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Ethylene and 1-butene copolymerization catalyzed by a Ziegler–Natta/Metallocene hybrid catalyst through a 2^3 factorial experimental design

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Abstract

In this work, a 2^3 factorial experimental design for the evaluation of ethylene–1-butene copolymerization was employed. 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 ratios. The catalyst activity and polymer characteristics were statistically analyzed through response surface methods. It was found that the catalyst type has a significant effect on activity, melt flow index and 1-butene content. Copolymers presented crystallinity values ranging from 46 to 58% and melt temperature in the 128–131 °C range. Copolymer comonomer content varied from 2 to 6% in weight.

Keywords: 2^3 Factorial design; Ziegler–Natta; Metallocene

1. Introduction

Polyethylene properties are modified when a small amount of α-olefin is incorporated into its main chain. Copolymer branching is related to α-olefin type and its distribution in the chain depends on the relative rates of comonomer propagation at the active polymerization center. This type of polyethylene copolymer is usually called linear low density polyethylene (LLDPE) [1].

In the last decades, olefins polymerization catalytic systems have been improved by catalysts' chemical modification or the discovery of entirely new catalytic systems. Kaminsky et al. [2] and Ewen [3] developed a series of metallocene compounds that, when cocatalyzed by methylaluminoxane (MAO), present high activity, producing polymers with special properties. New metallocene catalysts have been continuously reported in the literature [4].

The LLDPE produced with heterogeneous Ziegler–Natta catalysts is a more heterogeneous material when compared to metallocene LLDPE. It shows a broader molecular weight distribution (MWD) and a non-uniform comonomer distribution (the higher the molecular weight of polymer molecules, the lower the comonomer incorporation). These LLDPE characteristics are related to the occurrence of several active center types in Ziegler–Natta catalyst systems. On the other hand, homogeneous metallocene catalysts possess mainly one type of active center, which is more accessible to higher α-olefins, and is able to produce polymer with narrower comonomer and MWDs [5–7]. It is claimed that metallocene LLDPE presents superior mechanical and optical properties and worse processability performance when compared to Ziegler–Natta LLDPE.

It is worth mentioning that metallocene catalytic systems are essentially homogeneous and their practical application to industrial gas phase/slurry processes relies strongly on the

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utilization of inert supports. Solution processes use homogeneous catalysts to produce polymers that can dissolve in the reaction milieu. Such plants are best suited to the production of lower density and crystallinity polymers and copolymers such as VLDPE, plastomers or elastomers, as these will be soluble in the hydrocarbon solvent used or will melt at the process temperature. Homopolymers and copolymers of higher density and crystallinity, such as LLDPE, HDPE and polypropylene, are usually prepared in continuously slurry, fluidized-bed gas-phase or bulk monomer processes. These resins are insoluble in hydrocarbon solvents at the process temperatures commonly employed. The requirements imply modification on the polymerization conditions [8] and either immobilization that should also retain the 'single site' nature of the metallocene catalyst. Many different routes have been proposed in the literature [9,10–12].

The effect of reaction parameters on catalyst performance and polymer characteristics has usually been analyzed individually. The factorial experimental design helps verify whether or not there is a synergistic effect of the reaction parameters on polymerization performance and polymer properties. Experimental design has been frequently used in different research experiments [13–16] because it provides the best information regarding the effects of independent variables and their interactions on model parameters with the minimal number of runs. Runs must be randomized in order to minimize noise interference on final results. The empirical correlations obtained make it possible, then, to optimize the system responses according to each property evaluated.

The aim of this work was to employ a 2^3 factorial experimental design in order to evaluate the Ziegler–Natta/Metallocene (ZN/Met) hybrid catalyst behavior in an ethylene–1-butene copolymerization slurry process. The chemical nature of the ZN/Met hybrid catalyst used in this work has already been reported in a previous paper [17,18].

2. Experimental section

2.1. Materials

All the chemicals were manipulated using the Schlenk technique. A fourth generation Ziegler–Natta catalyst with approximately 2.2 wt% Ti and around 12 wt% DIBP (MCM1, Akzo Nobel Chemicals Inc.) and $CpTiCl_3$ (Boulder Scientific Company) were used as received. The alkyl-aluminum compounds, triethyaluminum (TEA) and tri*iso*butylaluminum (TIBA) (Akzo Nobel Chemicals Inc.) were employed in *n*-hexane solution. The *n*-hexane (IBRASOL) used in the catalyst preparation and copolymerization reactions was dried with a 3 Å molecular sieve.

2.2. Preparation of a hybrid ZN/Met catalyst (ZNM)

Dry *n*-hexane (8 ml) was added to a Schlenk tube containing $CpTiCl_3$ (1 mmol), followed by the dropwise addition of 0.7 ml of TIBA (2.8 mmol) under magnetic stirring. After 2 h at room temperature, the solution turned dark purple, nearly black; it was then 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 40 °C for 5 h at 300 rpm. The residual solid was washed with *n*-hexane and dried in nitrogen flow. The catalysts were characterized by their Ti, Cl and Mg content using ICP and XPS techniques [18]. The catalysts labeled ZNM20, ZNM22 and ZNM21 were prepared with titanium ZN/Met molar ratio equal to 2.0, 3.5, and 5.0, respectively. The titanium ZN/Met molar ratio is the titanium molar ratio between the titanium in Ziegler–Natta catalyst and titanium in metallocene compound.

2.3. 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 1 dm^3 of hexane at 7 bar and 75 °C for 2 h. An amount of 0.35 g of hydrogen was used in all reactions as a chain transfer in order to produce polymers with melt flow index (MFI) above 0.1 g/10 min [19,20]. Small vessels connected to the reactor allowed the comonomer and hydrogen to be measured and added it by following the pressure reduction on the vessels. The pressure setup was controlled by continuous addition of ethylene. The reaction conditions evaluated were: the catalyst type (ZNM20, ZNM21, and ZNM22), according to the titanium ZN/Met molar ratio; the total Al/Ti molar ratio; and the comonomer concentration. The order of addition of the reaction components into the reactor was solvent, triethylaluminium, catalyst, comonomer, hydrogen and ethylene.

2.4. Factorial experiment design

A 2^3 factorial experimental design with central point and one replication was used to study the ethylene–1-butene copolymerization [10–12]. The statistical data treatment was accomplished through the software Statistic 4.3. This software analyzes the statistical data based on the analyzis of variance (ANOVA table). This table is obtained from the sum of squares (SS) (Eq. (1)), degrees of freedom (df) and the mean square (MS) (Eq. (2)) of the independent variable and their interactions and residual. The *F*-test (square of effects/square of residual) and significance probability or *p*-value (Eq. (3)) are calculated in order to evaluate the significant effects. If the *F* calculated value is higher than the F_0 value related to a certain significance level (α), an effect is considered statistically relevant. Usually, the significance level (α) is set to 0.05 [21,22]. The *p*-value

represents the probability to obtain a specific value in the F distribution with $k-1$ variables and $k(n-1)$ df higher or equal to F_0 (k is the population number and n is the sample size). With the p-value, it is possible to evaluate if the dependent variables are significant, and how significant, and their interaction

$$\mathrm{SS} = \sum_{i=1}^{n}\sum_{j=1}^{n}\left(x_{ij} - 1/nk\sum_{i=1}^{n}\sum_{j=1}^{n}x_{ij}\right)^2 \quad (1)$$

$$\mathrm{SQ} = \mathrm{SS}/\mathrm{df} \quad (2)$$

$$p\text{-value} = P[F(k-1), k(n-1) > F_0] \quad (3)$$

2.5. Polymer characterization

The comonomer content in the copolymer was evaluated in film samples by infrared techniques, using a Nicolet 710 FT-IR spectrometer and a standard curve. The polymer MFI was determined in a Tinius Olsen MP 987 extrusion plastometer at 190 °C, using a 2.16 kg charge. The polymer melt temperature (T_m), 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.

3. Results and discussion

In this work, a ZN/Met hybrid catalyst was employed, prepared as previously reported [18], with the use of a fourth generation Ziegler–Natta catalyst, an $MgCl_2$ supported $TiCl_4$, and a metallocene compound ($CpTiCl_3$).

The hybrid catalysts have been prepared with the aim of introducing a new titanium species, such as metallocene, in the conventional Ziegler–Natta catalysts [9,10–12,17,18]. The metallocene compound $CpTiCl_3$ previously treated with tri*iso*butylaluminium (TIBA) leads to an alkylated titanium soluble compound ($(Cp)(i\,Bu)TiCl_2$) that is immobilized on the $MgCl_2$ surface. Based on the catalyst characterizations results, we have proposed that the titanocene species $Cp(i\,Bu)TiCl_2$ are fixed on the $MgCl_2$ surface besides the $TiCl_4$, already in the solid catalyst [18]. In this paper, our proposal is to evaluate this kind of catalyst in a ethylene–1-butene copolymerization through a factorial experiment.

The performance of the ZN/Met hybrid catalyst was evaluated in the ethylene–1-butene copolymerization using triethylaluminium as the cocatalyst. The runs were carried out employing a factorial experimental design and the independent variables were catalyst type, Al/Ti molar ratio and comonomer concentration. The levels of the independent variables shown in Table 1 were chosen based on ethylene homopolymerization preliminary results with the hybrid catalyst [17]. For the conditions range used, simulated data were checked with those obtained in randomic experimental conditions and they were very similar. Experimental conditions that are quite different from those used here must be checked in the future. Table 2 lists the full factorial experimental design employed in this work. All dependent variables were evaluated as a function of Al/Ti molar ratio, catalyst type and comonomer concentration.

Table 1
Factor levels of independent variables for ethylene–1-butene copolymerization

Independent variables (units)	Low level (−1)	Midpoint (0)	High level (+1)
Catalyst type[a]	5.0	3.5	2.0
Al/Ti (molar ratio)	200	600	1000
1-Butene (g/l)	29	44	59

[a] According to the titanium ZN/Met molar ratio, respectively, ZNM21, ZNM22 and ZNM20.

Table 3 lists the data of catalyst activity (kg pol/g cat h), polymer MFI (g/10 min), comonomer content (%), crystallinity (%) and melt temperature (°C), obtained according to the 2^3 factorial experimental design. The values of the dependent variables were calculated as the average of three runs.

Table 4 lists the significance probability (p-values) for all dependent variables. A dependent variable has a significant influence whenever the p-value is lower than 0.05. Surface response equations are expressed only in terms of relevant dependent variables.

Eq. (4) describes the surface response for catalyst activity as a function of the catalyst type (x), Al/Ti molar ratio (y) and 1-butene concentration in the polymerization medium (z), where the values of x, y and z vary in the range −1 to 1 (see Table 1). Fig. 1 shows the surface plot for catalyst activity as a function of (a) catalyst type and Al/Ti molar ratio, (b) catalyst type and 1-butene concentration, and

Table 2
2^3 Factorial experiment design codified factor level for ethylene–1-butene copolymerization

Experiment #	Catalyst type	Al/Ti molar ratio	1-Butene concentration
1	−1	−1	−1
2	−1	−1	−1
3	−1	−1	+1
4	−1	−1	+1
5	−1	+1	−1
6	−1	+1	−1
7	−1	+1	+1
8	−1	+1	+1
9	+1	−1	−1
10	+1	−1	−1
11	+1	−1	+1
12	+1	−1	+1
13	+1	+1	−1
14	+1	+1	−1
15	+1	+1	+1
16	+1	+1	+1
Midpoint	0	0	0
Midpoint	0	0	0

Table 3
Catalyst activity and copolymers MFI, comonomer content (C_4^-), crystallinity (X_c) and melt temperature (T_m) obtained with the ZN/Met hybrid catalysts

Catalyst	Al/Ti (m.r.)	[C_4^-] (g/l)	Catalyst activity (kg pol/g cat h)	MFI (g/10 min)	%C_4^-	%X_c	T_m (°C)
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 (2 dm^3 Büchi reactor): *n*-hexane = 1 l, time = 120 min, temperature = 75 °C, P_{H2} = 0.35 g/l, $P_{ethylene}$ = 7 bar.

finally (c) Al/Ti molar ratio and 1-butene concentration. As it may be seen by the surface slopes in Fig. 1(a)–(c), catalyst type (x), Al/Ti molar ratio (y) as well as their interaction (xy) have strong influence on catalyst activity (Fig. 1(a)). Both variables exhibit a positive effect, which means that the higher the amount of metallocene in the hybrid catalyst and the Al/Ti molar ratio, the higher the catalyst activity. The catalyst type influence could be related to the active centers' type in the hybrid catalyst. The catalyst ZNM20 has more metallocene Ti species, which are alkylated and more active than the $TiCl_3$ species; as a consequence, this catalyst showed higher activity than those prepared with less metallocene compound concentration (ZNM21 and ZNM22). The effect of Al/Ti molar ratio on activity is well known. There is usually an increase in activity until a certain value, being constant after that. For the interval of Al/Ti molar ratio of 200:1000 evaluated in this study, a continuous increase in catalyst activity was observed. The interaction between catalyst type and Al/Ti molar ratio (xy) is statistically relevant. The negative sign for the interaction term (xy) in Eq. (4) indicates that the rate of catalyst activity variation with respect to either catalyst type or Al/Ti molar ratio decreases when one of the variables is at its maximum level (+1)

$$\text{Activity} = 6.60 + 0.89x + 1.61y + 0.19z - 0.26xy - 0.17xz + 0.17yz \quad (4)$$

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

The comonomer concentration presented no relevant influence on catalyst activity, as it can be seen from the small values of surface inclination. This term may then be suppressed from the catalyst activity equation, which, after revaluation, results in Eq. (5), where the catalyst activity depends on the catalyst type (x) and Al/Ti molar ratio (y)

$$\text{Activity} = 5.600 + 0.890x + 1.610y - 0.256xy \quad (5)$$

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

The ANOVA table analysis showed that concentration of 1-butene (z) and its interaction with the other variables (xz and yz) was not relevant at a significance level of 5%. Therefore, these variables were also suppressed from Eq. (1). The same type of statistical analysis was performed for all the other response equations.

Fig. 2 shows the surface plot for the copolymers MFI described by Eq. (6)

$$\text{MFI} = 1.750 + 0.465x + 1.065y + 0.444xy \quad (6)$$

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

Catalyst type (x), Al/Ti molar ratio (y) and the interaction of these two independent variables (xy) had the most significant effect upon polymer MFI. Since all polymerizations were carried out with the same hydrogen quantity or chain transfer concentration, the MFI variations may be attributed to the catalyst type, and the alkyl-aluminum and comonomer concentration. As it is known, for the same polymer, the higher the MFI, the lower its molecular weight [19,20]. The chain transference in the Ziegler–Natta polymerization depends on the catalyst sensitivity towards hydrogen, which is influenced by the aluminum type and

Table 4
Significance probability (p-value) for all dependent variables—catalyst activity (Activity), MFI, comonomer content (%C_4^-), melt temperature (T_m) and crystallinity (%X_c)

	p-value				
	Activity	MFI	%C_4^-	T_m	%X_c
Catalyst (x)	0.000007	0.026413	0.023082	0.056086	0.06257
Al/Ti molar ratio (y)	0.000000	0.000143	0.002879	0.019536	0.204591
1-Butene (z)	0.093289	0.062128	0.000156	0.002471	0.026912
$x - y$	0.034066	0.032757	0.130081	0.763954	0.408041
$x - z$	0.137258	0.185197	0.487063	0.763954	0.204591
$y - z$	0.137258	0.110546	0.039210	0.763954	0.007604

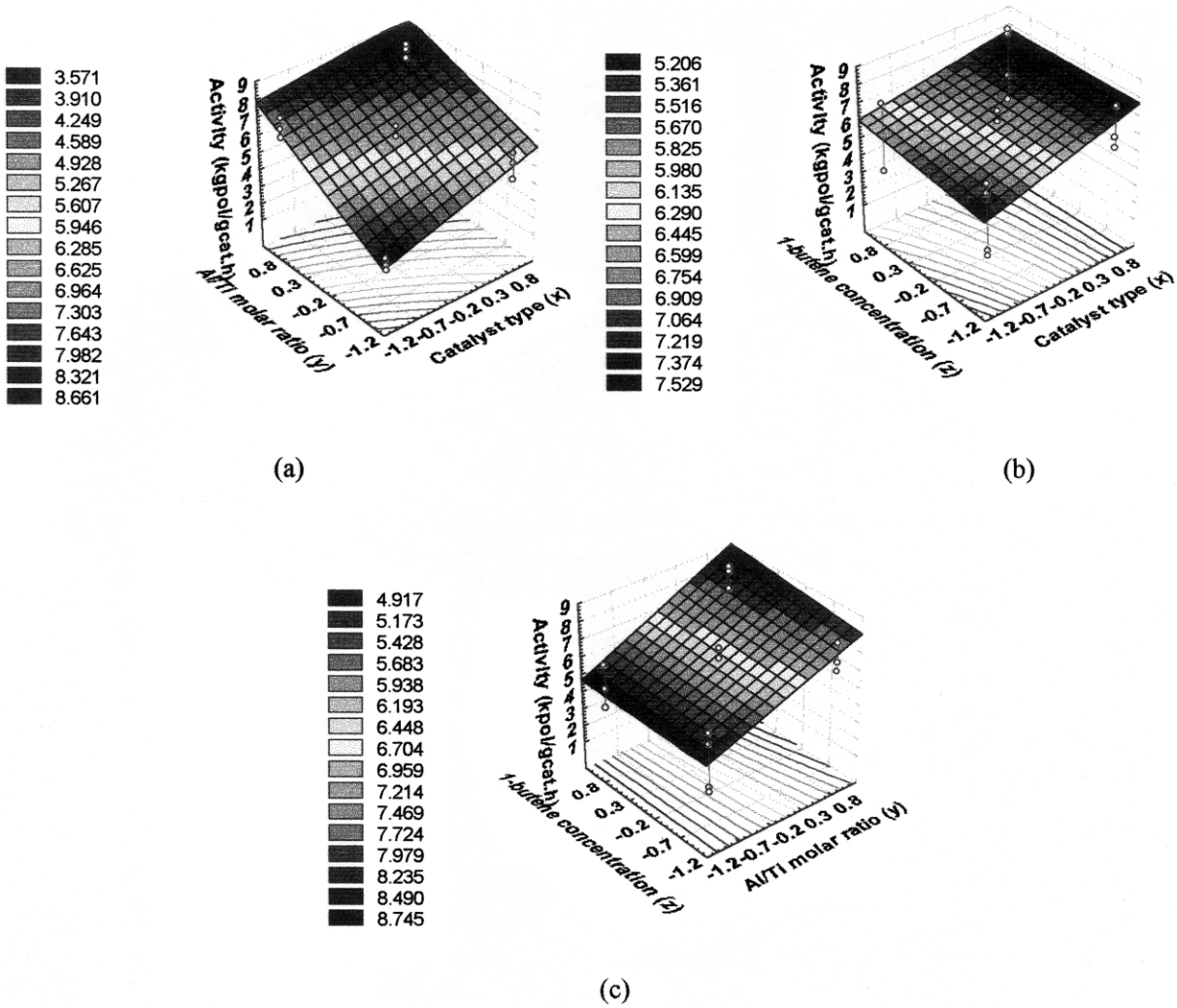

Fig. 1. Activity variation surface graph as a function of the catalyst type and Al/Ti molar ratio, as Eq. (4): (a) x versus y; (b) x versus z and (c) y versus z.

concentration. It is also known that the cocatalyst is a chain transfer agent, too. Comonomer concentration (in the range of 29–59 g/l) did not have any influence on MFI, so chain transfer to the comonomer did not seem to be significant in this case. The MFI was influenced by the catalyst type as well by the alkyl-aluminum concentration. Chain termination in metallocene active centers occurs mainly by β-elimination and the polymer usually has lower molecular weight than the one produced with the Ziegler–Natta catalyst. A higher amount of metallocene compound, with the hybrid catalyst, is expected to increase the MFI polymers produced. In this work, it was observed that the lower the catalyst titanium ZN/Met molar ratio, the higher the MFI polymers produced by this catalyst, due to the higher metallocene compound concentration. Moreover, the chain transfer mechanism to the alkyl-aluminum is favored by the increase in its concentration [20,23,24]. As in the case of catalyst activity, there was a synergic effect of both catalyst type and aluminum concentration on the MFI.

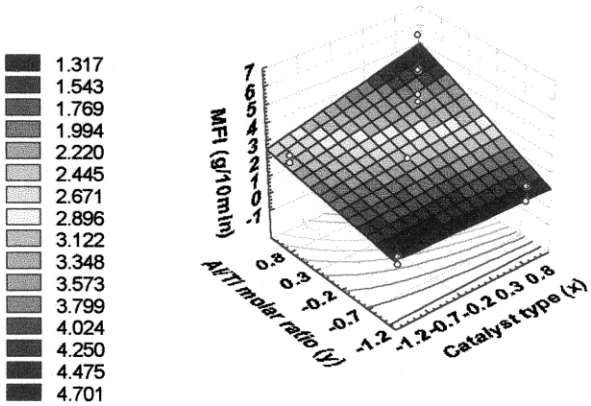

Fig. 2. Melt index variation surface graph as a function of the catalyst type and Al/Ti molar ratio, as Eq. (6).

Fig. 3 shows the surface response plot for comonomer content ($\%C_4^-$) described according to Eq. (7). The concentration of 1-butene (z) is the most significant variable. Catalyst type (x) and Al/Ti molar ratio (y) have also shown strong influence. In general, comonomer chain incorporation with metallocene catalysts is higher than with Ziegler–Natta ones, since the metallocene active center is

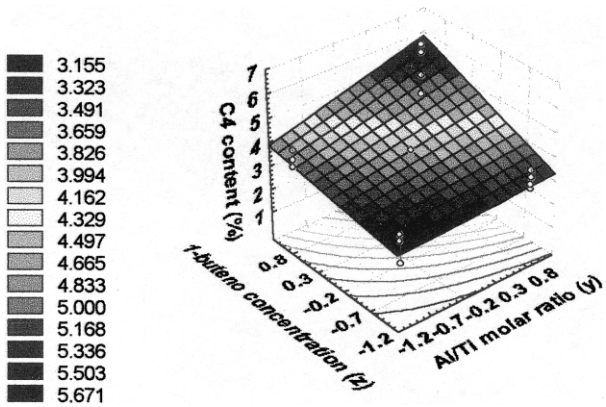

Fig. 3. Comonomer content variation surface graph as a function of the 1-butene concentration, as Eq. (7).

more accessible to the α-olefin [6,19]. Thus, the metallocene active center in hybrid catalyst should increase comonomer incorporation, as it is observed in Eq. (7). There was a synergic effect of Al/Ti molar ratio and comonomer concentration upon 1-butene content

$$\%C4^{-} = 4.0 + 0.325x + 0.475y + 0.712z + 0.287yz \quad (7)$$

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

Fig. 4(a) and (b) shows, respectively, the response surface for polymer crystallinity and melt temperature versus Al/Ti molar ratio and 1-butene concentration.

Crystallinity and melt temperature were essentially dependent on 1-butene concentration (z). Crystallinity was also influenced by the interaction between the Al/Ti molar ratio and 1-butene concentration. Melt temperature was also influenced by the Al/Ti molar ratio. The surface equation for polymer crystallinity ($\%X_c$) and melt temperature (T_m) are described by Eqs. (8) and (9), respectively

$$\%X_c = 51.9 - 1.312z - 1.687yz \quad (8)$$

Table 5
Influence of polymerization time on the catalyst activity, MFI and comonomer content (C_4^-) of LLDPE obtained with ZNM20 hybrid catalyst

Time (min)	Catalyst activity (kg pol/g cat h)	MFI (g/10 min)	C_4^- content (wt%)
20	18.4	1.6	5.4
40	12.1	1.4	5.3
60	11.7	2.7	5.6
80	9.2	3.0	4.9
120	9.1	2.4	5.4

$$T_m = 129.95 - 0.56y - 0.81z \quad (9)$$

where y is the Al/Ti molar ratio and z is the 1-butene concentration.

Copolymer crystallinity and melt temperature can also be related with another dependent variable, the comonomer content, as shown in Fig. 5. In this case, both copolymer variables showed a linear variation with the comonomer content in the polymer chain ($\%C_4^-$). Eqs. (10) and (11) describe how copolymer crystallinity and melt temperature vary with respect to the comonomer content

$$\%X_c = 56.86 - 1.47C4^{-} \quad (10)$$

$$T_m = 132.17 - 0.90C4^{-} \quad (11)$$

As it was expected, increases in the comonomer content cause a decrease in crystallinity and melt temperature. There is a decrease in melt temperature from 131 °C (for the copolymer with 2% 1-butene) to 126 °C (for the copolymer with 6% 1-butene). The insertion of a comonomer disrupts polyethylene chain homogeneity and symmetry due to the occurrence of short chain branches. Those short branches hinder chain crystallization into perfect crystallite formation and also reduce its size; therefore, the copolymer becomes less crystalline and shows lower melt temperature as compared to high density polyethylene [6,20,25,26].

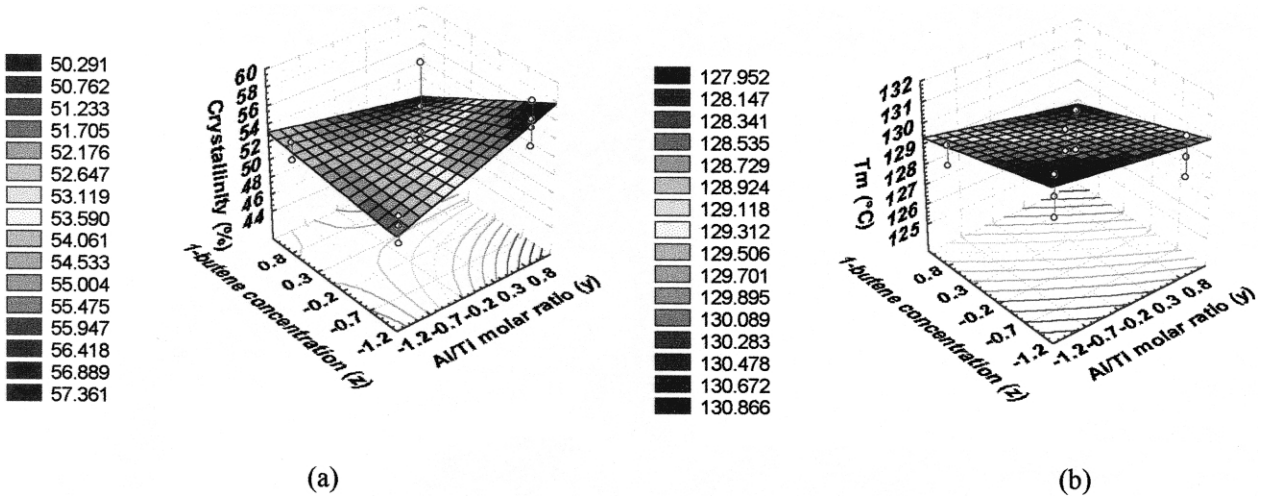

Fig. 4. Surface graph as a function of the Al/Ti molar ratio and 1-butene concentration for the (a) crystallinity and (b) melt temperature, as Eqs. (8) and (9), respectively.

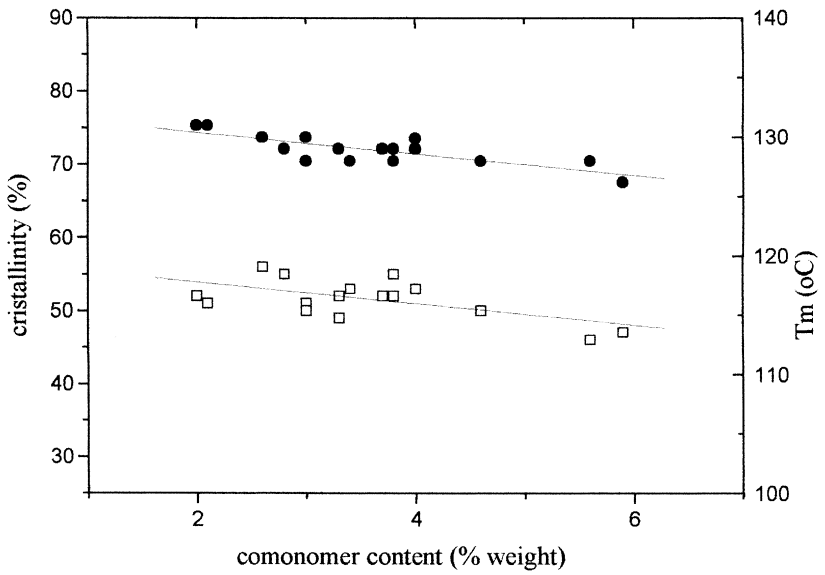

Fig. 5. Copolymers crystallinity (□) and melt temperature (●) as a function of the comonomer content.

The effect of reaction time on catalyst performance was also evaluated. Data regarding catalytic activity, MFI and comonomer content obtained with the ZNM20 catalyst at an Al/Ti molar ratio of 1000 and 1-butene concentration of 59 g/l are listed in Table 5. The content of 1-butene in the polymer did not change significantly with reaction time (around 5.0 ± 0.3%), which indicates that this catalyst might be suitable for well controlled copolymerization reactions.

Catalyst activity is seen to decrease with time (see Fig. 6), reaching a plateau at around 10 kg pol/g cat h after about 1 h of reaction. This is a moderately fast decaying catalyst which may reach reasonable average polymer yields (~4–6 kg/g cat) over typical industrial average reactor residence times (1–2 h). Eq. (12) describes how catalyst activity decays over time

$$\text{Activity(kg pol/g cat h)} = 9.04 + 8.9\exp(-(t-20)/19.6)(\text{min}) \quad (12)$$

4. Conclusion

Hybrid ZN/Met catalysts might represent an attractive alternative for ethylene/α-olefin copolymerizations. The combination of good particle morphology (which comes from well established fourth generation supported Ziegler–Natta systems) and a more uniform comonomer incorporation (coming from a single site metallocene catalyst) has

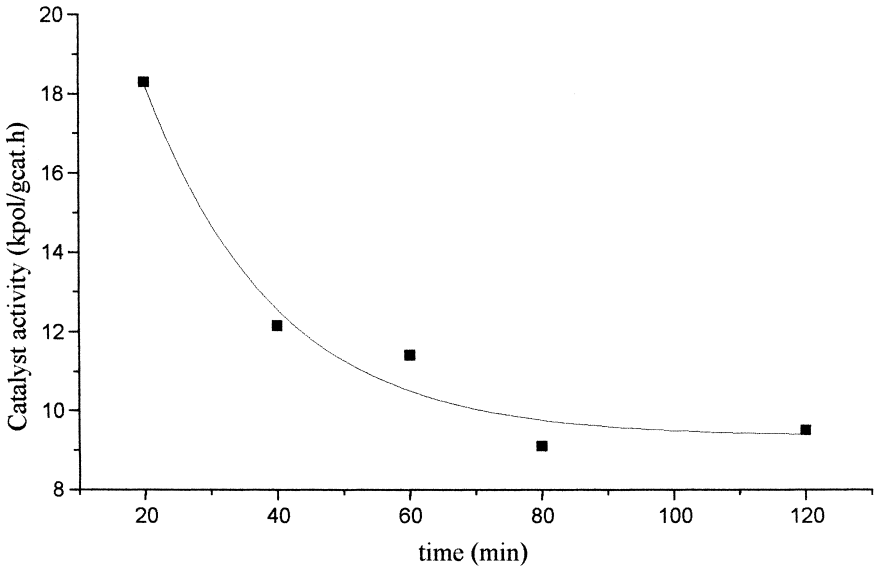

Fig. 6. Evaluation of catalytic activity versus time reaction.

the potential of achieving better polymer properties as well as improved reactor operability performance.

The use of statistical analysis and a full 2^3 factorial experimental design allowed the determination of the most important effects on the performance of a hybrid Ziegler–Natta/$CpTiCl_3$ catalyst formulation. Surface response analysis showed that catalyst type (ZN/Met ratio), Al/Ti molar ratio, as well as their interaction, have the most significant influence on catalyst activity and polymer MFI for the case of ethylene–1-butene copolymerization. All main effects including the interaction between Al/Ti molar ratio and 1-butene concentration exhibited relevant influence upon comonomer incorporation.

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References

[1] Schneider MJ, Mülhaupt R. Macromol Chem Phys 1997;198(4):1121–9.
[2] Andresen A, Cordes HG, Herwing J, Kaminsky W, Merk A, Mottweiler R, Penn J, Sinn H, Vollmer HJ. Angew Chem, Int Ed Engl 1976;15(10):630–2.
[3] Ewen JA. J Am Chem Soc 1984;106(21):6355–62.
[4] Alt HG, Küppl A. Chem Rev 2000;100(4):1205–22.
[5] Wu O, Wang H, Lin S. Chem Phys 1996;197:155–63.
[6] Hamielec AE, Soares JBP. Prog Polym Sci 1996;21(4):651–706.
[7] Suhm J, Schneider MJ, Mülhaupt R. J Mol Catal A 1998;128(1–3):215–27.
[8] Britto ML, Galland GB, Santos JHZ, Forte MMC. Polymer 2001;42(15):6355–61.
[9] Hlatky GG. In: Scheirs J, Kaminsky W, editors. Metallocene-based polyolefins, vol. 1.; 2000. p. 201–18. West Sussex.
[10] Hlatky GG. Chem Rev 2000;100(4):1347–76.
[11] Ban HT, Arai T, Ahn C-H, Uozumi T, Soga K. Curr Trends Polym Sci 1999;4:47–60.
[12] Ribeiro MR, Deffieux A, Portela MF. Ind Engng Chem Res 1997;36(4):1224–8.
[13] Bafna SS, Beall AM. J Appl Polym Sci 1997;65(2):277–88.
[14] Haswell SJ, Walmesley AD. Anal Chim Acta 1999;400:399–412.
[15] Shearer G, Tzoganakis C. J Appl Polym Sci 1997;65(3):439–47.
[16] Nachtigall SMB, Neto RB, Mauler RS. Polym Engng Sci 1999;39(4):630–7.
[17] Cunha FOV, Forte MMC, Zacca JJ. Polímero: Ciência e Tecnologia 2000;10(3):122–9.
[18] Forte MMC, Cunha FOV, Santos JHZ. J Mol Catal A-Chem 2001;175(1–2):91–103.
[19] Hindryckx F, Dubis P, Jérônime R, Marti MG. Polymer 1998;39(3):621–9.
[20] Brintzinger HH, Fischer D, Mülhaupt R, Rieger B, Waymouth RM. Angew Chem, Int Ed Engl 1995;34:1143–70.
[21] Bethea RM, Duran BS, Boullion TL. Statistical methodos for engineers and scientists. New York: Marcel Dekker Inc; 1975. p. 376–480.
[22] Brereton RG. Chemometrics applications of mathematics and statistics to laboratory systems. England: Ellis Horwood Limited; 1990. p. 11–84.
[23] Usami T, Yukitaka G, Takayama S. Macromolecules 1986;19:2722–6.
[24] Soares JBP. Macromol Theory Simul 1995;4:1085–104.
[25] Minick J, Moet A, Baer E, Chum SP. J Appl Polym Sci 1995;58:1371–84.
[26] Yoon JS, Chung CY, Lee IH. Eur Polym J 1994;30(11):1209–14.