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Chromium oxide/metallocene binary catalysts for bimodal polyethylene: hydrogen effects.

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Abstract

Bimodal resins came up to meet application requirements: low molecular weight for good processability and high molecular weight for mechanical properties. For obtaining this bimodality there are several strategies: physical melt mixing of the two components produced separately, a single catalyst in two different serial reactors and a single reactor technology employing a tailor made catalyst and/or switching conditions. This last method has many advantages such as lower investment costs, less process complexity and intimate mixing of high and low molecular weight components (improved product quality). By means of this single reactor technology, bimodal polyethylene was synthesized using a mesostructured catalyst based on Al-SBA-15 where two active centers, chromium and metallocene, were incorporated. Ethylene polymerizations were carried out over binary catalysts (hybrid and mixed Cr-metallocene) and the polyethylenes obtained were compared with those obtained with individual catalysts in order to determine the contribution of each active centre. As well, the effect on polymer properties of the partial pressure of hydrogen in the reactor was evaluated. Results indicate that the hybrid catalyst (metallocene supported over Cr-Al-SBA-15) and physical mixture (Cr-Al-SBA-15 mixed with met-Al-SBA-15) lead to bimodal polyethylenes which combine high molecular weight, crystallinity and melting point with good processability (high melt index).

Keywords: chromium catalysts, metallocene catalysts, binary catalysts, bimodal polyethylene, chain transfer agent, molecular weight distribution.

1. INTRODUCTION

The possibility of widening polymer properties profile remains a fruitful field of research aimed at producing more versatile materials. In this sense, bimodality has become an additional degree of freedom in tailoring polyethylene (PE) properties. A bimodal polyethylene consists of a mixture of low and high molecular weight polyethylene fractions [1], where the term “bimodal” comes from the shape of the gel permeation chromatography curve, that is, a bimodal molecular weight distribution (MWD). As known, MWD is clearly related with the rheological properties having a great influence on polymer processing behaviour. Since an increase in the molecular weight normally improves the mechanical properties of the polyethylene resins, there is a strong demand for polyethylene having high molecular weight, although it also involves processing difficulties [2,3]. Therefore, bimodal resins came up as a result of the need to meet application requirements, having the best of both parts: low molecular weight for processability and high molecular weight for good mechanical properties.

Nowadays, bimodal resins usually employed is the polyethylene classified as PE100 (i.e., pipe must withstand hoop stress of 10 MPa for up to 50 years at 20 °C, ISO 12162) [4,5]. PE100 provides important advantages over earlier grades because combines the strength and stiffness of high density polyethylene (HDPE) with the high stress crack resistance and processability of unimodal medium density grades [2,6-8].

Bimodal polyethylenes can be made by producing the components or fractions separately and then physically melt mixing into a uniform blend, but these blends usually present miscibility problems as a consequence of some phases segregation [5,9,10]. Since there is a wide knowledge about the polyethylene structure-properties relationship, numerous polymerization technologies have been developed in order to tailor the polymer architecture, which is basically fixed by the process configuration and the catalyst employed. In this context, a two-stage cascade polymerization process is the most employed technology for bimodal polyethylene using a Ziegler-Natta catalyst [3,4]. In general, in the first reactor a high hydrogen/ethylene ratio is used, resulting in a relatively low molecular weight, highly crystalline homopolymer. Then, the still active catalyst, embedded in the homopolymer, is transferred to a second reactor, with much lower hydrogen/ethylene ratio and the presence of a comonomer such as 1-butene or 1-hexene. However, there are many advantages of using a single reactor with two catalysts for obtaining simultaneously both fractions, such as lower investment costs, easier to control, less process complexity, intimate mixing of high and low molecular weight components (improved product quality) and simplified start-ups and shut-downs [6]. For this single reactor bimodal technology, a greatly advanced catalyst design is required. Several papers have been published about recent advances in olefin polymerization using binary catalysts [9-18]. They include hybrid catalyst, consisting on two catalysts loaded on a support [3,9,10,16,19-22], and mixed catalysts, which is a physical mixture of two independent catalysts that are introduced in the reactor together [3,9,10,13]. In this sense, if different active sites could be attached to the same support particle, it would be possible to obtain an in-situ blend of polyethylene chains with different predominant molecular weights in only one stage process. Even the combination of two or more catalytic systems not supported on the same particle but mixed in the same reactor could lead to more intimate blend of the bimodal components at a molecular level and, thus improved homogeneity in product properties.

Different olefin polymerization catalysts can be combined in order to obtain these catalytic systems. Catalysts derived from a heterogeneous Ziegler-Natta or Phillips catalyst and single-site catalyst component represent some of the most interesting examples of binary catalysis. In general, Ziegler-Natta or Phillips type catalyst components produce the high molecular weight fraction that provides the greater toughness performance of the polymer, whereas the single site component gives the low molecular weight, which provides the lubrication needed to process the resin. Most of examples are combinations of Ziegler-Natta and metallocene catalysts [9,10,12,13,19,20,22,23] and also two different metallocenes [14,16,24,25].

Several examples of Phillips and metallocene combinations can be found in the late 90s patent literature [26-30], gaining recently some attention [31,32]. The so-called Phillips-type catalyst is basically silica-supported chromium oxide or silylchromate-on-silica [33]. It is well known that ethylene polymers having a broad MWD can be obtained using these catalysts due to its multiple site character [34]. On the other hand, polymers synthesized with metallocene systems, known as single-site catalysts, present a narrow molecular weight distribution, which makes difficult for these polymers to be processed although high impact resistance, rigidity and crystallinity are achieved [35].

Recently we have reported the synthesis of a novel chromium oxide/metallocene hybrid catalyst for bimodal polyethylene developed by supporting a MAO/metallocene system on a mesostructured chromium catalyst prepared by direct synthesis [32]. In this catalyst, the better dispersion of chromium centres achieved by using the direct synthesis method [36] together with their presence inside silica walls allow a higher contribution of chromium sites in the overall productivity and, therefore, a greater contribution in the molecular weight distribution. In the present work, the hydrogen effect over this hybrid catalyst as well as over the parent physical mixture is explored.

It is well known that hydrogen is a chain transfer agent that allows controlling the molecular weight of the polymer product when using metallocenes as well as Ziegler-Natta catalysts [37-42]. As previously mentioned, it has been widely employed in the two-stage cascade polymerization processes for bimodal polyethylene [3,4,40] but also in a single slurry reactor [43] and with binary catalysts [9,10,25,31,44]. Typically, the molecular weight of the polyethylene produced with a Phillips catalyst is strongly dependent on the temperature of polymerization, and it is very little affected by the presence of hydrogen [33], while for metallocenes it was observed that hydrogen has a large effect not only on the product molecular weight but also on the catalyst activity [18,35]. Therefore, taking the advantage of the different behaviour of Phillips and metallocenes catalysts with hydrogen, a tailor-made catalyst could be obtained by combination of such systems balancing properly the molecular weight distribution and the catalyst activity with the goal of achieving an efficient bimodal polyethylene in a single reactor.

Based on the above mentioned considerations, a chromium–aluminium containing SBA-15 mesoporous catalyst was prepared by direct synthesis (Cr-Al-SBA-15) [32], as well as an aluminium-containing mesostructured SBA-15-type material [45], employed as support of the catalytic system (nBuCp)₂ZrCl₂/MAO (met-Al-SBA-15). Chromium and metallocene individual catalysts were used to prepare by one hand a physical mixture (Cr-Al-SBA-15 + met-Al-SBA-15). Besides, an hybrid catalyst was obtained by impregnation of (nBuCp)₂ZrCl₂/MAO over Cr-Al-SBA-15 (met-Cr-Al-SBA-15). Firstly, the influence of tri-isobutylaluminum (TIBA) amount in the reaction medium was analyzed with individual Cr-Al-SBA-15 and met-Al-SBA-15 catalysts since, as known, metal alkyl cocatalysts can improve or diminish the activity. For a chosen amount of TIBA, the effects of hydrogen concentration on the catalysts behaviour and polyethylene properties were analyzed comparing binary systems with individual catalysts in order to know the contribution of each kind of active site to the bimodal products.

2. MATERIAL AND METHODS

2.1. Catalysts preparation and characterization

The chromium–aluminium containing SBA-15 mesoporous catalyst (Cr-Al-SBA-15) was prepared as follows [36]: 4 g of triblock copolymer EO₂₀-PO₇₀-EO₂₀ (Pluronic 123, Aldrich) were dissolved in 150 ml of aqueous solution of HCl at pH 3. At the same time, 8.6 g of tetraethylorthosilicate (TEOS, 98%, Aldrich) and 0.276 g of aluminium isopropoxide (AIP, >98%, Aldrich) to get aSi/Al molar ratio = 30, and 0.55 g of

chromium(III) nitrate (99%, Aldrich) to reach the same Si/Cr molar ratio (30) were dissolved into 10 ml of the aforementioned aqueous HCl solution. Both mixtures were stirred for 4 h at room temperature and then, the latter was added over the first one. The final solution was stirred for 20 h at 40 °C and, subsequently, aged at 110 °C for 24 h under static conditions. The solid product was recovered by filtration, dried at room temperature overnight and calcined at 600 °C for 5 h (heating rate = 0.4 °C·min⁻¹) under air flow in order to remove the surfactant and oxidize Cr(III) to Cr(VI).

The Al-SBA-15 material was prepared according to the synthesis procedure reported by Yue et al. [45], which consists in the same steps as the above described for Cr-Al-SBA-15 without chromium precursor addition. Heterogeneous metallocene catalyst (met-Al-SBA-15) was prepared under inert nitrogen atmosphere using Schlenk techniques and a glove box, by impregnating 1 gram of the synthesized Al-SBA-15 with a liquid solution containing methylaluminoxane (MAO, 10 wt% in toluene, Aldrich) previously diluted with dry toluene (99 wt%, Scharlab) and bis(*n*-butylcyclopentadienyl)zirconium dichloride ((*n*BuCp)₂ZrCl₂, 97 %, Aldrich) [46]. The process was performed at room temperature in a stirred vessel during 3 hours. Finally, the solid was dried under nitrogen flow and stored in glove-box. The same procedure was followed to obtain the hybrid catalyst (met-Cr-Al-SBA-15), except by impregnation of 1 gram of Cr-Al-SBA-15 instead of Al-SBA-15 as support.

The physical mixture of both catalysts (Cr-Al-SBA-15 + met-Al-SBA-15) was prepared according to their individual catalytic activity with the aim of having a 50 % of contribution from each catalyst to the overall polymerization activity.

Catalysts textural properties were determined by nitrogen adsorption-desorption isotherms at 77 K obtained with a Micromeritics Tristar 3000 apparatus. Surface areas were calculated with BET equation whereas pore size distributions were determined by the BJH method applied to the adsorption branch of the isotherms. Mean pore size was obtained from the maximum of BJH pore size distribution. Aluminium, zirconium and chromium contents of the supported catalysts were determined by ICP-AES on a Varian Vista AX Axial CCD Simultaneous ICP-AES spectrophotometer.

2.2. Ethylene polymerization

Ethylene polymerizations were performed at 70 °C in a 2.0-L stirred stainless-steel reactor filled with of 1.0-L *n*-heptane (99 %, Scharlab) as diluent, and triisobutylaluminum (TIBA, 30 wt% in heptane, Witco) as scavenger. Ethylene (99.99 %, Air Liquide) was deoxygenated and dried through columns containing R-3/15 BASF catalyst, alumina and 3 Å molecular sieves. The flow rate needed to keep a constant pressure of 5 bars during the polymerization was measured with a mass-flow indicator (Bronkhorst Hi-Tec). When using hydrogen, it was loaded at the beginning of the polymerization. After 30 minutes, the polymerization was stopped by depressurization and polyethylene (PE) was recovered, filtered and dried for 12 hours at 70 °C. Polymerization activities (g PE/g_{CAT}·h) were calculated dividing the weight of dry PE produced by the weight of catalyst used in the reaction.

2.3. Polymer characterization

Molecular weight distributions were determined with a Waters ALLIANCE GPCV 2000 gel permeation chromatographer (GPC) located in the Polymer Technology Laboratory (LATEP) of Universidad Rey Juan Carlos. This apparatus is equipped with a refractometer, a viscosimeter and three Styragel HT type columns (HT3, HT4 and HT6) with exclusion limits of 1×10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of $1 \text{ cm}^3 \cdot \text{min}^{-1}$. The analyses were performed at $145 \text{ }^\circ\text{C}$. The columns were calibrated with narrow molar mass distribution polystyrene and with linear low density polyethylenes standards.

Polymer melting points (T_m) and crystallinities were determined in a METTLER TOLEDO DSC822 differential scanning calorimeter (DSC), using a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ in the temperature range $23\text{-}160 \text{ }^\circ\text{C}$. The heating cycle was performed twice, but only the results of the second scan were reported, because the former could be influenced by the mechanical and thermal history of the samples. Crystallinity was calculated considering that melting enthalpy of a 100 % crystalline polyethylene is 288.4 J/g .

Melt flow index (MI) was measured in a Melt Flow Tester 2000 at $190 \text{ }^\circ\text{C}$ under a 2.16 kg loading according to ISO 1133.

Dynamic mechanical analysis (DMA) was carried out with a DMA Q800 V 7.1 Build 116 from T. A. Instruments at fixed frequency (1 Hz) with a heating rate of $2 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ between -60 and $130 \text{ }^\circ\text{C}$, being the sample dimensions between the clamps $40 \times 13 \times 2 \text{ mm}$.

3. RESULTS AND DISCUSSION

3.1. Ethylene polymerization over individual chromium and metallocene catalysts

Table 1 summarizes textural properties obtained from nitrogen adsorption-desorption isotherms for Al-SBA-15 support and Cr-Al-SBA-15 catalyst. There is no significant variation related with the incorporation of chromium during the Al-SBA-15 synthesis. Differences can be observed when compared with pure silica SBA-15 materials, since the introduction of a heteroatom usually causes local distortions leading to higher textural properties since Al–O and Cr–O bonds are longer than Si–O bond [36,45]. Both synthesized materials have aluminium content close to 1.5 wt\% (Table 2), which corresponds to a Si/Al molar ratio of 30. Chromium content is a little bit higher than 1 wt\% , the fixed amount for commercial catalysts [33], while $\text{Al}_{\text{MAO}}/\text{Zr}$ molar ratio is near 190, according to previous studies [46].

The prepared single catalysts, Cr-Al-SBA-15 and met-Al-SBA-15, were polymerized in the presence of different amounts of tri-isobutylaluminum (Figure 1). As it is known, Phillips catalysts do not require cocatalysts, so at most, TIBA acts as impurities scavenger enhancing the catalyst activity [33]. However, metallocenes require a cocatalyst to reach a significant activity level, being methylaluminoxane the most employed one due to its unique effectiveness compared with other aluminium alkyls and metallocene activators [18]. In this work, methylaluminoxane is impregnated on the support to activate the metallocene $(n\text{BuCp})_2\text{ZrCl}_2$ while TIBA is added to the reactor

as an impurities scavenger although it can also act as cocatalyst [47]. Therefore, the amount of TIBA employed should be optimized since it can affect the activity of both chromium and metallocene catalysts. A maximum in the activity can be observed in Figure 1 for Cr-Al-SBA-15 and met-Al-SBA-15 catalysts at a given amount of TIBA. Aluminium alkyls enhance overall activity primarily by accelerating the development of polymerization rate; the induction time is shortened (and usually eliminated), and the polymerization rate then rises to its maximum more quickly. However, for Phillips catalysts larger amounts can result in loss of activity probably by an attack on the Cr-O-Si bonding link [33], although coordination of the reduced chromium with the aluminium alkyl has also been suggested as a possible reason for the loss in activity [48]. This coordination can also occur in metallocenes between zirconium and the aluminium alkyl causing either a reduction in the number of active sites or a change in active site type to a less active form [47,49]. In all the range studied, the catalytic activity of Cr-Al-SBA-15 is lower than the corresponding to met-Al-SBA-15 and, therefore the preferred amount of TIBA is 0.75 mL as it leads to the Cr-Al-SBA-15 highest polymerization activity.

The characterization of the polyethylenes obtained with both single catalysts at such reaction conditions is summarized in Table 3 (see data for $P_{H_2} = 0$ bar), which shows the typical differences between Phillips and metallocene polyethylenes related to multiple and single site character respectively. Cr-Al-SBA-15 produces a polymer with a broad MWD, having a polydispersity of 15.42; in contrast, polyethylene obtained by met-Al-SBA-15 has a polydispersity index of 2.25. The different MWD lead to distinctive flow characteristics of the melted resins that determines what kind of molding processes can be used. When the molecular weight distribution is broad, it makes the polymer more shear thinning during molding, that is, the short chains lubricate the movement of the long ones. The molten polymer therefore exhibits lower viscosity at high shear rate during extrusion, but under conditions of low shear rate, it exhibits higher viscosity, which increases the melt strength [50]. Apart from MWD, the average molecular weight also determines the processability, since a low melt flow rate corresponds to high molecular weight and, therefore this is the case for the polyethylene obtained with the Phillips catalyst (Cr-Al-SBA-15) as it is shown in Table 3.

As mentioned before, a bimodal resin based for example, on this high molecular weight polyethylene together with a polyethylene with lower molecular weight coming from metallocene catalyst would benefit from advantages present by the use of both fractions. However, the differences between the MWD of these two polyethylenes cannot lead to a bimodal polymer as it is shown clearly from the overlapping of distributions (Figure 2). Therefore, it is quite interesting to modify the molecular weight of the polyethylene obtained by the metallocene while maintaining the one produced by the chromium catalyst. In this sense, hydrogen is the most employed chain transfer agent and it is supposed to affect the molecular weight of the polyethylene produced by the metallocene catalyst while not so much to that produced by the Phillips catalyst [33,37-41].

The hydrogen effect was studied with the two individual catalysts, Cr-Al-SBA-15 and met-Al-SBA-15, at 0.2 and 0.5 bar of hydrogen partial pressure. Figure 3 shows the hydrogen effect on the catalytic activity revealing a decrease for both catalysts as the

hydrogen partial pressure increases. Although H₂ added to the reactor usually has no detrimental effect on the activity of Cr/silica [33], the sensitivity of chromium oxide catalysts can vary considerably, depending on the support, suggesting that various sites behave quite differently. Moreover, it has been reported that the addition of aluminium ions to Cr/silica can also sometimes increase the H₂ sensitivity although not as far as with Cr/alumina, which is highly responsive to H₂ as chain transfer agent [33]. Therefore, as the support contains aluminium (Al-SBA-15) some hydrogen effect in the catalytic activity is observed.

In the ethylene polymerization with metallocenes, the deactivating effect of hydrogen is due to the β -agostic coordination of hydrogen atom in the ethyl group (formed after hydrogen termination) with the monomer. No further polymerization can take place in the β -agostic coordinated sites and, therefore the more hydrogen that is present in the polymerization process, the more hydrogen terminations take place and more β -agostic coordinated sites [18,35,39,42]. These hydrogen terminations or chain transfer via hydrogenolysis lead to saturated end-groups and a decrease in the molecular weight is observed for polyethylene obtained with the metallocene catalyst (met-Al-SBA-15) (Table 3) [39-41]. With this catalyst an important increment in polyethylene polydispersity is also observed as hydrogen partial pressure increases, not due to peak broadening but to a higher molecular weight halo. This evidence could be related to the experimental conditions since hydrogen is added at the beginning of the polymerization [39,51].

On the other hand, the polyethylene produced with hydrogen by the chromium catalyst shows a slight increment in polydispersity index and, thus in the molecular weight distribution (Table 3, Figure 4) as the addition of hydrogen increases low molecular weight fraction at the expense of high molecular weight material [33], which results in increasing values of melt flow index (Table 3). No significant effect of hydrogen can be observed over thermal properties for polyethylene produced by Cr-Al-SBA-15, while an increment in crystallinity as well as a decrease in melting temperature is achieved with met-Al-SBA-15 (Table 3) due to the important role of hydrogen as chain transfer agent with metallocenes [39-41].

3.2. Ethylene polymerization over chromium-metallocene physical mixture and hybrid catalyst

Figure 5 shows activity results of the polymerizations carried out by using mixed and hybrid catalysts with different hydrogen partial pressures. Activities of individual catalysts are also included for comparison purposes. As observed, without adding hydrogen, hybrid catalyst presents higher activity than the physical mixture. Besides, it is more sensible towards the presence of this chain transfer agent, as indicates the higher decrease of the activity observed by increasing the hydrogen pressure from 0 to 0.5 bar.

These results seem to indicate that metallocene contribution to the total activity is higher for the hybrid system than for the combination of individual catalysts. This fact can be confirmed by polymer properties showed in Table 4. Thus, polyethylene produced by met-Cr-Al-SBA-15 without using hydrogen presents lower polydispersity (5.46) and molecular weight (384000) than those corresponding to the polyethylene

obtained with the physical mixture (16.6 and 570000, respectively). It is possible that this behaviour would be related to the preparation method of the hybrid catalyst since chromium activity is more affected by MAO species in this case (the impregnation of MAO/metallocene system is directly carried out over Cr-Al-SBA-15), than by mixing the individual catalysts [32].

By increasing hydrogen pressure, it is remarkable the increase of polydispersity and melt index observed in both cases (hybrid and mixed catalysts) which indicates a clear growth of the number of short chains. As explained above, the higher termination rate produced by hydrogen leads to polyethylene chains with lower molecular weight. In the same way that for individual catalysts, the presence of hydrogen also produced an increase of polymers crystallinity although in this case, no effect is observed on melting temperatures.

Figure 6 shows molecular weight distributions of polymers obtained with the hybrid and mixed catalysts by working with 0, 0.2 and 0.5 bar of hydrogen. As expected, by increasing hydrogen pressure, a great modification of the GPC curves is observed turning up a clear signal at low molecular weight corresponding to the shorter polyethylene chains. Thus, polymers obtained present a clear bimodality in their molecular weight distributions. In conclusion, hybrid and mixed catalysts can produce bimodal polyethylenes when hydrogen is added into the reactor. It is remarkable that obtained polymers combine high average molecular weight, crystallinity and melting point with good processability (high melt index, see Table 4).

Figure 7 shows DMA results for polyethylenes obtained at 0.2 bar H₂ with individual and binary catalysts. The variation of the storage modulus (E'), loss modulus (E'') and $\tan \delta$ with the temperature is presented for all the polymers. The storage modulus is related to the elastic capacity of the materials and it can be used as a measure of the necessary stress for producing a reversible deformation. As observed, for all the cases, it decreases by increasing the temperature showing a typical behavior of polymeric materials. This behavior is related to the increase of chains movements and relaxation times produced by raising the temperature [52,53]. The loss modulus is a measure of the energy consumed for chains displacements (energy necessary for movements and lost by friction). Thus, this parameter depends on the capacity of the materials for using the energy associated with an external stress to change their microstructure [54]. Values of E' and E'' are slightly lower for polymers coming from binary systems, especially at lower temperatures, probably due to the combination of their high molecular weight and crystallinity. Finally, the combination of E' and E'' values leads to $\tan \delta$ curve. Very similar curves of $\tan \delta$ can be observed for all the evaluated materials. Thus, results indicate that between 60 and 130 °C the four samples exhibit two transitions; specifically they correspond to the called β and α transitions. Although there is much controversy on the nature of these transitions, it is believed that their existence and location are related to the motions of the amorphous and crystalline parts of the polyethylene [52-54]. The β -transition is generally associated with the easier displacement of the amorphous part of polyethylene occurred between glass transition and room temperature and, therefore it is practically absent since it is homopolyethylene. On the other hand, α transition, usually located above 50 °C, could be attributed to the motion of polymer chain inside crystalline units before reach the

melting point. These movements lead to an increase of loss modulus reaching a maximum and thus, an increase of $\tan \delta$. Results of E'' curve indicate that polyethylene coming from metallocene achieves the maximum of loss modulus (α -transition) at lower temperature (47.4 °C) than the sample prepared by chromium (52.8 °C). This fact is probably related to its lower molecular weight and melting point (see Table 4) which make easier the movements of chains within crystalline units at lower temperature. For polymers coming from binary catalysts, the maximum of loss modulus is located at temperatures very similar to that obtained with chromium one (52.6 °C for hybrid catalyst and 52.0 °C for physical mixture) indicating a clear influence of chromium centres on microstructure of bimodal products.

4. CONCLUSIONS

The combination of both metallocene and chromium centres to prepare a mesostructured binary catalytic system allows the production of bimodal polyethylene in only one step polymerization process by using hydrogen as chain transfer agent. Hybrid catalyst (metallocene impregnated on Cr-Al-SBA-15) presents a higher contribution of metallocene sites than the physical mixture (Cr-Al-SBA-15 mixed with met-Al-SBA15) because, in the first case, Cr sites are more affected by the presence of MAO used during metallocene incorporation. Hydrogen has a strong influence on metallocene sites leading to an important reduction of the polymer chains length, whereas chromium centres are less sensible to the presence of hydrogen. Hybrid catalyst and physical mixture presented a similar behaviour by increasing partial pressure of hydrogen in the polymerization reactor, leading to a more pronounced bimodal molecular weight distribution. Results indicate that binary catalysts lead to bimodal polyethylenes which combine high molecular weight, crystallinity and melting point with good processability (high melt index). Finally, dynamic mechanical analysis points that α transition of polyethylenes coming from binary systems takes place at higher temperature than the corresponding to the sample obtained with metallocene catalyst due to the contribution of chromium centres to the microstructure of the bimodal product.

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