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Chromium oxide/metallocene binary catalysts for bimodal polyethylene: Hydrogen effects

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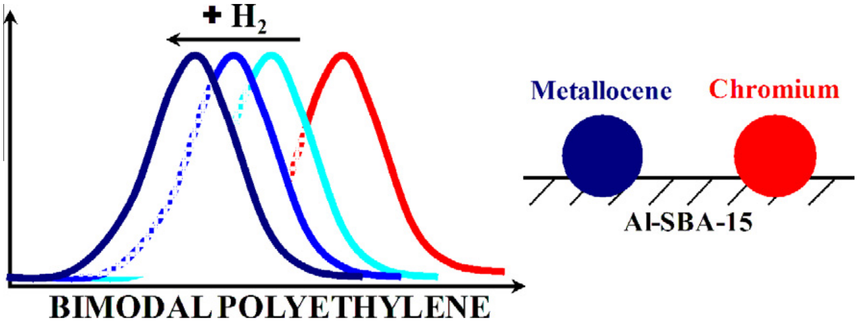
HIGHLIGHTS

- Bimodal polyethylene can be obtained by chromium–metallocene catalysts.
- These binary catalysts are able to run in one-step polymerization process.
- Chromium and metallocene catalytic centres present different behaviour with hydrogen.
- Properties of bimodal polymers can be adjusted by changing hydrogen concentration.
- Obtained bimodal polyethylenes combine high molecular weight with processability.

GRAPHICAL ABSTRACT



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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 centres, 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).

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

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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 shutdowns [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 1990s 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 a 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 $(n\text{BuCp})_2\text{ZrCl}_2$/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 $(n\text{BuCp})_2\text{ZrCl}_2$/MAO over Cr–Al-SBA-15 (met-Cr–Al-SBA-15). Firstly, the influence of tri-isobutylamunimum (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. Materials 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 EO_{20}-PO_{70}-EO_{20} (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