain transfer agent at the beginning of the

polymerization that affects more markedly to metallocene sites. Thus, the contribution of the low molecular weight fraction is smaller and the polymer presents lower polydispersity as well as lower HLMI values. In the same way, when using comonomers the contribution of the higher molecular weight chains is more prominent. Thus, the presence of both, hydrogen and comonomer, is necessary to achieve a bimodal polyethylene with suitable properties for high resistance applications.

In this regard, short-term mechanical properties of synthesized polyethylenes, such as yield strength as well as flexural modulus values, do not indicate any restriction for pipe application. The same occur observing the characterization of resistance to rapid crack propagation (RCP) through Charpy impact energy measurements, for which just polyethylenes synthesized only in the presence of hydrogen present impact energy below than that corresponding to PE100 grade. Therefore, just considering short-term mechanical properties, polyethylenes obtained without hydrogen, seem to have also appropriate characteristics for pipe manufacture. However, for this application, long-term mechanical properties are of fundamental importance, being Slow Crack Growth (SCG) resistance one of the major long-term failures in polyethylene pipes. Paying attention to short and, even more, to long-term characteristics measured, it can be concluded that Met-Cr-Al-SBA-15 catalytic system, under specific reaction conditions (both hydrogen and comonomer), produces polyethylene that perfectly fits the standard for the manufacture of pipes. Remarkably, when hydrogen is fed at once the properties are closer to those required for the last generation of PE100RC grades.

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