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Influence on properties and phase structure of single gas-phase reactor made impact polypropylene copolymers

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ABSTRACT

Impact polypropylene copolymers (IPC) are materials important for many commercial applications. These materials are usually synthetized by different methods involving two consecutive reactions: in liquid, gas or liquid-gas phase. This work presents a method of synthesis in a laboratory scale based on two sequential steps in only one reactor in gas phase. Variables such as H_2 addition, reaction time, and composition during the second step were studied, and their influence on the formation of propylene-ethylene copolymer materials with different properties was analyzed. The IPC materials so obtained were characterized by analytical temperature rising elution fractionation (TREF), calorimetric methods (DSC), ^{13}C nuclear magnetic resonance (^{13}C NMR), gel permeation chromatography with an infrared detector (GPC-IR5), Charpy impact, and scanning electron microscopy (SEM).

The isotactic polypropylene matrix (iPP) obtained in the first step of the gas-phase process displays spherical morphology and lower mean particle size than those obtained in the liquid-phase process, even though the polymer grains experimented a certain tendency to agglomerate.

In particular, hydrogen addition caused a significant decline in the catalyst productivity and dramatically shortened the length of the propylene homopolymer chains. Similarly, the presence of hydrogen on the synthesis of ethylene-propylene copolymers was demonstrated to lead to materials with very low molecular weight, low ethylene incorporation, and rubbery phases irregularly distributed along the iPP matrix and therefore with poor impact properties.

On the other hand, ethylene-propylene copolymers synthesized without hydrogen yielded a suitable combination of molecular weights and molecular weight distribution that can contribute to good polymer processing and were proven to incorporate adequate amounts of ethylene mainly randomly distributed into the iPP matrix. SEM measurements revealed that the amorphous rubbery phase was homogeneously dispersed in the iPP matrix, and the Charpy test allowed to rank these materials as IPC.

Finally, fractionation of IPC materials by preparative TREF provided information about the microstructure formation. Subsequent studying of molecular weights and composition of the fractions by GPC-IR, analytical TREF, and DSC measurements based on the ethylene-propylene composition and ethylene distribution in the molar mass molecules was shown to enable the design of IPC materials. Additionally, the optimal IPC material was compared with the best IPC using liquid-phase polymerization, and the results showed that the range of ethylene-propylene composition, as well as the ethylene distribution in IPC molar mass molecules, correlated with IPC mechanical behavior.

1. Introduction

Polypropylene (PP) is a widely used thermoplastic material due to its excellent mechanical properties. However, isotactic polypropylene (iPP) has been known to have very poor low-temperature impact properties. An efficient method to improve the impact strength of iPP is to add elastomers or ethylene copolymers to the iPP matrix. Among them, the in-reactor blending of iPP with other polyolefins (especially ethylene-propylene rubber [EPR]) by sequential multistage polymerization seems to be the best method for iPP impact strength improvement [1]. The excellent impact property, especially at low temperatures, makes these materials, commonly named impact

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polypropylene copolymers (IPCs), important for many commercial applications [2]. IPC materials are synthesized by solid catalyzed olefin polymerization in a multistage process [3] consisting of a set of reactors in series [4]. In the first stage, iPP molecules are synthesized. The powder flows entering in a second reactor connected in series, and ethylene and propylene are added to produce rubbery domains that embed into the iPP matrix. IPC molecules obtained from this sequential polymerization are very complex and include amorphous and crystalline propylene-ethylene copolymers with different monomer length distributions and molar masses [5]. Therefore, the different crystalline and noncrystalline components make IPC excellent materials for several impact-related applications even at low temperatures [6].

Hybrid technology development is an area of active research. Thus, slurry, gas phase, and/or a combination of both types of reactors connected in series are used for synthesizing IPC materials [7]. If slurry and gas-phase polymerization reactors are compared, the distinctive feature of liquid-phase systems is the use of a solvent, which requires some additional equipment, such as solvent stores, solvent purification, solvent removal, and powder drying sections. Thus, gas-phase processes are more compact and simpler, and therefore, there is a reduction in the building and operating costs of the plants, as well as a diminution of their environmental impact over the conventional liquid-phase processes [8,9]. Moreover, the slurry processes complicate the synthesis of some polymers according to the density property variations along the synthesis since the polymer solubility can be affected. Another disadvantage of the liquid-phase processes over the gas-phase processes is that the solution viscosity boosts as the molecular weight increases. This increment can limit the reactor performance and productivity reaction. Therefore, a major advantage of the gas-phase processes is it has no constrictions by solubility and viscosity, which allows synthesizing polymers with a significant range of comonomer content, enabling the synthesis of the IPC materials. Thus, commercial gas-phase processes such as Unipol, Innovene, and Novolen account for approximately 45% of propylene [10]. Union carbide gas phase UNIPOL PP Process Technology (UNIPOL) is a gas-phase technology that occurs in a fluidized bed reactor system [11]. Fluidization is achieved through a blower, which circulates the gas and provides mixing to ensure the adequate distribution of the polymer and catalyst components throughout the bed. For impact copolymers, a second smaller fluidized bed is linked in series with the first reactor; this second reactor is fed by both propylene and ethylene monomers. The homopolymer made in the first reactor, which still contains the active catalyst, is transferred to the second reactor, where the catalyst continues to react with the olefin mixture to produce the rubber phase of the IPC [12].

The INEOS Technologies Innovene polypropylene (PP) process is a widely used gas-phase process to produce polypropylene. A typical Innovene polypropylene process configuration consists of one horizontal stirred-bed gas-phase reactor to form a propylene homopolymer or random copolymer and one downstream horizontal stirred-bed gas-phase reactor to produce impact propylene copolymers [13].

In this work, an approach based on two sequential steps in a single gas-phase reactor triggered by a Ziegler–Natta catalyst was used to obtain IPC materials. The variables of this process have been studied, and the morphological characteristics of IPC materials were compared with those previously obtained by our group in a liquid-phase process [14]. Mechanical performance was obtained from the notched Charpy impact strength. Thermal properties in solution and solid state were determined using temperature rising elution fractionation (TREF) and differential scanning calorimetry (DSC) methods. Molecular microstructure was acquired using liquid state ^{13}C nuclear magnetic resonance (^{13}C NMR) and gel permeation chromatography (GPC), and finally the morphology and distribution of the EPR phase in the iPP matrix was determined using scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Propylene, ethylene, and hydrogen were supplied by Praxair SA (99.99%) and the solvent n-heptane by Scharlab SA (99%). All polymers were synthetized using a standard $TiCl_4/MgCl_2$ Ziegler–Natta catalyst containing 2.5 wt% Ti, triethylaluminum was used as a cocatalyst and scavenger (TEA 1M in n-heptane, supplied by Witco), and cyclohexylmethyldimethoxysilane (C-donor, Wacker Química Ibérica SA) was used as an external donor. Sodium chloride used for every experiment in gas phase was supplied by Scharlab SA.

2.2. Synthesis procedure

Reactions were carried out in a 2-l autoclave reactor. A jacketed steel vessel allowed heating the reaction volume with a water bath by a thermostat (Julabo) at 70 °C for all the runs. Monomers were fed through calibrated gas flow meters, supplied by Bronkhorst Hi-Tec. The most important difference of the gas-phrase process over the liquid-phase process was the stirrer. Thus, a gas-phase helical stirrer was designed to obtain a homogeneous medium without a solvent (Fig. 1a). The helical stirrer forced the powder mixture to move upward along the reactor wall and downward along the stirrer shaft under the influence of gravity. A lower propeller stirrer had been mounted to whirl up the powder on the bottom of the reactor. The cooling system was modified, and the coil placed inside the reactor, which allowed the internal refrigeration usually used in the liquid-phase reactor, was removed, and the thermocouple was placed next to the axis through the center of the stirrer.

Fig. 1b shows the polymerization procedure that requires two steps: (1) homopolymerization and (2) copolymerization. In this work, polypropylene homopolymer and IPC with different amounts of ethylene monomer and with or without hydrogen addition have been synthesized in gas phase. The homopolymer was named iPP with a subscript gas phase (g) followed by a number indicating the addition of hydrogen in bar. The IPC with different amounts of ethylene was named iPP with a subscript gas phase (g) followed by a value with the time in minutes of ethylene-propylene added. The IPC with different amounts of hydrogen with ethylene was named iPP with a subscript gas phase (g) followed by a number indicating the addition of hydrogen between dashes and a value with the time in minutes of ethylene-propylene added.

Inert sodium chloride was used for every experiment to prevent catalyst particles from sticking to each other and to the reactor wall. Sodium chloride also improved the heat transfer from the reacting particles to the reactor wall [15,16]. It was calcined at 150 °C during 24 h and introduced in the reactor previous to the catalytic system with overpressure of propylene.

1 mL of TEA and 0.08 mL of C-donor were precontacted in n-heptane due to its influence on catalyst activity [17] and then added to 20 mg of catalytic system. 1.5 mL of TEA was added into the reactor as a scavenger. TEA (scavenger) and the catalytic system were added into the reactor at 70 °C, and the desired amount of hydrogen was added according to Fig. 1b.

The main polymerization stage was maintained at 60 min, and the propylene monomer was fed to keep the pressure at 8 bars. The second step of the polymerization was only carried out to synthesize IPC with or without hydrogen. After the first step, the reactor was vented, and ethylene/propylene in a ratio of 50/50 was fed at 8 bars at different times. After the polymerization reaction, the polymers were washed with water to dissolve the sodium chloride, and they were recovered by filtration and dried.

2.3. Characterization of the samples

Characterizations of samples were carried out using different