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Review

Influence of stereospecificity and molecular weight on mechanical properties of iso-syndio-polypropylene obtained by combination of metallocene catalysts

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ABSTRACT

Polypropylene with special properties can be obtained using two supported metallocene catalysts of different stereospecificities: rac-$Me_2Si(2\text{-}Me\text{-}benz[e]Ind)_2\ ZrCl_2$ [CAT-B] as an isotactic catalyst precursor and $Ph_2C(Cp)(9\text{-}Flu)ZrCl_2$ [CAT-C] as a syndiospecific catalyst precursor supported on silica/MAO. These catalysts were evaluated either isolated or as a binary system. Catalysts physical mixtures and hybrid catalysts were prepared at three proportions, and tested in propylene polymerization. The effect to the activity and presence of hydrogen in the structural and mechanical properties of resultant polypropylenes were investigated. The influence of the binary systems containing more than half of the syndiotactic fraction on the molecular and mechanical properties respect to the isotactic polypropylene was evaluated. The great contribution of the sPP was observed in the polypropylene synthesized with the catalysts physical mixtures in absence of hydrogen. These samples showed a reduction of the crystallinity leading to an increase in the stress at break, because the flexion resistance is reduced. Polymers obtained with hybrid catalysts have an average molecular weight and crystallinity nearly to isotactic polypropylene with a break at very low strains, and high modulus.

1. Introduction

Since the discovery of stereo selective olefin polymerization in 1958 [1], and the development of polypropylene (PP) by Natta using Ziegler type catalysts, PP has become one the most commercially important thermoplastic. Two years later, syndiotactic polypropylene (sPP) was considered only a scientific curiosity because it showed unprofitable properties due to the low stereoregularity of the macromolecules synthesized with Ziegler-Natta catalyst [2]. But in the middle of 1980s, a rebirth of sPP was observed due to the possibility of obtaining this thermoplastic with the new single-site metallocene catalyst [3]. Some of these new catalysts were highly syndiospecific and therefore suitable for producing very crystalline sPP with a high melting temperature. The physical and chemical properties of metallocene sPP resulted completely different from those ones presented by isotactic polypropylenes. It fact, they exhibit better toughness, greater heat stability, tear resistance, ductility, elasticity and transparency, among other advantages.

The reason for the aforementioned differences in properties of both stereoisomers lies on the alternating position of methyl groups

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Abbreviations: [CAT-B], $Me_2Si(2\text{-}Me\text{-}benz[e]Ind)_2\ ZrCl_2$ as an isotactic catalyst precursor; [CAT-C], $Ph_2C(Cp)(9\text{-}Flu)ZrCl_2$ syndiospecific as a syndiotactic catalyst precursor; [iPP-B], polypropylene obtained by [CAT-B]; [sPP-C], polypropylene obtained by [CAT-C]; [iPP-B] + [sPP-C], polypropylene produced by physical mixture; [iPP-B]/[sPP-C], polypropylene produced by hybrid catalyst

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along the sPP macromolecules. Such configuration gives a high flexibility to the chain together with a high density in the molten state, providing a great resistance to large-scale molecular motions. These features account for a relatively low value of melting temperature as well as a low value of the maximum attainable degree of crystallinity and the slower rate of crystallization when compared with isotactic polypropylene (iPP).

Polymer blends are now regarded as an economical alternative to the development of new polymers. Materials with improved end use properties can be obtained by blending polymers with different molecular characteristics. Therefore, the possibility to produce a polypropylene mixture consisting on the polymer fractions produced by metallocene catalysts differing in their stereospecificity can provide intermediate characteristics to the polymer. Consequently, this kind of polypropylenes can present thermoplastic elastomeric properties without a decrease in barrier properties keeping the processability thanks to the isotactic fraction of the polymer [4,5].

The economical and attractive route to produce polypropylene with multimodal molecular weight distributions (MWD) and controlled molecular weight (M_w) is the combination of a binary or multicomponent catalytic system in a single reactor with the subsequent cost saving. The details of the polymerization mechanism of polypropylene involving binary zirconocene systems are unclear because the interaction between propagating chains on dissimilar metallocenes is discernible if the catalyst species differ in stereospecificity.

On the other hand, most existing processes for the production of polypropylene working in gas phase or “slurry”, so it is necessary to immobilize the metallocene catalyst, which is inherently homogeneous, on an inert support [6,7] as can be SiO_2 [8–11]. Supported catalyst have advantages over their counterparts not supported, resulting in polymers with higher molecular weight also required smaller amount of cocatalyst (MAO) for activation and enable the control of polymer particles size and shape [12]. There are different methods of heterogeneization [11,13–15]. The advantage of using a direct heterogeneization, where the metallocene is active by MAO and then anchored onto the support, is that allows producing polymers with higher molecular weight than those afforded by the appropriate homogeneous catalysts [9] as were evaluated in a previous work [16] and maximizes the number of active centers by activating the metal component in solution, producing high catalytic activities even for low AL/Zr ratios.

It is well known that hydrogen is a chain transfer agent that allows controlling the molecular weight of the polymer products when using metallocene as well as Ziegler-Natta catalysts [17,18]. Hydrogen has a positive effect on the catalyst activity while polymer molecular weight decreases because β-H transfer to Zr after secondary monomer insertion is favoured.

Based on the above mentioned and considering the importance to develop new propylene based materials in the world market, the aim of this work was to evaluate the influence of the addition of a syndiospecific polypropylene having elastoremic characteristics on an isotactic polypropylene, where the percentages of iPP and sPP, their molecular weight, isotacticities, and melting transition temperatures (T_m) can all be modified. Trying to reach this goal, two heterogeneous metallocene of different stereospecificities have been selected: the isotactic catalyst rac-Me_2Si(2-Me-benz[e]Ind)$_2ZrCl_2$ denoted as [CAT-B] and the syndiotactic catalyst Ph_2C(Cp)(9-Flu)$ZrCl_2$ denoted as [CAT-C]. Individual and binary catalytic systems were heterogeneized using silica as support. The catalysts activity and the polypropylene properties obtained with binary systems have been determined and compared with polypropylenes obtained by the individual supported catalysts in order to evaluate their influence in the mechanical properties. Additionally, the hydrogen effect on the molecular weight of polypropylene blends have been evaluated.

2. Experimental part

2.1. Catalysts preparation

Commercial silica from INEOS Silicas Ltd was employed as support. Silica was calcined according to the procedure reported in a previous work [19]. Nitrogen adsorción/desorcion analysis at 77 K were obtained with a Micromeritics Tristar 3000 apparatus. Textural properties were presented in Table 1.

2.1.1. Individual heterogeneous systems

Metallocene precursor was prepared under inert nitrogen atmosphere using Shlenck techniques by impregnating 1.0 g of silica with a 12 mL of methylaluminoxane (MAO, 10 wt% in toluene, Sigma-Aldrich) in toluene (≥99.5%, Sigma-Aldrich) at room temperature for 15 min. The process was stirred in a rotary evaporator for 3 h until the solvent was evaporated. The concentration of Al and Zr in the grafting solution was calculated to achieve 23 wt% and 0.57 wt% in the solid catalyst respectively, corresponding to a Al/Zr molar ratio of 136. The same process was followed to obtain [CAT-B] rac-Me2Si(2-Me-benz[e]Ind)$_2$ $ZrCl_2$ (Boulder Scientific company) and [CAT-C] Ph_2C(Cp)(9-Flu)$ZrCl_2$ [CAT-C] (Boulder Scientific company). Both metallocene structures are shown in Scheme 1.

Polypropylenes obtained by [CAT-B] and [CAT-C] will be named as [iPP-B] and [sPP-C], respectively.

Table 1
Textural properties corresponding to the silica after calcined threatment.

Support	V_{pore} (cm^3/g)	Area BET (m^2/g)	$D_{medium\ pore}$ (nm)
Silica	1.14	256	28