

**COMPARISON OF ETHYLENE/1-HEXENE
COPOLYMERIZATION PERFORMANCE USING
METALLOCENE CATALYSTS SUPPORTED
ON BOTH SILICA AND BRAZILIAN
MINERAL CLAY**

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Abstract

Ethylene/1-hexene copolymerization was carried out using $(n\text{-BuCp})_2\text{ZrCl}_2$ catalyst supported on two different carriers (silica and bentonite), and compared to homogeneous copolymerization. The reactions were carried out at

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50°C and 80°C employing different amounts of comonomer. The polymerization parameters, such as catalyst activity and copolymer thermal properties were examined. In reactions at 80°C, the catalyst performed significantly better with the addition of comonomer when silica was used as support. However, the activity decreased when a bentonite-supported catalyst was employed. In both heterogeneous polymerizations, the amounts of comonomer incorporated in the polyethylene chains were lower than those with the homogeneous counterpart, although, the homogeneous polymer system presented higher melting temperatures.

1. Introduction

Ethylene copolymerization with higher olefins is employed for the production of the commercially important linear low-density polyethylenes. Using different α -olefins as comonomer, the produced polymers contain varied size chain branches, leading to properties tailored to specific applications. When 1-hexene is incorporated in polyethylene chains, the resulting four carbon atoms branches are responsible for the decrease in crystallinity in the final product, improving both the processability and optical properties [3]. The amount of comonomer and its intramolecular distribution in the polymer chains can vary considerably, depending on the catalytic system employed in the copolymer synthesis. Even though conventional Ziegler-Natta catalyst systems are still very widely used in the commercial production of LLDPEs, extensive studies have been directed to metallocene and post-metallocene catalysts. The use of metallocene systems helps attain polymer materials with a high degree of compositional uniformity [4].

Ethylene/ α -olefins copolymerization has been still increasingly evaluated in heterogeneous systems [1, 2, 7, 12-14]. The type of support, as well as the appropriate technique for the heterogenization of both metallocene and MAO, has a significant influence on the catalyst's behaviour. Metallocene supported catalysts tend to incorporate lower amounts of comonomer in comparison with homogeneous systems [4]. Along with development of metallocene catalysts, it has become possible to produce copolymers according to the required application. Therefore, polymer materials produced with the use of metallocene catalysts have

prompted great scientific and industrial interest. These catalysts produce copolymers with homogeneous comonomer distribution in the polymer backbone (intermolecular homogeneity) and also narrower molecular weight distribution, meaning an improved controlled molecular microstructure, in comparison to the copolymers produced with traditional Ziegler-Natta catalysts [6].

The aim of the present work was to evaluate the performance of mineral clay as a support for metallocene catalyst in ethylene-hexene copolymerization and to compare the results with the traditional silica-supported catalyst. Also, the differences in catalyst activity and comonomer incorporation were analyzed. The successful use of mineral clay as support for coordination catalyst is of utmost importance in the field of industrial scale production of polyolefin nanocomposites by *in situ* polymerization technique.

2. Experimental

2.1. Materials

Two types of support for the catalyst bis(*n*-butyl-cyclopentadienyl) zirconium dichloride, (*n*-BuCp)₂ZrCl₂, were employed: (1) thermally treated commercial silica gel (Sylopol 948, supplied by Grace Davison), with 309m²/g specific area and particle size in the range of 27μm to 84μm; and (2) commercial sodium bentonite (Bentogel® Petro, from Bentonisa do Nordeste S.A./Brazil), both used as received after thermal treatment. The silica used as support material was heated to 400°C (2°C/min) during 4 hours. The clays were dried at 120°C under airflow during 24 hours. Methylaluminoxane (10% in toluene) and the metallocene complex were supplied by Crompton GmbH, Germany, and used as received. White Martins Gases Industriais (Praxair)-Brazil supplied ethylene at petrochemical grade purity, which was further purified by passing through columns filled with an activated 4Å molecular sieve and copper catalyst. Toluene was supplied by Ipiranga Petroquímica, and was used after treatment in a 3Å molecular sieve,

followed by reflux and distillation under a dry nitrogen and sodium/benzophenone system. Hexane was supplied by Petroflex and was used after being passed through a 3Å molecular sieve and bubbled with dry nitrogen for 1 hour. 1-hexene (97% purity) was supplied by Sigma-Aldrich and was used after being dried under a 4Å molecular sieve for 48 hours.

2.2. Catalyst preparation

All operations were carried out under nitrogen, using the Schlenk technique. MAO was employed in the support pre-treatment (5mmol Al/g) at room temperature during 12 hours, followed by washing with toluene at 90°C to remove cocatalyst residue. For the support impregnation, a solution of homogeneous (*n*-BuCp)₂ZrCl₂ in hexane was employed. The catalyst solution was left in contact with the pre-treated support. The metallocene concentration used was 0.05mmol per gram of support. The suspension obtained was kept under magnetic stirring for 12 hours, and then dried in a fluidized bed under N₂ until constant weight. The catalyst activity was calculated by considering 100% Zr impregnation on the support.

2.3. Copolymerization reactions

The prepared catalysts were evaluated in ethylene/1-hexene copolymerization at 50°C and 80°C and different amounts of comonomer, with 2 bar ethylene. The polymerizations were carried out in a Büchi glass reactor coupled to magnetic stirrer. The homogeneous catalyst concentration in the reaction medium was 50µM and the Al/Zr molar ratio applied was 1000 (MAO). For the supported catalyst, 100mg was used. The reactor was filled with 100mL of hexane under nitrogen atmosphere, followed by cocatalyst injection. Then, 1-hexene was added after introducing MAO in the reactor. Different amounts of comonomer were employed (10, 15, and 25mL). Ethylene was introduced and the catalyst was injected to start the polymerization. The reaction was stopped after 30 minutes by adding ethanol/HCl 5%. The copolymers were purified with ethanol and dried until constant weight.

2.4. Polymer characterization

The copolymers' thermal characteristics, such as melting temperature (T_m) and crystallinity degree (X_c), were obtained by differential scanning calorimetry (DSC) by using a Perkin-Elmer DSC-7 device at a heating rate of 10°C/min. Approximately 3.0mg of polymer sample was sealed into aluminum pans. The temperature was raised from 40 to 150°C at 10°C/min under nitrogen atmosphere. The sample was kept for 10 min at this temperature to eliminate the heat history before cooling at 10°C/min.

Fourier transform infrared spectrometry (FTIR) was used to determine the terminal group concentrations in the polymer chains, and subsequently to estimate the molecular weights of the polymers. The number-average molecular weights (M_n) were evaluated by using a calibration curve obtained from polyethylene samples, with their molecular weights pre-determined by gel permeation chromatography (GPC). The incorporated comonomer content was calculated from the FTIR analysis, according to the method of Faldi and Soares [12]. The FTIR analyses of the polymers were conducted in a Perkin Elmer FT-IR device operating in the range of 700 - 400 cm^{-1} , 50 scans, and resolution of 4 cm^{-1} . The composites were evaluated as 50mm thick films. The reactivity ratios were calculated by using the Finemann-Ross equation.

3. Results and Discussion

3.1. Effect of comonomer 1-hexene in copolymerization

Ethylene/1-hexene copolymerization using one homogeneous and two heterogeneous catalysts supported on bentonite (BET) and silica (Si) were performed at varying temperature and comonomer concentration in the reaction medium. Table 1 presents the results obtained under different polymerization conditions.

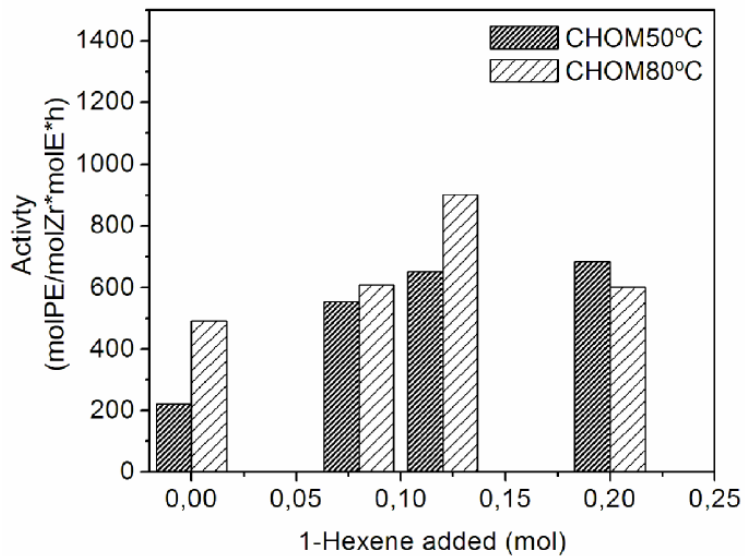
Table 1. Ethylene homopolymerization and ethylene/1-hexene copolymerization with the catalyst system $(n\text{-BuCp})_2\text{ZrCl}_2 / \text{MAO}$

| Polymer | T_p^* | 1-exene | Incorporated | | T_m | X_c |
|----------|---------|----------------|----------------------------------|----------|-------------|-------|
| | (°C) | added (mol) | 1-hexene ^a (% mol) | a^{**} | (°C) | (%) |
| C00HOM50 | | 0 | 0 | 221.5 | 132.0 | 61 |
| C10HOM50 | | 0.08 | 5.7 | 553.6 | 100.1/104.0 | 18 |
| | 50 | | | | | |
| C15HOM50 | | 0.12 | 6.9 | 652.7 | 94.9/99.9 | 4 |
| C25HOM50 | | 0.20 | 12.4 | 685.3 | 81.3 | 1 |
| C00HOM80 | | 0 | 0 | 491.2 | 129.1 | 68 |
| C10HOM80 | | 0.08 | 14.0 | 609.3 | 82.2 | 1 |
| | 80 | | | | | |
| C15HOM80 | | 0.12 | 16.0 | 902.0 | ud | 0 |
| C25HOM80 | | 0.20 | 22.8 | 601.5 | ud | 0 |

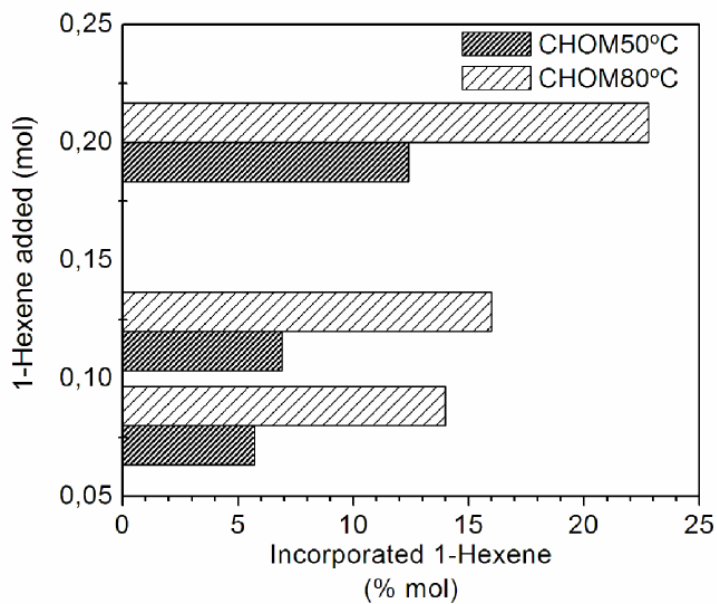
Polymerization conditions: 100mL hexane; T_p^* -polymerization temperature; time: 30 min; ethylene pressure: 2 bar; [Zr] = 0.005mmol catalyst; MAO [Al]/[Zr] = 1000; a^{**} catalytic activity (ton PE / mol Zr * mol ethylene * h); T_m -melting temperature; X_c -crystallinity degree; ^aobtained from calibration curve according to the literature [12]; and ud- undefined.

An increase in catalyst activity along with an increase of both polymerization temperature and hexene concentration was observed. The melting temperature and crystallinity degree were influenced by the incorporated comonomer content. Polyethylene crystals were not found at high polymerization temperature and high comonomer content, since branching was introduced in the polymer chains. The characteristics shown by copolymer C25HOM80 indicate that it is amorphous, due to the high comonomer incorporation in the polymer chains (Table 1).

Figure 1(a) shows the increase of the catalyst activity with increased comonomer concentration for the homogeneous system, which indicates the phenomenon known as the *comonomer effect*. This behaviour can be explained by the increase of 1-hexene incorporation in the polymer chains (Figure 1(b)), which reduces the crystallinity degree and increases polymer solubility in the reaction medium, causing catalytic sites to be more exposed and accessible, which in turn leads to higher catalytic activity. An increase of the incorporated comonomer content was observed as the temperature rose, which can be explained by a decrease in ethylene concentration at higher temperatures.



(a)



(b)

Figure 1. (a) Catalytic activity and (b) incorporated comonomer versus 1-hexene concentration in the homogeneous system.

Table 2 presents the polymerization results employing the catalysts supported on silica (Si) and on sodium bentonite (BET). The supported catalytic systems were evaluated in relation to the effect of comonomer content in the reaction medium, type of support employed in the catalytic synthesis, 1-hexene incorporation, melting temperature, crystallinity degree, and polymerization temperature over catalytic activity.

Table 2. Ethylene homopolymerization and ethylene/1-hexene copolymerization employing supported catalysts

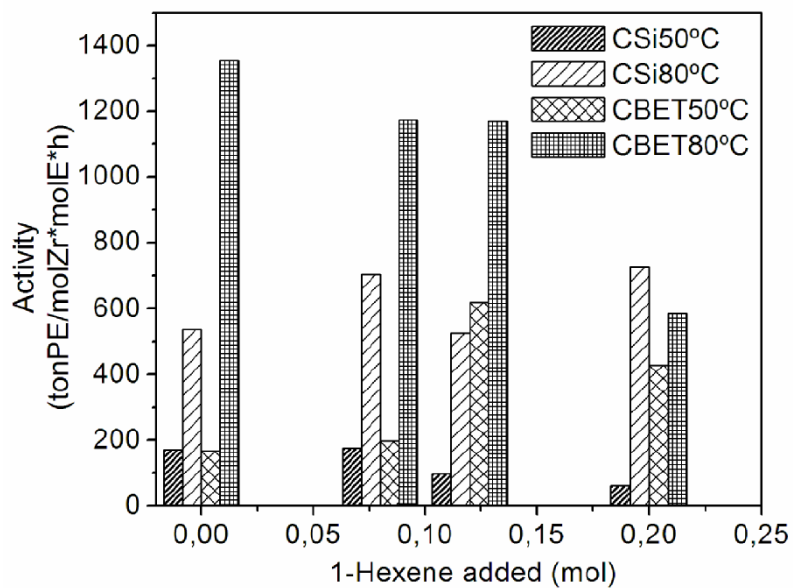
| Polymer | T_p^* | 1-hexene | Incorporated | | T_m | X_c |
|----------|---------|----------------|----------------------------------|---------------|-------------|-------|
| | (°C) | added (mol) | 1-hexene ^a (% mol) | α^{**} | (°C) | (%) |
| C00Si50 | | 0 | 0 | 170.3 | 133.9 | 54 |
| C10Si50 | | 0.08 | 4.8 | 175.6 | 102.9-106.0 | 14 |
| | 50 | | | | | |
| C15Si50 | | 0.12 | 7.2 | 96.3 | 89.7 | 7 |
| C25Si50 | | 0.20 | 6.0 | 60.3 | 83.2 | 4 |
| C00Si80 | | 0 | 0 | 536.9 | 131.5 | 68 |
| C10Si80 | | 0.08 | 8.2 | 702.5 | 86.3 | 2 |
| | 80 | | | | | |
| C15Si80 | | 0.12 | 8.6 | 524.9 | ud | 0 |
| C25Si80 | | 0.20 | 18.7 | 723.8 | ud | 0 |
| C00BET50 | | 0 | 0 | 167.2 | 133.9 | 55 |
| C10BET50 | | 0.08 | 5.4 | 197.0 | 97.5 | 17 |
| | 50 | | | | | |
| C15BET50 | | 0.12 | 6.7 | 620.1 | 93.1 | 5 |
| C25BET50 | | 0.20 | 10.9 | 428.4 | 70.7 | 1 |
| C00BET80 | | 0 | 0 | 1354.3 | 130.2 | 64 |
| C10BET80 | | 0.08 | 8.2 | 1173.5 | 89.5 | 2 |
| | 80 | | | | | |
| C15BET80 | | 0.12 | 10.4 | 1167.9 | 86.5 | 1 |
| C25BET80 | | 0.20 | 19.9 | 584.8 | ud | 0 |

Polymerization conditions: 100mL hexane; T_p^* -polymerization temperature; time: 30min; ethylene pressure: 2 bar; [Zr] = 0.005mmol catalyst; MAO [Al]/[Zr] = 1000; ** catalytic activity (ton PE / mol Zr* mol ethylene*h); T_m -melting temperature; X_c -crystallinity degree; ^aobtained from calibration curve according to the literature [12]; and ud- undefined.

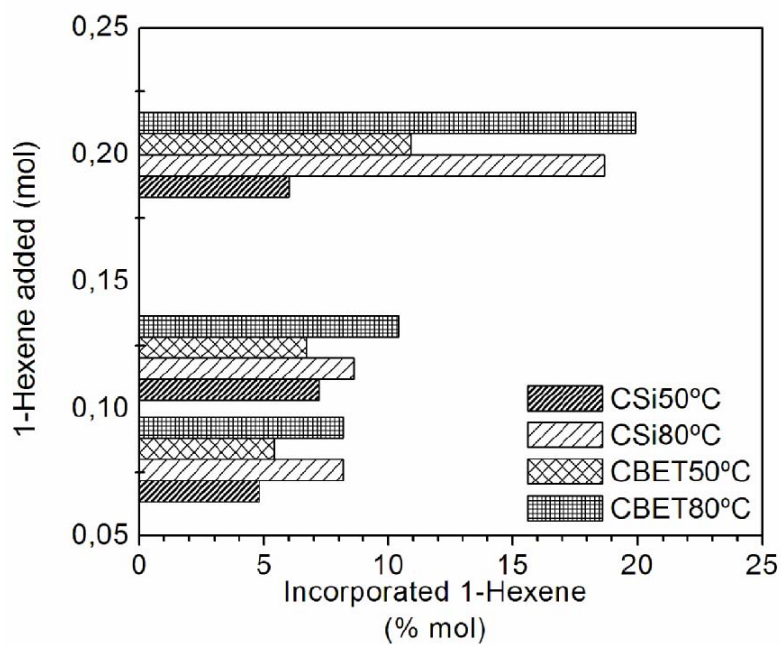
We observed an increase in catalytic activity with increasing polymerization temperature for both homogeneous and heterogeneous systems (Table 1). The lowest activity was observed for the catalyst supported on silica in polymerizations at 50°C. This fact could be related to the low solubility of the resultant polymer at low temperatures, which make the catalytic species covered, therefore retarding the monomer diffusion to the catalytic species [14]. However, the activity at 50°C using bentonite-supported catalyst increased. We speculate that bentonite platelet surface provide lower sterical hindrance than that of silica surface, making the comonomer more accessible to the active centers.

Figures 2(a) and 2(b) show the relationship between catalytic activity and 1-hexene concentration in the feed, as well as the incorporated comonomer percentage for both supported systems. As pointed out previously, both supported systems behave differently in polymerizations at 50°C; catalyst activity enhanced significantly with bentonite-supported catalyst as comonomer content increases, while it decreased with the use of silica-supported catalyst. However, at 80°C, the opposite have occurred, i.e., activity in the bentonite-supported system showed a strong decrease along with an increase in 1-hexene content (Figure 2(a)). It seems that the access of the sites fixed on the clay lamella have freely reacted with the comonomer, therefore decreasing the overall catalyst activity.

Figure 2(b) depicts how temperature and type of support used can influence 1-hexene incorporation. We observed that BET-supported catalyst, at 50°C and 80°C, achieved higher incorporation percentages than the silica-supported catalyst. As the amount of 1-hexene increased in the feedstock, the former catalyst produced copolymers with higher comonomer content. At 80°C, the 1-hexene incorporation content was even higher, due to low ethylene concentrations in the reaction medium, which facilitates 1-hexene incorporation in the growing chains, although changes in rate constant may be also important.



(a)



(b)

Figure 2. (a) Catalytic activity and (b) comonomer incorporation versus comonomer concentration for supported systems.

3.2. Effect of incorporated 1-hexene on the thermal properties

α -Olefin units in the polymer chains produce short branches, affecting the chain folding and preventing lamellae formation, which leads to spherulite formation. Consequently, defective crystals can also be formed [5, 6, 8, 9, 11]. Thus, an increase in the incorporation of 1-hexene in polymer chains leads to a decrease in melting temperatures and crystallinity degree of the synthesized copolymers. According to the literature [5, 6, 8, 9, 11], this decrease of T_m for higher comonomer levels can be explained by two factors: The formation of different crystal sizes and crystalline lattice imperfections. The presence of comonomer in ethylene chains produces branching, which reduces crystal sizes and causes a decrease in the crystallinity degree.

Figures 3 (A)-(C) show the influence of 1-hexene incorporation on the polymer melting temperature employing the catalyst systems. As 1-hexene incorporation increases, both melting temperature and crystallinity degree decreased for all the systems studied (homogeneous and BET and silica-supported systems). 1-hexene incorporation produces branches, which hinders lamellar folding [5, 6, 8, 9, 11]. Copolymers obtained from both homogeneous and heterogeneous systems showed higher T_m variations, although for the same comonomer composition, the homogeneous system always had higher melting temperatures. Moreover, it should be emphasize that melting temperature is influenced also by polymer molecular weight. In the obtained copolymers, M_n was very low with the incorporation of hexane and this could also be one of the reasons that melting temperature resulted very low.

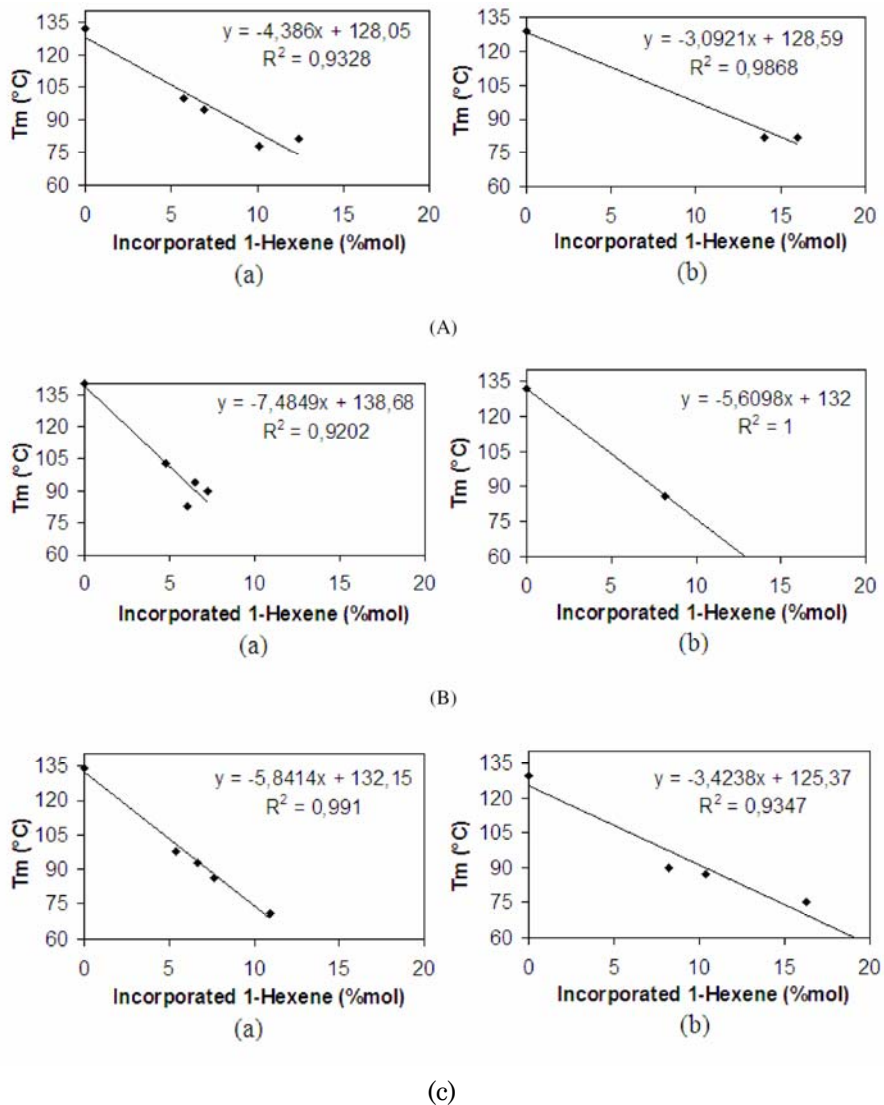


Figure 3. Melting temperature versus 1-hexene incorporation at (a) 50°C and (b) 80°C with: (A) homogeneous metallocene; (B) silica-supported catalyst; and (C) BET-supported system.

The effect of 1-hexene incorporation on melting temperatures indicates that in the reactions performed at 80°C, the copolymers presenting similar 1-hexene content incorporated in the polymer chains presented higher T_m 's in comparison to those obtained at 50°C. At low temperatures, the copolymers presented shorter ethylene sequences, leading to lower melting temperatures.

The same tendency could be observed for the supported systems, that is, a decrease in the melting temperatures for copolymers having the same composition in comparison to those obtained in the homogeneous system. This means that the ethylene sequences are shorter, and this could be due to a higher amount of 1-hexene incorporated. Also, catalysts supported on silica produced copolymers with shorter ethylene sequences in comparison to catalysts supported on BET.

The endotherms of copolymers synthesized with homogeneous and with BET and silica-supported catalysts (Figures 4 (A)-(C)) show a bimodal peak. Copolymers obtained by metallocene catalysts have homogeneous interchain composition, although the monomer distribution can be intramolecularly heterogeneous. As a result, the crystals have different melting temperatures.

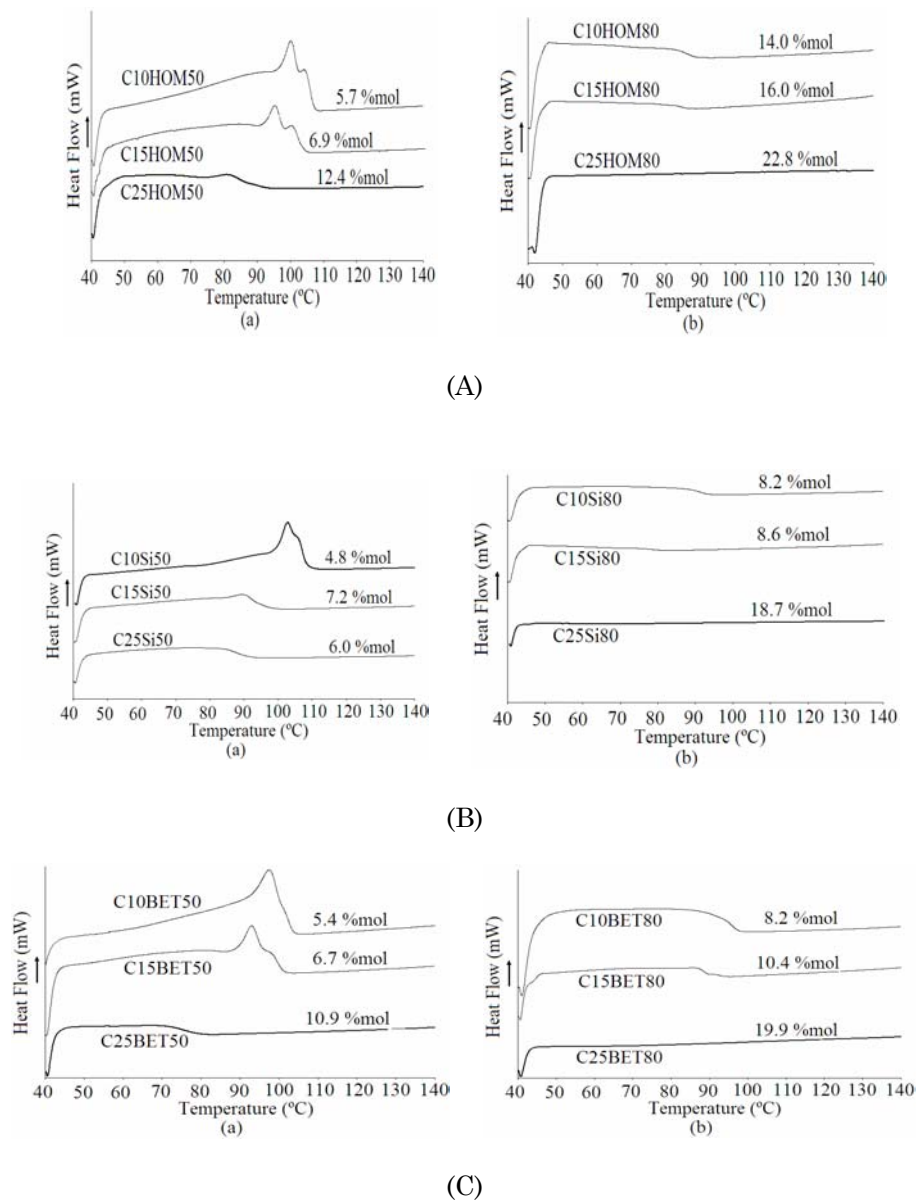


Figure 4. Melting endotherms of copolymers synthesized at (a) 50°C and (b) 80°C with: (A) homogeneous metallocene; (B) silica-supported catalyst; and (C) BET-supported system.

According to copolymer microstructure studies performed by Marques and Marinha [8], at lower levels of incorporated 1-hexene, the presence of a wide distribution of ethylene sequences with differing lengths in the polymer chains was observed, originating thicker crystals in the case of long ethylene sequences. However, in copolymers with high comonomer content, 1-hexene units interrupt ethylene sequences, making them smaller and thus producing crystalline sections with lower melting temperatures.

The presence of bimodal peak in the thermograms of the copolymers synthesized with homogeneous and supported catalysts at 50°C employing 0.08 and 0.12mol of 1-hexene in the feedstock can be observed. This behaviour was not expected, considering that metallocene systems are single-site catalysts and thus virtually every chain should have the same composition. This is the consequence of interchain heterogeneity, which in turn is the result of a wide distribution of ethylene sequences of different lengths in every chain, generating crystalline sections of different sizes. This distribution of ethylene sequences grows along with the increase of 1-hexene content in the copolymer [10]. An increase in polymerization temperature is responsible for a reduction of ethylene concentration in the reaction medium. Also, an increase in [1-hexene]/[ethylene] ratio implies a higher comonomer content, causing both the bimodal peak to disappear and the melting temperature to decline. All of these lead to the presence of higher 1-hexene content in the chains, compromising the formation of more perfect crystals.

3.3. Effect of incorporated 1-hexene on polymer molecular weight

The molecular weight was also influenced by comonomer content. In the homogeneous system, with increasing comonomer content, the number-average molecular weight decreased sharply (Table 3). At 80°C, copolymers had lower molecular weights in comparison to those obtained at 50°C. Considerable formation of vinyl groups could be observed in all copolymers synthesized at both temperatures, with only a slight increase at 80°C.

Table 3. Number-average molecular weight of copolymers synthesized with homogeneous catalyst and its respective normalized absorbance

| Polymer | T_p (°C) | 1-hexene | | | $M_n * 10^{-3}$ | |
|----------|---------------|----------------|--------------------|--------------------|-----------------|--------------------|
| | | added (mol) | A_{965}/A_{4323} | A_{908}/A_{4323} | | A_{888}/A_{4323} |
| C00HOM50 | | 0 | 0.11 | 0.50 | 0.01 | 58.2 |
| C10HOM50 | | 0.08 | 0 | 13.00 | 0.80 | 2.7 |
| | 50 | | | | | |
| C15HOM50 | | 0.12 | 0.13 | 17.60 | 1.14 | 1.9 |
| C25HOM50 | | 0.20 | 0 | 30.56 | 2.08 | 1.1 |
| C00HOM80 | | 0 | 0.34 | 2.52 | 0.05 | 12.6 |
| C10HOM80 | | 0.08 | 0.54 | 59.04 | 0 | 0.6 |
| | 80 | | | | | |
| C15HOM80 | | 0.12 | 0.67 | 70.37 | 0 | 0.5 |
| C25HOM80 | | 0.20 | 0.54 | 92.56 | 0 | 0.4 |

Moreover, the type of support had no significant influence on the number-average molecular weight of copolymers synthesized at both temperatures. These were higher than those synthesized with homogeneous catalyst (Table 4).

Table 4. Number-average molecular weight of copolymers obtained by catalysts supported on silica and bentonite (BET) and their respective absorbance

| Polymer | T_p (°C) | 1-hexene added (mol) | A_{965} (cm^{-1}) | A_{908} (cm^{-1}) | A_{888} (cm^{-1}) | A_{4323} (cm^{-1}) | $M_n * 10^{-3}$ |
|----------|---------------|----------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|-----------------|
| C00Si50 | | 0 | 0.049 | 0.084 | 0 | 0.6039 | 167.0 |
| C10Si50 | | 0.08 | 0 | 0.336 | 0.0190 | 0.0461 | 4.8 |
| | 50 | | | | | | |
| C15Si50 | | 0.12 | 0 | 2.125 | 0.1130 | 0.1564 | 2.6 |
| C25Si50 | | 0.20 | 0.060 | 2.762 | 0.1690 | 0.2454 | 3.0 |
| C00Si80 | | 0 | 0.150 | 0.923 | 0 | 0.7502 | 25.7 |
| C10Si80 | | 0.08 | 0 | 0.023 | 2.3590 | 0.0872 | 1.3 |
| | 80 | | | | | | |
| C15Si80 | | 0.12 | 0.080 | 8.189 | 0.4754 | 0.2238 | 0.9 |
| C25Si80 | | 0.20 | 0.073 | 9.417 | 9.4170 | 0.1493 | 0.3 |
| C00BET50 | | 0 | ud | ud | ud | ud | Ud |
| C10BET50 | | 0.08 | 0 | 1.544 | 0.0730 | 0.1915 | 4.4 |
| | 50 | | | | | | |
| C15BET50 | | 0.12 | 0 | 0.996 | 0.0591 | 0.0698 | 2.4 |
| C25BET50 | | 0.20 | 0.021 | 2.726 | 0.1706 | 0.1728 | 2.2 |
| C00BET80 | | 0 | 0.153 | 0.398 | 0.0066 | 0.5403 | 35.6 |
| C10BET80 | | 0.08 | 0.064 | 5.296 | 0.3549 | 0.1697 | 1.1 |
| | 80 | | | | | | |
| C15BET80 | | 0.12 | 0.051 | 3.490 | 0.2276 | 0.1137 | 1.1 |
| C25BET80 | | 0.20 | 0.059 | 10.071 | 0.7200 | 0.1104 | 0.4 |

The molecular weights of copolymers obtained with catalyst supported on silica were slightly higher than those obtained on BET-support. The copolymers obtained with BET, as catalyst support had molecular weights very close to those of the copolymers synthesized with silica. As expected, an increase of both 1-hexene content in the feedstock

and polymerization temperature implied a decrease of polymer molecular weight due to the increase of the chain transfer reactions by β -hydrogen elimination.

3.4. Determination of monomer reactivity ratios: copolymer microstructure

The reactivity ratios of the monomers (r_1 for ethylene and r_2 for 1-hexene) were determined from copolymerization results with both catalytic systems (homogeneous and heterogeneous). Fineman and Ross plots for homogeneous catalyst at 50°C and 80°C are depicted in Figure 5(A) (a) and (b), respectively. Similarly, Figures 5(B) and 5(C) also show the behaviour of catalysts supported on silica and on bentonite, respectively. In all cases, high correlation coefficients were obtained.

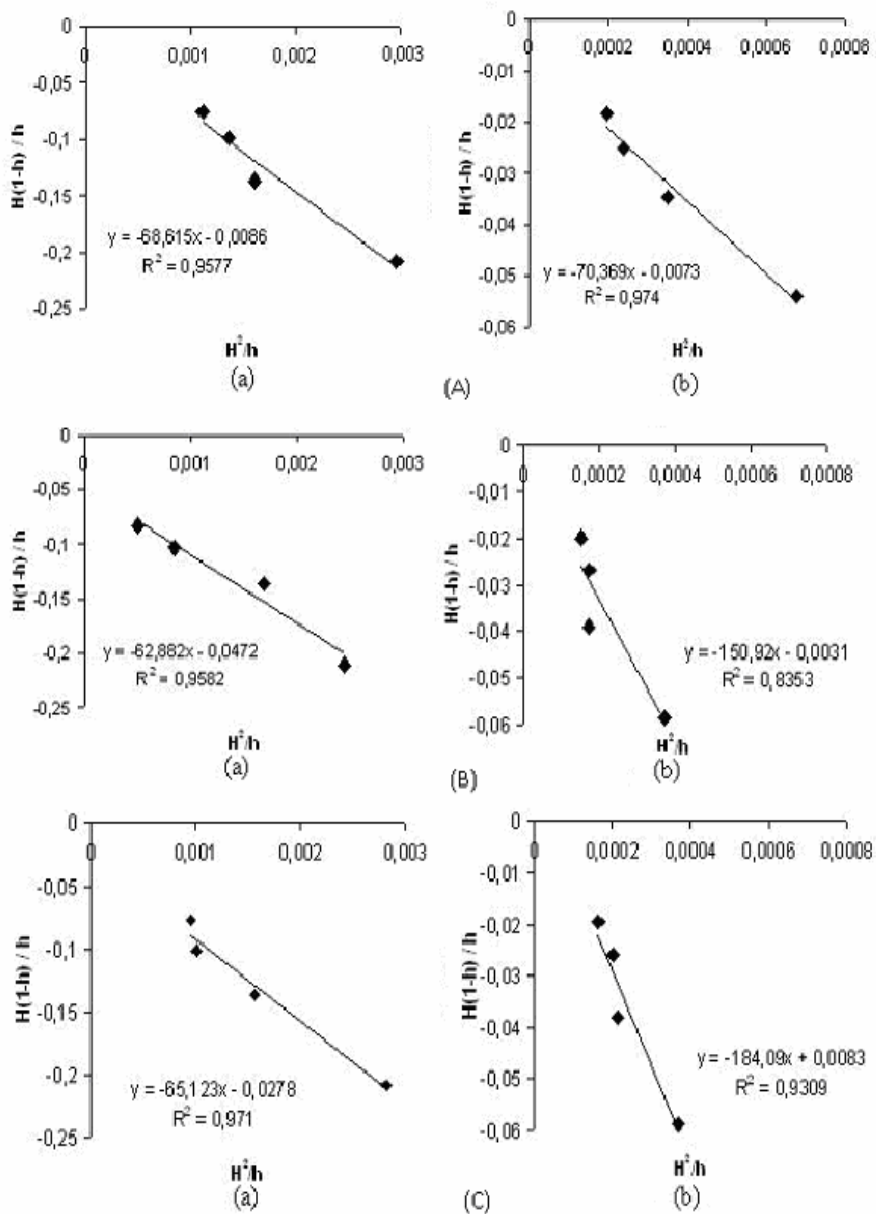


Figure 5. Fineman and Ross plot for the calculation of monomer reactivity ratio at (a) 50°C and (b) 80°C with: (A) homogeneous metallocene; (B) silica-supported catalyst; and (C) BET-supported system.

Table 5 presents the values obtained for ethylene and 1-hexene reactivity ratios in different catalytic systems. The 1-hexene reactivity ratios (r_2) were very low at all temperatures and in all catalyst systems. The determination method employed in this work was not accurate enough to evaluate r_2 results. Ethylene units were present in larger amounts in polymer chains, with the 1-hexene units being practically isolated among ethylene blocks. Values of r_2 close to zero are a clear indication of that. Marques and Marinha [8] obtained reactivity ratio values for both ethylene/1-hexene copolymerization at 80°C for homogeneous catalyst systems ($r_1 = 90.49$, $r_2 \cong \text{zero}$) and mordenite-supported catalyst systems ($r_1 = 120.86$, $r_2 \cong \text{zero}$), which also indicates a tendency to yield the same copolymer structure.

Table 5. Monomers reactivity ratios in the polymerization catalyzed by both homogeneous and supported systems

| Catalytic system | T_p (°C) | Reactivity ratio values | | |
|---|---------------|-------------------------|---------------------|---------------------|
| | | r_1 | r_2 | $r_1 \cdot r_2$ |
| (<i>n</i> -BuCp) ₂ ZrCl ₂ /MAO | 50 | 68.61 | $\cong \text{zero}$ | $\cong \text{zero}$ |
| (<i>n</i> -BuCp) ₂ ZrCl ₂ /MAO | 80 | 70.36 | $\cong \text{zero}$ | $\cong \text{zero}$ |
| (<i>n</i> -BuCp) ₂ ZrCl ₂ /SiO ₂ /MAO | 50 | 62.88 | $\cong \text{zero}$ | $\cong \text{zero}$ |
| (<i>n</i> -BuCp) ₂ ZrCl ₂ /SiO ₂ /MAO | 80 | 150.92 | $\cong \text{zero}$ | $\cong \text{zero}$ |
| (<i>n</i> -BuCp) ₂ ZrCl ₂ /BET/MAO | 50 | 65.12 | $\cong \text{zero}$ | $\cong \text{zero}$ |
| (<i>n</i> -BuCp) ₂ ZrCl ₂ /BET/MAO | 80 | 184.09 | $\cong \text{zero}$ | $\cong \text{zero}$ |

1 = ethylene; 2 = 1-hexene.

The values of r_1 did not vary with the temperature increase in the case of the homogeneous catalyst. However, for copolymerization employing supported systems at 80°C, the r_1 values increased considerably. Since the supported systems have a tendency to produce copolymers with smaller ethylene sequences [8], it is possible for the r_2 values in these systems to be closer to zero in comparison to the values in homogeneous catalysts. The support's sterical effect probably prevents the formation of 1-hexene sequences in the polymer chains.

4. Conclusion

In ethylene/1-hexene copolymerization at 80°C, the bentonite-supported system achieved higher catalyst activity in comparison with both silica-supported and homogeneous systems. Copolymers synthesized with both silica and bentonite-supported catalysts showed higher number-average molecular weights in comparison to the homogeneous catalysts. However, the increase of both comonomer content in the reaction medium and polymerization temperature led to a marked decrease in the molecular weight. The 1-hexene incorporation capacity was higher for the homogeneous catalyst, followed by bentonite and silica-supported systems at 50°C and 80°C. The melting temperatures of copolymers with similar composition, obtained by the homogeneous catalyst, were higher in comparison to both the bentonite and silica-supported systems. This is due to the fact that copolymers synthesized through supported catalysts have a tendency to yield alternating distribution of comonomer in the polymer chains.

This paper confirms the extraordinary performance of mineral clay-metalocene heterogeneous catalysts in the copolymerization of ethylene-hexene. This could lead to LLDPE/clay nanocomposite. The study of the thermal and mechanical properties of these materials is the subject of future publication.

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