
Polyethylene of ultra-high molecular weight (UHMWPE) for biomedical applications

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ABSTRACT

In this study the polymerization of ethylene was studied, using the metallocenes Cp_2ZrCl_2 and $(n\text{ButilCp})_2\text{HfCl}_2$ supported in mesoporous silica SBA-15 type, by two different methods. The effect of the presence of the support and of metallocene heterogenization methods used, direct impregnation of catalyst on the support pretreated with the organoaluminum cocatalyst and impregnation of the pre-activated catalyst on the support, on the catalytic activity was analysed. The supported systems developed were used to prepare nanocomposites of ultra-high molecular weight polyethylene, (UHMWPE) by *in situ* polymerization. These nanocomposites comprise a matrix of polyethylene formed inside the pores of SBA-15 particles and were characterized in order to evaluate their properties through several techniques such as: differential scanning calorimetry, X-ray diffraction, termogravimetric analysis, hardness and stress-strain tests. The results indicate that the methodology used in preparing the supported catalyst influences catalytic activity, as well as the characteristics of the nanocomposites. It has been found that the impregnation SBA-15 treated with MAO was more advantageous since it leads to higher catalytic activities for ethylene polymerization. In terms of the final characteristics of the nanocomposites based on the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system gave rise to more crystalline, hard and able to suffer less deformation materials.

1. Introduction

The UHMWPE is a high density polyethylene which has extremely long chains. It is a fairly hard material with high impact resistance, fatigue, abrasion and very resistant to a wide variety of products acids, solvents, oxidants and fuels. In terms of applications, has a wide use in biomedical products, with respect to sutures, heart valves, prosthetic manufacture of hip and knee replacement of damaged and painful femur, tibia and patella

surfaces. The application also resides in coating materials in corrosive environment, pipes, pumps and various types of packaging products.

The materials were produced polymer nanocomposites, which are two phases consisting of a polymeric matrix reinforced with a small fraction of an inorganic compound, with dimensions on the nanometer scale systems. The presence of small amounts of these inorganic compounds in the polymer matrix provides a significant improvement in the mechanical, electrical and thermal resistance

properties. The technique used for the preparation of intercalated nanocomposites is the in situ polymerization. In this methodology the catalyst, the monomer and the inorganic compound are introduced directly into the polymerization reactor. This technique enables a more uniform distribution of the inorganic filler in the organic matrix which becomes crucial when you want to prepare more homogeneous and high quality materials. The selection of the metallocene complex have been carried out in mind the desired molar mass ranges. The catalysts used for the polymerization of ethylene were Cp_2ZrCl_2 and $(n\text{ButilCp})_2\text{HfCl}_2$. The zirconium catalyst, a catalyst is well-studied, gives polyethylenes with molar mass M_n in the range of 200 to 300 000 and essentially serves here as the reference system, while the catalyst of hafnium allows to obtain values of M_n and higher, up to 600 000 and greater.

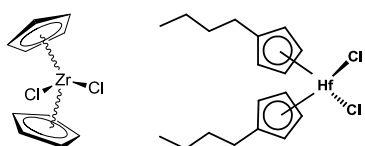


Figure 1 - Representation of metallocene structure Cp_2ZrCl_2 and $(n\text{ButilCp})_2\text{HfCl}_2$, respectively.

For these compounds can act as catalysts and produce polymers, the presence of a cocatalyst to promote the formation of the active site is needed. The cocatalyst selected was methylaluminoxane (MAO) which is the most commonly used in the activation of metallocenes.

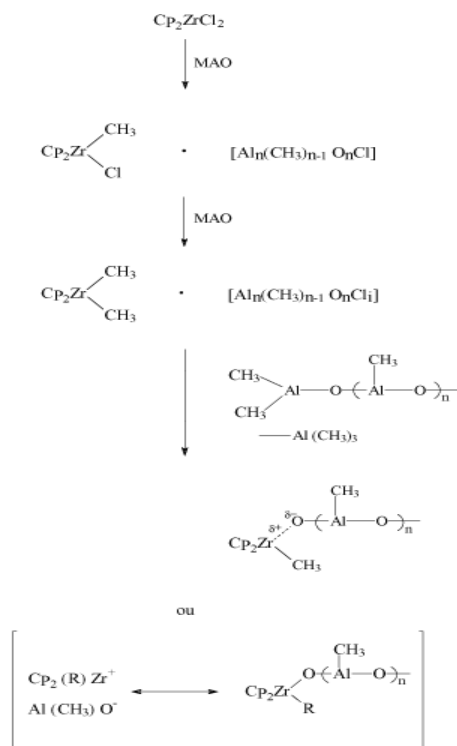


Figure 2 - Formation of the active species in $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ systems.

The heterogeneity of the catalytic system (catalyst / cocatalyst) may be performed in a variety of media. The successful use of a given material depends on the support as interactions between the user and the immobilized complex and the characteristics of the support itself. The support used for the polymerization of α -olefins was mesoporous silica SBA-15 is a very stable and inert under the polymerization conditions and the material has a high porosity, surface area, low cost. This porous silica has ordered hexagonal structure with uniform straight channels and which will facilitate immobilization of metallocenes, giving rise to a more homogenous distribution of the surface, and improve the accessibility during the activation by MAO monomer, and insertion. The SBA-15 will have a dual role, will act as support and as reinforcing agent the polymeric matrix. The immobilization strategies were used impregnating the support with the pre-activated catalyst (PA), and pretreatment of the support with the cocatalyst (MAO-SBA). In the first method there is a pre-contact between the catalyst and the cocatalyst and only then there will be an impregnation of the support with the resulting solution. In the second method there is a pretreatment of the support with MAO catalyst is added and eventually into the polymerization reactor. Compared with the direct method of impregnation, these techniques allow to increase the number of active centers and give catalysts with high activity.

2. Experimental

All manipulations were performed under inert nitrogen atmosphere using the standard Schlenk technique. Nitrogen (N45 Air Liquide) was purified by passing through columns of molecular sieves 4A and 13X. The solvent, toluene, was dried with 4A and 13X molecular sieves (Aldrich) and subsequently purified by distillation under an inert nitrogen in the presence of sodium (5 g / L) and benzophenone (1 g / L) atmosphere before use. The amount of catalyst and cocatalyst to be employed were chosen according to the experimental methods developed previously. The supported catalysts were used in the form of suspension with a solid weight, and contents of Zr and Hf, as well as known volume of toluene. All procedures done to Cp_2ZrCl_2 catalyst were also carried out similarly to $(n\text{ButilCp})_2\text{HfCl}_2$. The mesoporous material was dried at 300°C with a heating rate of $5^\circ\text{C} / \text{min}$, remaining for two hours in air reconstituted and one hour in an inert atmosphere. After cooling, the SBA-15 is transferred into a dry Schlenk inerted subsequently be used for the impregnation.

2.1 Preparation of supported catalyst

- i) Impregnating the support with the pre-activated catalyst (PA)

In a Schlenk inerted was added 1.9 mL of a solution of Cp_2ZrCl_2 (98%, Aldrich) in toluene preactivated 1.7×10^{-3} M MAO (7 wt% Al, Akzo) (Al / Zr = 150) to a suspension of 150 mg of SBA-15 in 5 ml of toluene. The suspension obtained is placed under stirring for 1h30 with shielding from ambient light. After this period, the supernatant of the suspension is tested by testing the supernatant, see section supernatant test to verify that the immobilization of the organometallic compound in the solid was complete. If this does not occur, is repeated to prepare a new suspension using a smaller amount of Cp_2ZrCl_2 solution.

- ii) Pretreatment of the support with MAO (SBA-MAO)

Inerted schlenk is a heavy one ounce of support. Board 25 mL of toluene and stirred until complete dispersion of the solid. Is added, then 1.3 mL of MAO and the resulting suspension is placed under stirring for 16 hours. After this period, the solid is washed 3 times with 20 mL portions of substantially fresh toluene, and dried under vacuum to eliminate the solvent. This procedure pretreatment with MAO leads to a content of 3.0 mmol Al / g solid. After drying, add 1.5 ml of the solution 1.7×10^{-3} M Cp_2ZrCl_2 in toluene so as to make the impregnation of the pretreated support. The suspension obtained is poured under stirring during 5 min with protection from ambient light. Again we resort to testing the supernatant to confirm the immobilization of the metallocene.

2.2 Polymerizations

The polymerization reactions were performed in a glass reactor with a volume of 250 ml and equipped with a magnetic stirrer and closed with a septum and a capsule. The glass container is dried in an oven at 75°C , assembled while still hot and cooled under vacuum before it can be used later. This reactor is connected to a network of gas / vacuum through a needle inserted through the septum and all solutions and suspensions are also injected through this needle septum. All this system is placed in a water bath at 25°C with agitation provided by an Ika RCT Basic plate, set to 1200 rpm. The closed reactor is purged with five cycles of vacuum / nitrogen before being heated under vacuum with a heat gun to about 200°C . After cooling, distilled toluene are introduced in order to obtain a total of 50 ml to initiate polymerization. The atmosphere and the solvent are saturated with ethylene at 1.2 bar (Air Liquide, purified by columns with molecular sieves 4A and 13X), with the holding of five rapid cycling between vacuum/ethylene. The polymerization reaction is

stopped by adding about 20 ml of methanol acidified with hydrochloric acid, during production of one gram or half gram of polymer. This is then filtered and washed twice with methanol for several hours, dried and weighed.

2.2 Characterization techniques

All nanocomposite films were prepared at 230°C . To measure the weight variation with temperature of a sample was used the apparatus of TA Instruments Q500. The analysis was performed in a controlled atmosphere of air and nitrogen, the heating rate was $10^\circ\text{C} / \text{min}$, and the studies were conducted at temperatures from 30 to 800°C . For the DSC technique, the protocol used for all samples were as follows: -40 to 190°C heating, followed by cooling from 190 to -40°C , and finally heating from -40 to 190°C with a speed for the different cycles of $10^\circ\text{C} / \text{min}$. The calorimeter used was a TA Instruments Q100. The analyzes of the nanocomposites through X-ray diffraction to average (MAXS) and high angles (WAXS) were performed. Samples were recorded in the reflection mode by using a Bruker D8 Advance diffractometer, provided by a PSD Vantec detector (Bruker, Madison, Wisconsin). We used a $\text{CuK}\alpha$ ($\lambda = 0.1542 \text{ nm}$) radiation operating at 40 kV and 40 mA. The optical parallel beam was adjusted by the parabolic Göbel mirror with a horizontal incident Soller slit of $0,12^\circ$ and LiF monochromator. The equipment was calibrated with multiple standards. Employed a scanning mode to the detector, these diffraction scans were collected with a range of $2\Theta = 1$ to 43 , with a pitch of $2\Theta 0,024^\circ$ and 0.2 sec per step. The indentation tests were performed at room temperature on a Shimadzu analyzer (model DUH211S) equipped with a triangular type Berkovich diamond indenter. Stress-strain tests were performed at two different temperatures, 25°C in a Instron dynamometer, model 3366, with a load of 100N and 90°C in a Minimat dynamometer with a 20N load cell. In both cases, the test tubes were obtained starting from films with a length 10 mm, cut with a die in a press Wallace, Model C71509. In the tests there was a deformation reached 34 mm, then the final length of 44 mm was obtained. The drawing rate applied to both temperatures was $1 \text{ mm} / \text{min}$, so that each test lasted 2000 s.

3. Results and discussion

3.1 Characterization of mesoporous silica, SBA-15

The SBA-15 is the nanometric inorganic component used in this study for the synthesis of nanocomposites and here has a dual role as holder and as reinforcing agent the polymeric matrix. The parameters of Table 1 were calculated from nitrogen

adsorption experiments and are consistent with the values reported in literature for such materials.

Table 1 - Texture parameters of the SBA-15.

Support	S_{BET} (m^2g^{-1})	V_p (cm^3g^{-1})	A_{ext} (m^2g^{-1})	D_p (\AA)
SBA-15	743	1,12	87	70

S_{BET} : specific surface area.

V_p : specific pore volume.

D_p : average pore diameter ($D_p = 4V_p/S_{\text{BET}}$).

3.2 Study of the behavior in polymerization of ethylene and of complex Cp_2ZrCl_2 and $(n\text{butyl})_2\text{HfCl}_2$ supported on SBA-15

The catalysts prepared according to the methods above, were tested in the homopolymerization of ethylene two values for Al / Mt, one down, right 500 being used, in order to limit any possible effect on leaching of the catalyst support during the polymerization, and other 5000 high, thereby maximizing higher activities. For ease of comparison, the polymerization activity of these catalysts (based on Zr and Hf) are shown in figures 3 and 4.

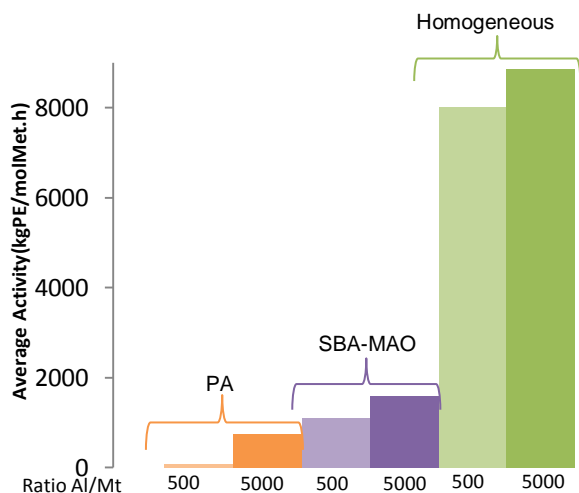


Figure 3 - Polymerization activities for $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ homogenous system and supported on SBA-15 Second different methodologies.

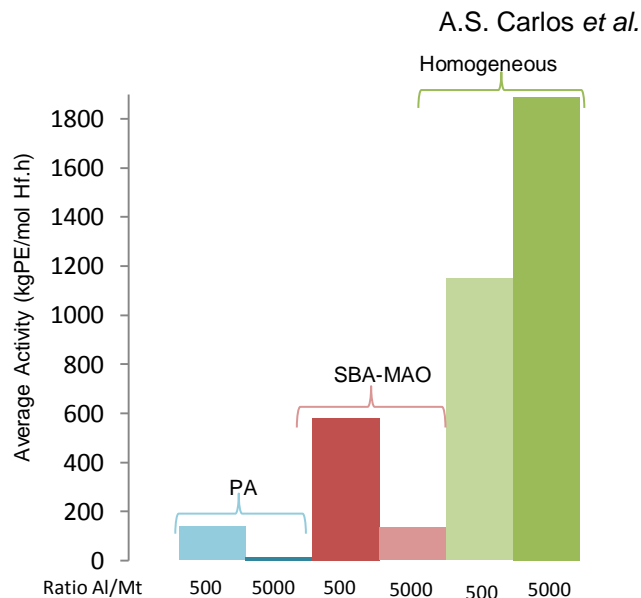


Figure 4 - Activities for the polymerization system $(n\text{ButilCp})_2\text{HfCl}_2/\text{MAO}$ homogeneous and supported on SBA-15 under separate methodologies.

Analyzing the graphs it appears that the highest activities are obtained with homogeneous phase catalyst. The metallocene heterogenization on the surface of the SBA-15 activity leads to significantly lower values. Comparing the two methods of immobilization can be seen that the highest activities are obtained when the pretreatment is employed with MAO. In this case, the active species not formed directly on the support surface, but rather on the resulting intermediate layer of MAO. Also observed is an effect of the ratio Al/Mt in catalytic activity that is distinct for each of the transition metals studied. For the Zr-based systems there is, in the range of Al/Zr studied, an increase of activity with this reasoning. Already for systems of Hf such behavior is only observed for the catalyst in homogeneous phase. One possible explanation relates to the well-known reduction of the value of Al / Zr required to achieve maximum activity when the catalyst is immobilized on the support. Thus in the case of supported catalysts Hf maximum activity should now meet to values of Al/Hf between 500-5000. The heterogeneity of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system causes a greater drop in activity observed in the system $(n\text{ButilCp})_2\text{HfCl}_2/\text{MAO}$. So between the systems supported the difference in activity is attenuated. It is further noted that the reduction of activities between the homogeneous and the heterogeneous system is stronger for $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system than for the Hf-based counterpart.

3.3 Characterization of Nanocomposites

The nanocomposites were characterized by thermal level (thermogravimetric analysis, TAG, and differential scanning calorimetry, DSC) crystalline (X-ray diffraction) and mechanical (indentation tests and stress-strain).

3.3.1 Study of the thermal properties

The thermogravimetric technique provides information about the contents of SBA-15 existing in each of the nanocomposites through the degradation processes occurring analyzed for the two atmospheres, oxidizing and inert.

There is thermogravimetric curves in the degradation process occurs in an inert atmosphere in a single phase, while for the atmosphere occurs in several stages. This mechanism is more complex in this atmosphere due to presence of air oxygen, which favors the formation of different intermediate species used for each gas. For nanocomposites which have a high content of SBA-15, there is a small step degradation at low temperatures, due to the effect of the mesoporous silica, which acts as a catalyst for decomposition reactions, as described in the literature [13, 14, 20]. It is also observed that degradation occurs at higher temperatures for SBA-MAO method.

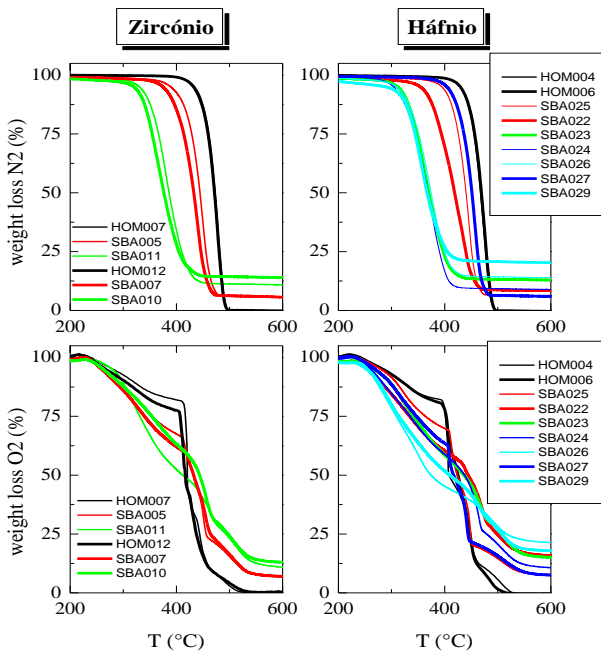


Figure 5 - Decomposition of the samples under study for inert and oxidizing atmosphere for the two catalysts.

In DSC, the materials were subjected to three cycles was held first an essay heating, after the material has to be cast, carried out a cooling and lastly the second heating process, the entities generated in the controlled cooling. These steps will provide information on existing transitions in samples processed in movie form.

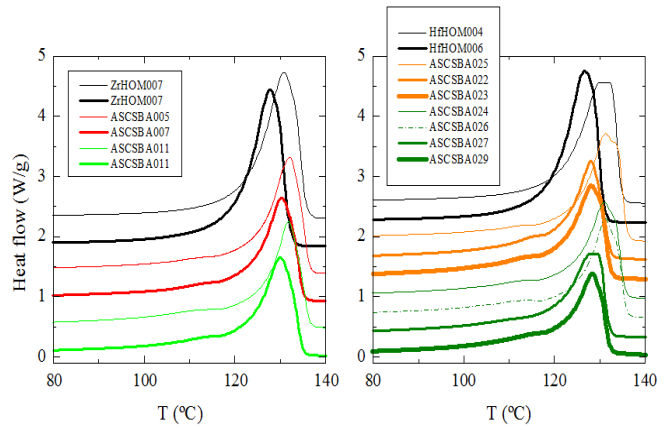


Figure 6 - DSC thermograms for the first melting process of the nanocomposites under study.

Heating cycles show a primary endothermic process, the maximum is around 130 °C superimposed with a much lower peak intensity located around 110 °C. The major band is associated with fusion of regular crystals of polyethylene, while the projection on the lower temperatures is attributed to the PE chains of crystals which are inside the tubes of SBA-15. The latter crystals are smaller than those of the outer polyethylene chains and therefore melt at lower temperatures as a result of the confinement phenomenon, since its growth is restricted to the size of said channels. It is evident also that the synthesized samples with hafnium have a certain bimodal, ie asymmetry of the melting endotherms, indicating a fact that the size distribution of the crystals is less homogeneous for these samples than for those prepared with zirconium.

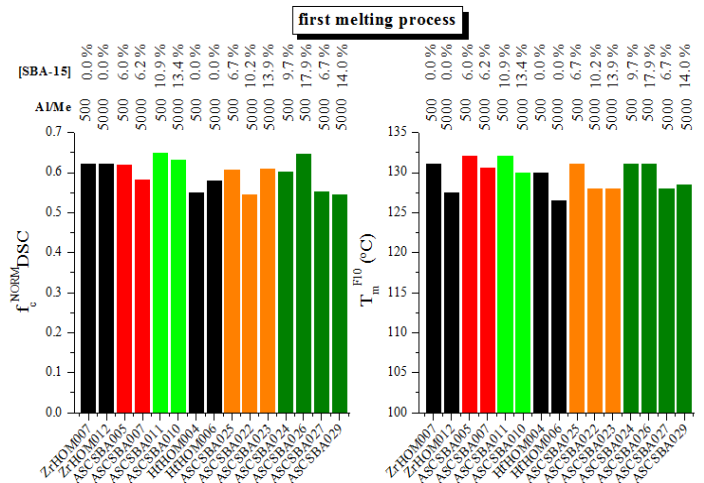


Figure 7 - Graphic summary of crystalline fractions (fcNORM) and melting temperatures (T_m) for the first fusion (F10) obtained in DSC.

The results show a common characteristic for all samples regardless of the catalyst used and the presence of SBA-15, the samples with an Al/Mt ratio = 500 exhibit superior to those observed for samples with a ratio of 5000. For T_m Zirconium samples there is a relationship for the same ratio Al/Zr and different methods, there is an increase in the crystalline fraction for samples PA. Compared with

homogeneous samples it is observed that the temperatures of first melting increase in nanocomposites, but the difference is not very significant, as the standard crystalline fraction, this are largely unaltered. For samples Hafnium observed in general that the nanocomposites synthesized with an Al/Mt ratio of 500 f_c^{NORM} have an increased T_m and for the first fusion.

3.3.2 Study of the crystal structure

The diffraction X-ray technique is useful for structural characterization of semicrystalline polymers such as polyethylene. Polyethylene crystallizes under normal conditions in an orthorhombic cell. This is characterized by having distinct diffractions, 110 and 200 located at 23° and 21° , respectively, at 2θ (CuK α radiation ($\lambda = 0.1542$ nm)). The materials studied show additional complexity. SBA-15 possesses a broad range caused by an ordering ordered hexagonal structure of its channels, and the low range is a totally amorphous material, or has an isotropic halo which coincides with the angular interval in the diffraction pattern polyethylene. Thus, the correct determination of the crystalline polyethylene fraction requires subtracting the contribution of the halo of SBA-15 the total diffractogram.

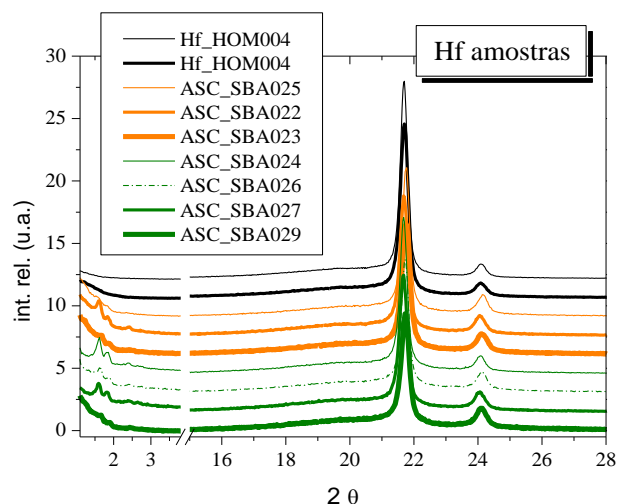


Figure 9 - RX diffractograms for nanocomposites by the system (nButilCp) $_2$ HfCl $_2$ /MAO.

It is observed that the values of $f_c^{RX,NORM}$ for the various samples of Table 2 are very similar to each other and lower than the homogeneous samples. Compared with the DSC data, it appears that the values are always lower than $f_c^{DSC,NORM}$. This difference may be explained by the fact that the X-ray diffraction does not detect the PE crystallites that are within the channels of SBA-15, obtaining a value less than the actual [13]. These crystals count on the results from DSC endothermic peak area around 110-115 ° C.

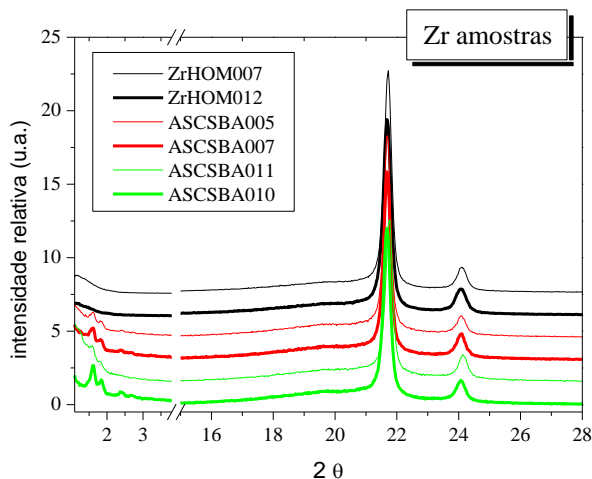


Figure 8 - RX diffractograms for nanocomposites obtained by Cp $_2$ ZrCl $_2$ /MAO system.

Table 2 - Crystallinity normalized RX ($f_c^{RX,NORM}$) compared to the crystallinity calculated by DSC ($f_c^{DSC,NORM}$) for nanocomposites studied.

Zirconium	Method	Al/Mt	TGA	$f_c^{RX,NORM}$	$f_c^{DSC,NORM}$
Zr-HOM-007	Homog	500	0,0	0,63	0,62
Zr-HOM-012	Homog	5000	0,0	0,61	0,62
ASC-SBA-005	SBA-MAO	500	6,0	0,54	0,62
ASC-SBA-007	SBA-MAO	5000	6,2	0,53	0,58
ASC-SBA-011	PA	500	10,9	0,52	0,65
ASC-SBA-010	PA	5000	13,4	0,54	0,63
Hafnium					
Hf-HOM-004	Homogéneo	500	0,0	0,58	0,55
Hf-HOM-006	Homogéneo	5000	0,0	0,59	0,58
ASC-SBA-025	SBA-MAO	500	6,7	0,57	0,61
ASC-SBA-022	SBA-MAO	5000	10,2	0,52	0,55
ASC-SBA-023	SBA-MAO	5000	13,9	0,54	0,61
ASC-SBA-024	PA	500	9,7	0,52	0,60
ASC-SBA-026	PA	500	17,9	0,52	0,65
ASC-SBA-027	PA	5000	6,7	0,49	0,55
ASC-SBA-029	PA	5000	14,0	0,50	0,54

3.3.3 Study of the mechanical properties

In the indentation test, the determination of hardness, consisting primarily of monitoring print dimensions (indentation) resulting from the penetration of an indenter on the surface of the material. Figures 10 and 11 show the results obtained for the modulus of microhardness for nanocomposites studied.

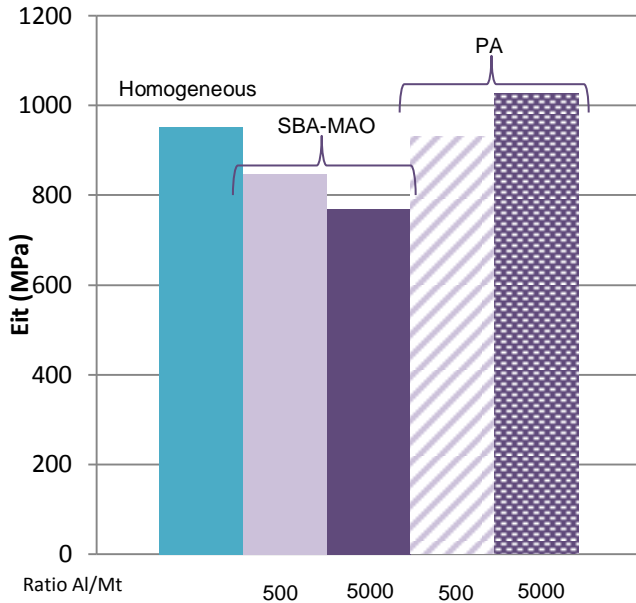


Figure 10 - Values of microhardness module for Cp₂ZrCl₂/MAO system of reference samples and nanocomposites.

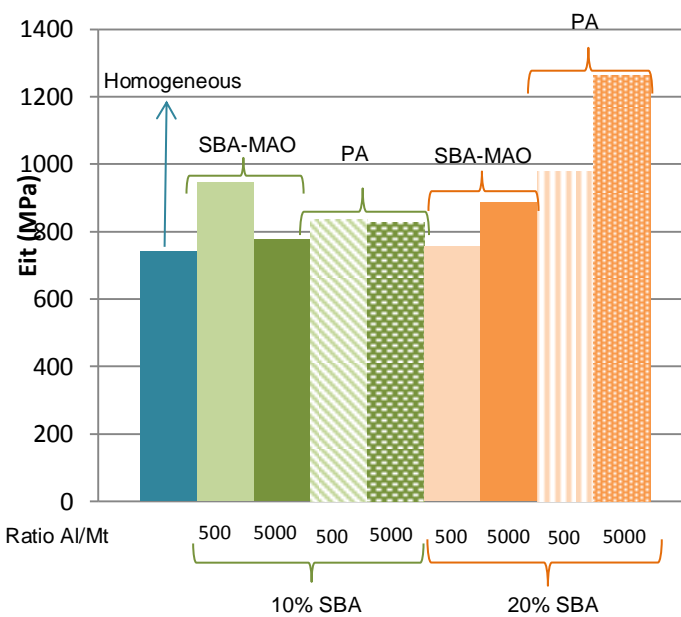


Figure 11 - Microhardness modulus values for the system (nButilCp)₂HfCl₂/MAO of reference samples and nanocomposites.

For the system (nbutilCp)₂HfCl₂/MAO, the strictest samples are those with the highest

percentage of SBA-15, which would be expected due to its reinforcing effect, conclude that for this system nanocomposites produced by impregnation holder with the pre-activated catalyst (PA) have the highest values. The cause could be the fact that in these conditions of treatment, the active phase has become strongly bound to the support. As compared to the average of the homogeneous sample values it appears that this has the lowest value of all, what you would expect, but the difference is not very significant. No regard to Cp₂ZrCl₂/MAO system, the average of the samples homogeneous is located above the other measurements, although it was performed by the same procedure. It is also the case here that caused by PA nanocomposites exhibit more advantageous values, despite variations are not very significant. There are few micro-hardness data for polymer matrix composites for the case study. The thickness of the films is about 150 microns may be sufficient to estimate the measure due to the fact that they have to take the sample to a glass slide. This event linked to a degree of heterogeneity that may exist in some samples may be responsible for these results indentation. These results that do not show significant variations and very visible trends.

The stress-strain diagrams were obtained by subjecting the material to tensile tests, where a cylinder of standard dimensions is deformed at constant speed, record the force required to stretch the material and this deformation. The diagrams provide information about the rigidity (Young's modulus), flow point (from the permanent strain), tensile strength and toughness, these last two magnitudes are related to the strength of the material. The Young's modulus or modulus of elasticity (E) is the ratio of the stress and strain in the direction of the applied load. It is known that this module has a direct relationship with the stiffness of the material, ie the higher the value, the greater the stiffness of the material and therefore there will be less deformation before rupture.

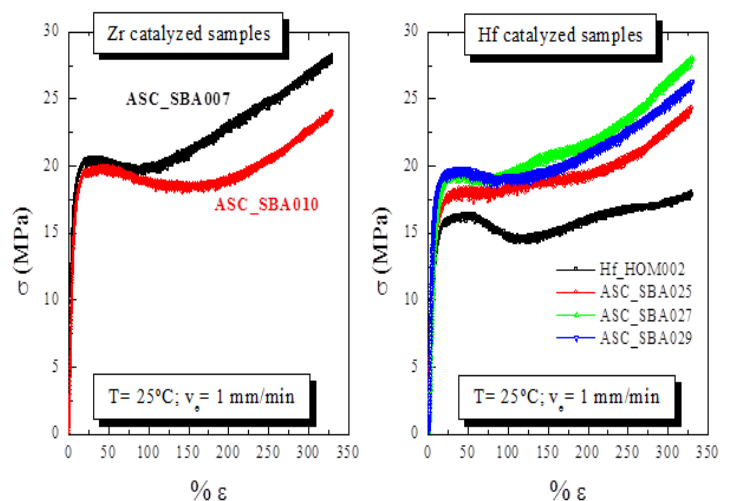


Figure 12 - Results of the stress-strain tests at 25°C with a drawing speed of 1mm / min for nanocomposites studied.

The differences found in the samples of zirconium put in evidence that the ASC-SBA-007 sample has a slightly higher modulus than the ASC-SBA-010 nanocomposite despite its content in SBA-15 is much lower and there is also a change in the crystalline fraction. The reason for this behavior does not seem surprising; the elastic part of the deformation process curve could be associated with the fact that the PA method appears to be less effective than the SBA-MAO (ratio Al/Mt is the same for both) in order to allow the foot to crystallize within the channels of SBA-15, as evidenced by the DSC data in the region of 110-120 °C. The intensity for ASC-SBA-010 sample should be higher than for ASC-SBA-007 and not a significant difference is observed, on the contrary are practically the same magnitude. For the shape of the curves in the stretching process it is found that ASC-007 SBA-hybrid has a higher deformation capacity. For ASC-SBA-010 sample stretching is more limited due to the higher content of SBA-15 and its higher crystallinity. With respect to samples of hafnium checks that the ASC-SBA-025 sample has a Young's modulus value above BSA-SBA-027 sample, but this is explained by the crystal morphology of this sample. Taking into account the other parameters it is inferred that this also shows heterogeneity. Comparing the homogeneous mixture with the other, there is a difference in elastic modulus due to the incorporation of mesoporous load. The high modulus value for ASC-SBA-029 sample is evidenced by the high content of SBA, but not the rest of the parameters. This event again justifies the reduced efficiency of the method PA in order to allow the foot to crystallize within the channels of SBA-15. Comparing the two systems it is found that the nanocomposites through the system $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ have higher Young's modulus values indicating a higher stiffness and less deformation capacity at 25 °C.

Were also carried out tests of the stress-strain at 90 °C which can be consulted on following figure 13.

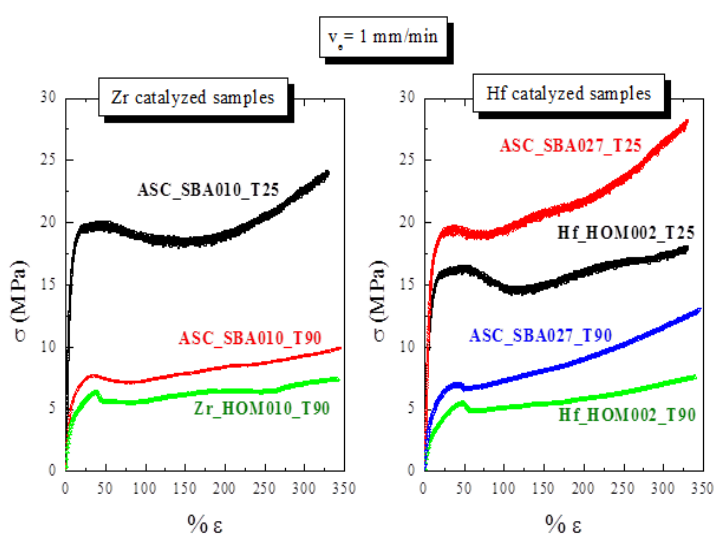


Figure 13 - Results of the stress-strain tests at 90 °C with a drawing speed of 1mm / min for nanocomposites studied. Also incorporated curves for tests at 25 °C.

Figure 13 also contains a homogeneous sample (HOM-Zr-Hf-010 and HOM-002) for both catalysts, only to see the difference in deformation between materials in the presence of mesoporous load. Differences in crystallinity, the crystal size and uniform size distribution of the crystals become greater than the Young's modulus in ASC-SBA-10 sample, although it was expected since most significant differences which has twice the contents of SBA-15 compared to BSA-SBA-027 sample. Now comparing the tests for two different temperatures, it is inferred that the results are dependent on this variable. It is observed that at 90 °C have a lower value of the modulus of elasticity, which means that nanocomposites at this temperature deform with ease. These results are particularly important at a practical level, since it allows to obtain an improved mechanical performance at 25 °C without modifying the processing conditions.

4. Conclusions

There were two types of supported catalysts for the polymerization of ethylene, using two impregnation strategies SBA-15. This analysis showed that the type of support, catalyst and the method of preparation used in the immobilization this has a direct effect on polymerization activity. The use of this mesoporous silica with a pore diameter greater favors the confinement of active species within their own channels, which benefits the stability of the active species and regulating activity via a selective effect on MAO catalyst. The carrier confinement effect also leads to polymers with specific morphology. All these characteristics of SBA-15 proved to be particularly important for a maximum of catalytic activity in the polymerization of ethylene. The knowledge of the behavior of the catalyst systems $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ and $(n\text{ButilCp})_2\text{HfCl}_2/\text{MAO}$ in ethylene polymerization becomes also possible to use mesoporous materials such as SBA-15 type inorganic filler to prepare nanocomposites by in situ polymerization.

It proves that the presence of MAO favors the attachment of the metallocene and a content thereof for each system under study in order to maximize the catalytic activity is needed. The best values occurred for the Cp_2ZrCl_2 catalyst with SBA-MAO method and a high ratio Al/Mt.

It is also inferred that the PA method appears to be less effective than the SBA-MAO in order to allow the foot to crystallize within the one-dimensional mesoporous pores of the silica.

Conclude that a $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system is advantageous, both in terms of activity as in thermal and mechanical properties. These samples have to be more stable, crystalline, hard and capable of undergoing less deformation.

The characterization results confirm that the

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