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2^3 FACTORIAL EXPERIMENT DESIGN IN A ETHYLENE AND 1-BUTENE COPOLYMERIZATION CATALYZED BY A ZIEGLER-NATTA/METALLOCENE HYBRID CATALYST

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In this work was employed a 2^3 factorial experiment design for the evaluation of ethylene-1-butene copolymerization and the following reaction parameters were used as independent variables: catalyst type, Al/Ti molar ratio and 1-butene concentration. The copolymerization was carried out using hybrid Ziegler-Natta/Metallocene catalysts with different titanium molar ratio between the Ziegler-Natta catalyst and metallocene one. The catalyst activity and polymer characteristics were evaluated by surface curves. The catalyst type has a significant effect on the activity, melt flow index (MFI) and 1-butene content. The copolymers obtained showed crystallinity values from 46 to 58% and melt temperature in the range of 128 to 131°C. The polymer comonomer content varied from 2 to 6%.

Introduction

The LLDPE produced by heterogeneous Ziegler-Natta catalyst show a broader molecular weight distribution (MWD) and non-uniform comonomer distribution when compared to those produced by metallocene ones. The polymer also present higher comonomer content in the lower molecular weight chains and vice-versa. These LLDPE characteristics are related to the several active center types, usually formed on the solid catalysts. On the other hand, homogeneous metallocene catalysts have only one type of the active sites, more accessible to superiors α-olefins, and these produce polymers with more homogeneous comonomer incorporation and distribution in the chain, and a narrower MWD. [1-3] The LLDPE produced with this characteristic is claimed to have poorest processabillity than that one produce with Ziegler-Natta catalyst.

It is worth mentioning that the metallocene catalytic systems are essentially homogeneous and its heterogeinization represents a challenge to be solved at industrial level, once that the last generation processes use heterogeneous catalysts. So, the study of the metallocene heterogeneous catalyst behavior, in suspension or gas phase processes, it is very important in order to evaluate the polymer properties and compare these with those ones of the commercial polymers already produced. Usually the effect of the reaction parameters on the catalyst performance and polymer characteristics has been analyzed individually. The factorial experiment design help ones to verify if there is or not a synergistic effect between the reaction parameters on the polymerization performance and polymer properties.

The aim of this work was to employ a 2^3 factorial experiment design for to evaluate the Ziegler-Natta/Metallocene hybrid catalyst behavior in the ethylene-1-butene copolymerization slurry process.

Experimental

Preparation of a hybrid ZN/Met catalyst (ZNM)

Dry *n*-hexane (8 mL) was added into a Schlenk tube containing $CpTiCl_3$ (1mmol), followed by the dropwisely addition of 0.7 mL of TIBA (2.8 mmol) under magnetic stirring. After 2 hours at room temperature, the solution turned dark purple, nearly black, then it was added to a suspension of Ziegler-Natta catalyst (2 mmol of Ti) in *n*-hexane, in a glass reactor equipped with mechanical stirring. The mixture was kept at 40ºC for 5 hours at 300 rpm. The residual solid was washed with *n*-hexane and dried in nitrogen flow. The catalysts were characterized by its Ti, Cl and Mg content using ICP and XPS techiniques.[7] The catalysts used in this study ZNM20, ZNM22 and ZNM21 were prepared with titanium molar ratio ZN/Met equal 2.0: 3.5: 5.0 respectively.

Ethylene-1-butene copolymerization

The copolymerization was carried out in a 2 dm^3 Büchi reactor equipped with mechanical stirring and temperature control. The reactions were performed in 1dm^3 of hexane at 7 bar and 75 °C for 2 hours. 0,35 g of hydrogen were used in all reactions. The following reaction conditions were evaluated: catalyst type (ZNM20, ZNM21 and ZNM22) according to the titanium ZN/Met molar ratio, Al/Ti molar ratio and comonomer concentration. The component addition order in the reactor was the following: solvent, triethylaluminium, catalyst, comonomer, hydrogen and ethylene.

Factorial experiment design

A 2^3 factorial experiment design with central point and one replication was used to study the ethylene-1-butene copolymerization. The statistical data treatment was accomplished through the software Statistic 4.3 in experimental design modulate. This program use the one-way ANOVA table to analyze the statistical data.[4]

Polymer characterization

The comonomer content in the copolymer was evaluated in film samples by infrared techniques, using a Nicolet 710 FT-IR spectrometer using a standard curve. The polymer melt flow index (MFI) was determined in a Tinius Olsen MP 987 extrusion plastometer at 190 °C, using a 2.16 kg charge. The polymer melting temperature (Tm), as well crystallinity were determined by differential scanning calorimeter (DSC) using TA DSC 2910 equipment connected to the Thermal Analyst 2100 Integrator, at a heating rate of 10 °C/min.

Results e Discussion

In this work was used a Ziegler-Natta metallocene hybrid catalyst prepared with a 4th generation Ziegler-Natta catalyst, a $MgCl_2$ supported $TiCl_4$ catalyst, and $CpTiCl_3$ as metallocene compound.

The Table I displays the data of catalyst activity (kgPol/gcat.h), the polymer melt flow index (g/10'), comonomer content (%), crystallinity (%) and melt temperature (°C), all dependent variables obtained according to 2^3 factorial experiment design. The values of the dependent variables were the medium of three runs.

Table I

The Equation 1 describes the surface variation for the catalyst activity as function of the catalyst type (x), Al/Ti molar ratio (y) and 1-butene concentration (z) in the polymerization medium. The catalyst type (x) and Al/Ti molar ratio (y) has a strong influence in catalyst activity, both variables have a plus signal, which means that as higher the amount of metallocene in the hybrid catalyst and the Al/Ti molar ratio as higher will be the catalyst activity. The effect of Al/Ti molar ratio in activity is well know, and usually there is an increase of the activity with this until certain value and after that is constant. For the interval of Al/Ti molar of 200 to 1000 evaluated in this study it was observed on continuos increase of the catalyst activity. The interaction between catalyst type and Al/Ti molar ratio (xy) has a significant synergic effect. The signal of the terms of interaction between two independent variables is negative when the influence of one variable on the other is higher in the lower interval values. Or in the other way the surface inclination decrease in the higher interval values related to that one in the lower interval values.

$$\textbf{Activity} = 6.60 + 0.89\,x + 1.61\,y + 0.19\,z - 0.26\,xy - 0.17\,xz + 0.17\,yz \quad \textbf{(Eq.1)}$$

Where, x is the catalyst type; y is the Al/Ti molar ratio and z is the 1-butene concentration.

As the comonomer concentration did not have influence on the catalyst activity (low variation of the surface inclination) this term can be supressed in the catalyst activity equation (Equation1), which can be simplified (Equation 2). This influence or not of one variable can be see by the significance factor (α) determined by F test, i.e., if it was higher then 0.05 the independent variable or the interaction between this variables has no significative effect on dependent variables. How in this case the α factor was higher than 0.05 for 1-butene concentration (z), and the interaction of 1-butene concentration and the others variable (xz and yz) these terms could be suppressed. The same procedure was doing for the other equations.

$$\textbf{Activity} = 5.600 + 0.890\,x + 1.610\,y - 0.256\,xy \quad \textbf{(Eq.2)}$$

Where, x is the catalyst type and y is the Al/Ti molar ratio.

For the MFI statistical data variation (Equation 3) the most significant independent variables were the catalyst type (x), Al/Ti molar ratio (y) and the interaction of these variables (xy). In all polymerizations were used the same hydrogen concentration, so the molecular weight variation and consequently MFI values could be attributed to type of catalyst, alkylaluminium and comonomer concentration. However the comonomer concentration did not have influence on the MFI in the range of 29 to 59 g/L, so the chain transference for the comonomer was not increase of content of the metallocene in the catalyst (catalyst type) and increase of alkylaluminium concentration as well knows. As was observed on the catalyst activity there was a synergic effect of both catalyst type and aluminum concentration on the MFI.

$$\textbf{MFI} = 1.750 + 0.465\,x + 1.065\,y + 0.444\,xy \quad \textbf{(Eq.3)}$$

Where, x is the catalyst type and y is the Al/Ti molar ratio.

For the 1-butene content incorporated into the produced copolymer (Equation 4) the most significant variables was the 1-butene concentration (z). However, the catalyst type (X) and the Al/Ti molar ratio (y) also have had a strong influence in the comonomer incorporation in the polymeric chain. There was also a synergic effect of Al/Ti molar ratio and comonomer concentration on the 1-butene content.

$$\% C_4^-. = 4.0 + 0.325 x + 0.475y + 0.712z + 0.287yz \quad \textbf{(Eq.4)}$$

Where, x is the catalyst type; y is the Al/Ti molar ratio and z is the 1-butene concentration.

The crystallinity (%Xc) and melt temperature (Tm) were essentially dependent of the 1-butene concentration (z), Equation 5 and 6 respectively. The crystallinity was also influenced by the interaction between the Al/Ti molar ratio and 1-butene concentration.

$$\%Xc = 51.9 - 1{,}312 z - 1{,}687yz \quad \textbf{(Eq.5)}$$

$$Tm = 129.95 - 0.8z \quad \textbf{(Eq.6)}$$

Where, y is the Al/Ti molar ratio and z is the 1-butene concentration

Conclusion

The use of the a 2^3 full factorial experimental design and the treatment of data thought surface equation permit one to visualize better the influence of the independent variables and the synergic effect of these on the dependent variables evaluated. The surface equation results showed that the catalyst type and Al/Ti molar ratio such as the interaction between them have had the most significant factor the variation of catalyst activity and MFI in the ethylene-1-butene copolymerization. For 1-butene incorporated all study variables and the interaction between Al/Ti molar ratio and 1-butene concentration have had a significant effect.

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Table I. Catalyst activity and melt flow index (MFI), comonomer content (C_4), cristallinity (Xc) and melt temperature (Tm) of copolymers obtained with the Ziegler-Natta/Metallocene hybrid catalysts.

Catalyst	Al/Ti (m.r.)	C_4^- (g/L)	Activity ($kg_{pol}/g_{cat}.h$)	MFI (g/10 min)	C_4 (%)	X_c (%)	Tm (ºC)
ZNM 21	200	29	2.7	0.67	2.1	51	131
ZNM 21	200	29	2.4	0.26	2.0	52	131
ZNM 21	200	59	3.1	0.75	3.7	52	129
ZNM 21	200	59	3.2	0.85	3.8	52	129
ZNM 21	1000	29	5.9	1.80	2.6	56	130
ZNM 21	1000	29	6.4	1.80	2.8	55	129
ZNM 21	1000	59	7.0	2.20	4.6	60	128
ZNM 21	1000	59	7.0	1.70	3.8	55	128
ZNM 20	200	29	5.1	1.15	3.0	51	130
ZNM 20	200	29	5.7	0.29	3.3	49	129
ZNM 20	200	59	5.6	0.19	3.0	50	128
ZNM 20	200	59	4.2	1.08	3.3	52	129
ZNM 20	1000	29	7.5	2.20	3.4	53	128
ZNM 20	1000	29	7.6	2.60	3.1	58	130
ZNM 20	1000	59	8.0	4.00	5.9	47	126
ZNM 20	1000	59	8.3	6.00	5.6	46	128
ZNM 22	600	44	6.9	2.40	4.0	56	129
ZNM 22	600	44	6.3	2.50	4.0	53	130

Copolymerization conditions ($2dm^3$ Büchi reactor): n-hexane=1L, time =120 min, temperature = 75 ºC, P_{H2} = 0,35 g/L, $P_{ethylene}$= 7 bar .