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Production of LPE/BPE blends using homogeneous binary catalyst system: influence of the polymerization parameters on polymer properties

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Abstract

Linear polyethylene/branched polyethylene blends (LPE/BPE) were prepared using the homogeneous binary catalyst system composed by Ni(α-diimine)Cl_2 (**1**) (α-diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) and *rac*-ethylenebis($IndH_4$)$ZrCl_2$ (**2**) ($IndH_4$ = 4,5,6,7-tetrahydro-1-η^5-indenyl) activated with methylaluminoxane in hexane at three different polymerization temperatures (0, 30 and 50 °C) and by varying the zirconium loading molar fraction (x_{Zr}). The polymerization runs carried out at 30 °C have shown that the productivity decreases linearly with x_{Zr}. On the other hand, at 0 and 50 °C, a non-linear dependence was observed between the x_{Zr} and the productivity. The molecular weight of the LPE/BPE blends varied from 222 to 470×10^3 g mol^{-1} with polydispersities around 2.0. Differential scanning calorimetry results showed that the dependence of the T_m values with respect to the x_{Zr} it is higher for the LPE/BPE blends produced at 0 °C. Dynamic mechanical thermal analysis shows the formation of different polymeric materials where the stiffness varies according to the x_{Zr}. The surface morphology of the BPE/HDPE blends produced at 30 °C revealed a low miscibility between the PE phases resulting in the formation of a 'cobweb structure' (for $x_{Zr} = 0.25$) after etched with hot *o*-xylene.

Keywords: Ethylene polymerization; LPE/BPE blends; Homogeneous binary catalyst system

1. Introduction

The demands for polymeric materials with an unique combination of properties are ever growing. A cost efficient solution to meet the demands is the use of polymer blends. Particularly, the blends of linear and branched polyethylene have received much attention during the last decades especially due to their interesting chemical and physical properties [1–4]. Usually, polymer blends can be obtained either by a mechanical mixture of two or more melted polymers or by dissolving appropriated polymers followed by precipitation. Additionally, an alternative method has been introduced based on binary catalyst systems which consists of combining, in a single reactor, two or more types of catalysts to produce polymers with different and controlled M_w and M_w/M_n [5–11]. Recently, we have reported the use of binary catalyst systems such as Ni(α-diimine)Cl_2 (**1**) (α-diimine = 1,4-bis(2,6-diisopropyl-phenyl)-acenaphthenediimine)/*rac*-ethylenebis($IndH_4$)-$ZrCl_2$ (**2**) [12] ($IndH_4$ = 4,5,6,7-tetrahydro-1-η^5-indenyl) and 1/{$T_p^{Ms^*}$}$TiCl_3$ [13,14] ($T_p^{Ms^*}$ = hydridobis(3-mesityl-pyrazol-1-yl)(5-mesitylpyrazol-1-yl)borate) in the production of polyethylene blends. Our initial studies have revealed that the productivity as well as the properties of the polymer are strongly influenced by the polymerization parameters. For instance, we previously described that the homogeneous binary catalyst system **1/2** when activated by methylaluminoxane (MAO), and using toluene as solvent produce different grades of polyethylene with narrow polydispersities and M_w in the range of 222–571×10^3 g mol^{-1}. By varying the polymerization temperature, a complete phase segregation of the polyethylenes at 50 °C as result of enhancement of branching degree in the polyethylene produced by 1/MAO was observed.

In this paper, as a follow-up to our preliminary communication involving the homogeneous binary catalyst system **1/2** in presence of MAO [12], we report the influence of polymerization conditions, such as solvent, and the temperature of polymerization on productivity and polyethylene blend properties.

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2. Experimental

2.1. Materials

Ni(α-diimine)Cl_2 (**1**) (α-diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) was synthesized following procedures described in the literature [15]. *rac*-ethylene-bis($IndH_4$)$ZrCl_2$ (**2**) ($IndH_4$ = 4,5,6,7-tetrahydro-1-η^5-indenyl) was granted by OPP Chemical and used as received. Ethylene, provided by OPP Chemical, and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (13 Å) prior to use. MAO (5.21 wt% Al, in toluene, average molar mass 900 g mol^{-1}) was purchased from Witco and used without further purification. Hexane was refluxed and distilled over sodium diphenylketyl complex prior to use.

2.2. Polymerization procedures

All polymerization reactions were performed in a 1.0 l Pyrex glass reactor connected to a constant temperature circulator and equipped with mechanical stirring and inlets for argon and ethylene. The reactor has been rinsed with 100 ml of a 0.04 mol l^{-1} $Al(iBu)_3$ solution in hexane prior to use. Under argon atmosphere were introduced sequentially the proper amounts of hexane and MAO solution, and then the system was saturated with ethylene. After complete saturation with ethylene at atmospheric pressure and thermal equilibration of the system, the polymerization reactions were started by adding solutions of **1** and/or **2** to the reactor. The total volume of the reaction mixtures was 450 ml for all polymerizations. The polymerization reaction was stopped by the addition of 1 ml of methanol. The polymer was washed with acidic ethanol, then water and ethanol, and dried in a vacuum oven at 60 °C for 12 h. On the basis of the results of multiple runs, we estimate the accuracy of the productivities to ± 8%.

2.3. Fractionalized precipitation of the PE blend components

The fractionalized precipitation of the PE blend components was carried out by dissolving the polymer blend sample in *o*-xylene at 145 °C followed by a controlled cooling down to 80 °C by 5 °C steps, in which the polymer solution was kept stirring for 1 h. At 80 °C the precipitated polymer (linear polyethylene, PE) was collected by filtration, washed with hot *o*-xylene (6 × 30 ml), and dried in a vacuum oven for 24 h at 70 °C. The *o*-xylene was removed from the combined filtrates under vacuum and the remaining polymer (branched polyethylene, BPE) dried in a vacuum oven for 24 h at 60 °C.

2.4. Film preparation

Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) data were evaluated from films. Polyethylene films were prepared in a Carver press Monarch series, model 3710 ASTM. The polymers were pre-heated for 2 min at 160 °C between the press plates without pressure and then pressed for 2 min at 3 kgf cm^{-2} at the same temperature. After this time, the pressure was released and the films were control-cooled down to room temperature at the cooling rate of 10 or 18 °C min^{-1}, or quenched in water–ice bath or liquid nitrogen. The film thickness was 0.15 mm ± 0.02.

2.5. Polymer characterization

Melting temperatures were determined by means of DSC with a Thermal Analysis Instruments DSC-2010 using a heating rate of 10 °C min^{-1} after twice previous heating to 190 °C and cooling to 40 °C at 10 °C min^{-1}. DMTA was carried out using a MK II DMTA Polymer Laboratories instrument operating in the tensile mode. The sample dimensions were 0.15 × 7.0 × 12 mm^3. Measurements were taken at 1 Hz. The temperature was raised from −150 to 150 °C, at a scanning rate of 2 °C min^{-1}. The molecular weight (M_w) was evaluated by gel permeation chromatography (GPC) with the Waters 150CV system equipped with three columns Styragel HT3, HT4 and HT6 (10^3, 10^4 and 10^6 Å, respectively) and a refractive index detector. Analyses were undertaken using 1,2,4-trichlorobenzene as solvent (with 0.5 g l^{-1} of Irganox 10/10 as antioxidant) at 140 °C and the M_ws were calculated using a universal calibration curve built with polyethylene, polypropylene and polystyrene standards (American Polymer Standard Corporation).

2.6. Blend morphology

The morphology of the blends were studied by using a Scanning Electron Microscope (JEOL JSM 5800). Samples were fractured under liquid nitrogen and the fractured surfaces were coated with gold.

3. Results and discussion

3.1. Effect of x_{Zr} and temperature on productivity

The ethylene polymerization reactions were carried out using methylaluminoxane-activated Ni(α-diimine)Cl_2 (**1**) (α-diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) and *rac*-ethylenebis($IndH_4$)$ZrCl_2$ (**2**) ($IndH_4$ = 4,5,6,7-tetrahydro-1-η^5-indenyl) in hexane at 0, 30 and 55 °C. Table 1 shows the results of polymerization runs by varying the zirconium loading molar fraction (x_{Zr}) [16].

The ethylene polymerization reactions performed employing **1** and **2** separately showed that **1**/MAO exhibited a productivity of 2.44 × 10^3 kg of PE mol[Ni]$^{-1}$ h^{-1} at 0 °C

Table 1
Ethylene polymerization using homogeneous binary catalyst system composed of Ni(α-diimine)Cl_2 (**1**) (α-diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) and *rac*-ethylenebis($IndH_4$)$ZrCl_2$ (**2**) ($IndH_4$ = 4,5,6,7-tetrahydro-1-η^5-indenyl) in hexane under atmospheric ethylene pressure, [M] = 5 μmol, [Al]/[M] = 500, and using MAO as cocatalyst

Entry	x_{Zr}[a]	T_p (°C)	T (min)	Polymer yield (g)	Productivity[b] ($\times 10^{-3}$)	T_m (°C)	χ (%)	M_w ($\times 10^{-3}$)	M_w/M_n
1	0.00	0	15	3.05	2.44	116	29	600	1.8
2	0.25	0	15	1.42	1.14	122	31	440	1.9
3	0.75	0	30	0.68	0.27	127	32	400	2.2
4	1.00	0	30	–	–	–	–	–	–
5	0.00	30	30	3.50	1.42	–	–	210	2.0
6	0.25	30	20	2.09	1.25	127/130	9	220	2.3
7	0.33	30	20	2.30	1.38	127/130	13	210	2.1
8	0.50	30	20	2.17	1.30	128/131	18	240	2.0
9	0.67	30	20	1.70	1.12	129	31	240	2.3
10	0.75	30	20	2.05	1.23	134	33	250	2.1
11	1.00	30	20	2.02	1.23	134	42	290	2.0
12	0.00	50	30	1.07	0.43	–	–	150	1.8
13	0.25	50	30	3.24	1.30	134	32	260	2.3
14	0.50	50	20	2.64	1.60	139	38	270	2.3
15	0.75	50	20	3.90	2.35	139	42	220	2.1
16	1.00	50	20	7.13	4.28	139	42	230	2.0

[M] = total amount of metal (Zr + Ni) in the polymerization reaction.
[a] x_{Zr} = [Zr]/([Zr] + [Ni]).
[b] kg of PE mol$[M]^{-1}$ h^{-}.

while **2**/MAO showed inactive at this polymerization temperature (compare entry 1 and 4). Conversely to the polymerization results obtained in toluene [12], at 30 °C the productivity of both systems are similar with values ranging from 1.42 to 1.23 × 10^3 kg of PE mol$[M]^{-1}$ h^{-1} (entries 5 and 11). On the other hand, **2**/MAO showed maximum productivity at higher temperatures (50 °C, 4.28 × 10^3 kg of PE mol$[Zr]^{-1}$ h^{-1} in accordance with the results obtained previously [13].

It is noteworthy to mention that the use of hexane instead of toluene provokes significant changes in the productivity mainly in case of **2**/MAO. For instance, the productivities found for this system in the polymerization reaction carried out in hexane at 30 and 50 °C were ca. of 4.2 fold lower than those obtained in toluene under identical polymerization conditions. The lower activity of **2**/MAO is attributable to the lower solubility of MAO in hexane.

Polymerization runs carried out varying x_{Zr} and temperature, with constant amount of MAO, showed that the productivities are strongly dependent on these parameters. At low temperature (0 °C) the productivity decreased as the x_{Zr} increased in the polymerization medium as consequence of the inactivity of **2** at this polymerization temperature. At 30 °C, the productivities varied from 1.12 to 1.42 × 10^3 kg of PE mol$[M]^{-1}$ h^{-} indicating a very low dependence of the productivity with respect to x_{Zr}. Furthermore, for the polymerization reactions using x_{Zr} in the range of 0.25–0.75 the observed productivities were comparable to that one obtained for **2**/MAO (entries 6–10 vs entry 11). As expected, at higher temperature (50 °C) the productivity increased as x_{Zr} increased in the polymerization medium considering the higher activity of the catalyst precursor **2** at this temperature. In that case, the productivities varied from 0.43 to 4.28 × 10^3 kg of PE mol$[M]^{-1}$ h^{-} (Fig. 1).

At 0 and 50 °C, a non-linear dependence was observed between the x_{Zr} and the productivity. The productivities found using combined catalysts are lower than those obtained employing the catalysts separately and this effect is more pronounced at 0 °C. For instance, the productivity found for x_{Zr} = 0.75 at 0 °C (0.27 × 10^3 kg of PE mol$[M]^{-1}$ h^{-}) is 2.3 times lower than the predicted productivity (0.61 × 10^3 kg of PE mol$[M]^{-1}$ h^{-}) [17].

3.2. Effect of x_{Zr} and temperature on polymer properties

The influence of x_{Zr} and temperature on polyethylene

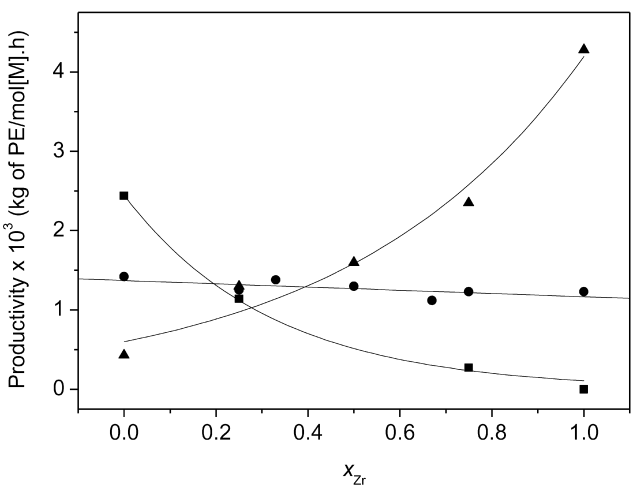


Fig. 1. Dependence of productivity on x_{Zr} for polymerization of ethylene at 0 °C (■), 30 °C (●) and 50 °C (▲).

microstructure have been evaluated by means of DSC, GPC and scanning electron microscopy (SEM). The results are summarized in Table 1.

At 0 °C **1**/MAO produces polyethylene sample with high molecular weight of 600×10^3 g mol^{-1}. It is interesting to note that despite of non-activity of **2**/MAO at 0 °C, the molecular weight of the polyethylene blends decreases with increasing x_{Zr}. For instance, the molecular weight drops from $M_w = 600 \times 10^3$ g mol^{-1} when carried out employing $x_{Zr} = 0$ to $M_w = 400 \times 10^3$ g mol^{-1} using $x_{Zr} = 0.75$.

As expected, the enhancement of the polymerization temperature to 30 °C, gives for **1**/MAO, polyethylene with lower molecular weight ($M_w = 210 \times 10^3$ g mol^{-1}) as consequence of an increase of β-hydride elimination rate [18]. Although these catalyst precursors produce PEs with different M_w (entry 5 vs 11), this homogeneous binary system generated PEs with M_w in the range of 220–250×10^3 g mol^{-1} and a monomodal molecular weight distribution behavior was observed for all cases.

At higher temperature (50 °C) the M_w of the polyethylenes produced by **1**/MAO and **2**/MAO were slightly lower than the PEs produced at 30 °C. Furthermore, no significant changes in M_w were observed by varying x_{Zr}. On the other hand, the M_w of the PE produced by homogeneous binary system are similar to those ones produced at 30 °C varying between 220 and 260×10^3 g mol^{-1}.

It is worth noting that the M_w of the PEs produced in hexane using **1**/MAO and **2**/MAO catalyst precursors separately were higher than those produced in toluene [12] under the same polymerization conditions. Conversely, an opposite trend is observed using the binary catalyst system where it was noticed that the production of polyethylenes with higher M_w in the polymerization reactions was carried out in toluene.

The polyethylene produced at 0 °C using **1**/MAO was found to exhibit melt transition (T_m) of 116 °C. Conversely to the thermal behavior noticed for the PE blends produced in toluene [12], single melting and crystallization peaks were observed in the blends produced in hexane (entries 1–3). Interestingly, despite of the apparent non-activity of the catalyst precursor **2** at this polymerization temperature, the combination of the catalyst precursors promotes an increase in the T_m. For instance, the polymerization reactions carried out using $x_{Zr} = 0.25$ or 0.75 generate LPE/BPE blends with T_m of 122 and 127 °C, respectively.

The linear polyethylene/branched polyethylene blends (LPE/BPE) produced at 30 °C showed T_m varying from 127 to 134 °C with crystallinities ranging between 0 and 42%. In this case, the increase of crystallinity as the x_{Zr} increase in the polymerization medium is attributable to the presence of higher amounts of LPE in the blend composition.

At 50 °C the influence of **1** on the T_m was only observed for $x_{Zr} = 0.25$ and 0.33 where the LPE/BPE blends displayed T_m of 134 °C. Up to $x_{Zr} = 0.33$, the T_m values were constant (139 °C) indicating clearly the predominance of the characteristics of **2** upon the polymer blends produced as a consequence of its higher productivity at this polymerization temperature.

Comparing the DSC results of the polymer samples produced at 0, 30, and 50 °C varying the zirconium molar fraction (Fig. 2), it was observed that the higher dependence of the T_m values with respect to the x_{Zr} has been noticed for the polyethylene blends produced at 0 °C, and this one decreases as the polymerization temperature increases suggesting that at lower polymerization temperatures the miscibility between the PE phases is more effective.

In the DSC curves of the PE blends produced at 30 °C (Fig. 3) it is observed that the presence of BPE affect the LPE crystallization behavior leading to the broadening or even the appearance of a bimodal melting peak. This behavior is more pronounced with higher amount of BPE ($x_{Zr} = 0.25$) and it can be related to the growth of defective PE spherulites.

3.3. Thermal properties of the polyethylene blends

Taking into account the similar productivities presented by the catalyst precursors **1** and **2** at 30 °C the thermal dynamic mechanical properties of the polyethylene blends were investigated using DMTA. The dependence of storage moduli (E') and mechanical damping (tan δ) with x_{Zr} are shown in Fig. 4. Below −60 °C, all polymer samples had nearly the same stiffness.

The PE produced by **1** ($x_{Zr} = 0.00$) showed a sharp decrease in the storage modulus from $10^{9.0}$ Pa at −55 °C to $10^{6.5}$ Pa at 80 °C, as consequence of the high branching degree of the PE (107 branches/1000 backbone chain carbon atoms) obtained under these polymerization conditions [19]. The moduli of the PE obtained with $x_{Zr} = 1.00$ decreased gradually from $10^{9.2}$ to $10^{8.2}$ in the temperature range of −6 to 120 °C, indicating the presence of a large amount of linear PE (LPE). For the LPE/BPE blends produced using $x_{Zr} = 0.25$, 0.33, and 0.50 it was observed a similar

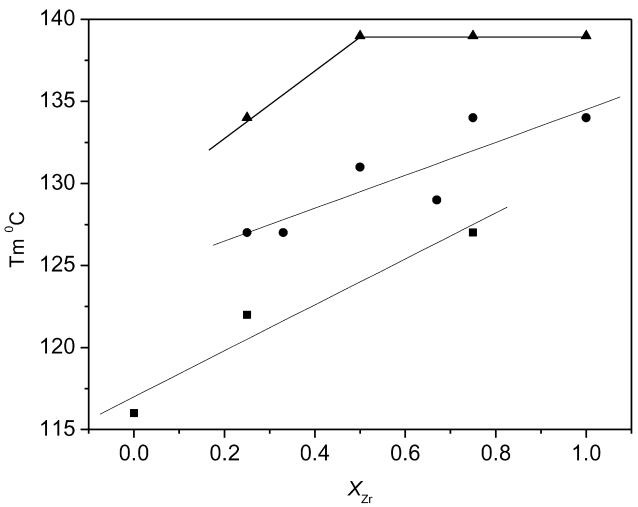


Fig. 2. Dependence of the melting transition (T_m) on x_{Zr} for polymerization of ethylene at 0 °C (■), 30 °C (●) and 50 °C (▲).

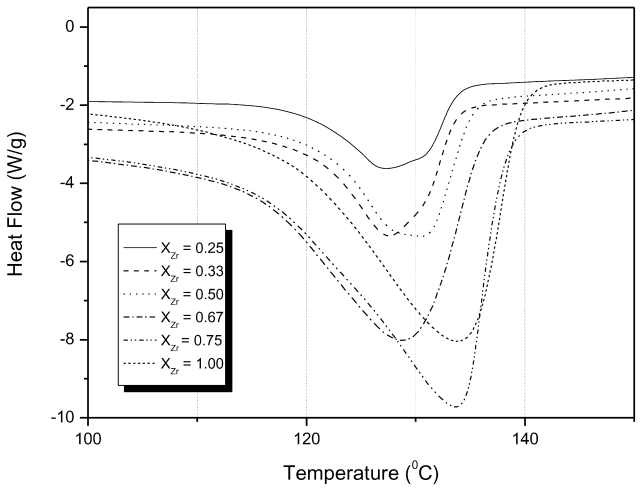


Fig. 3. DSC curves of the PE blends produced in hexane at 30 °C.

behavior with E' values intermediate between those ones obtained employing exclusively the catalyst precursors **1** and **2**. In that case the storage modulus decreased from $10^{9.1}$ at −55 °C to less than $10^{7.0}$ at about 120 °C. These values indicate the presence of a large amount of branched PE in the polymer blends. On the other hand, the similarity between the storage moduli of the polymer blend produced using $x_{Zr} = 0.75$ with the one presented by the polyethylene produced by **2** ($x_{Zr} = 1.00$) indicated that the polymer blend is almost totally composed of linear polyethylene.

Among the α-, β-, γ-transitions [20] observed in the polymer samples when the mechanical damping (tan δ) is plotted against temperature, the second order transition denominated as β-transition is the most representative in this study. This transition has been previously attributed to the contribution of the interfacial content [21].

As expected, the polyethylene produced at 30 °C employing $x_{Zr} = 0.00$ showed a marked β-transition at −30 °C due to a high degree of branching [18,21]. As expected, the intensity of the β-transition increased by 1.6 orders of magnitude compared to the polyethylene produced at 30 °C under ethylene pressure of 5.2 atm [14]. In addition, this transition is slightly shifted to lower temperature (−39 °C) as a consequence of the production of a higher branched polyethylene.

For the LPE/BPE blends, it was observed that the intensity of the β-transition decreased as x_{Zr} increases, as can be seen in Fig. 4. This feature is attributable to the presence of a higher amounts of catalyst precursor **2** which is responsible for the production of LPE. The LPE/BPE blends produced using $x_{Zr} = 0.75$ did not present a β-transition as a consequence of the high amount of LPE in the blend composition. In the case of polyethylene obtained using the catalyst precursor 2 ($x_{Zr} = 1.00$) the β-transition is not observed due to the absence of branching on the polyethylene.

For the LPE/BPE polymer blends generated using $x_{Zr} = 0.25–0.50$ the appearance of a shoulder in the temperature range of −24 and −4 °C was observed suggesting an interference of the LPE in the motions of the interfacial region characterized by the crystalline core and the amorphous domains.

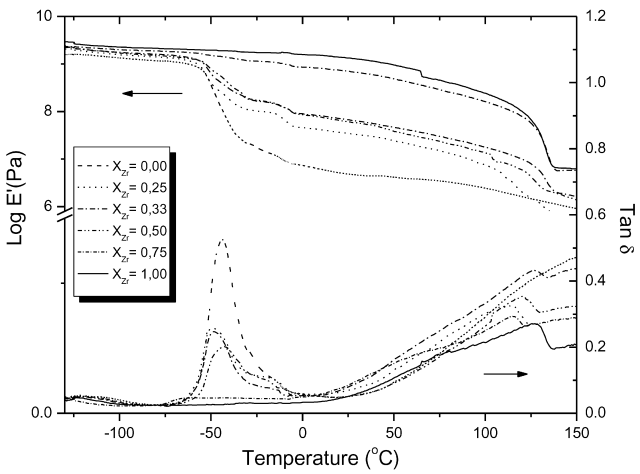
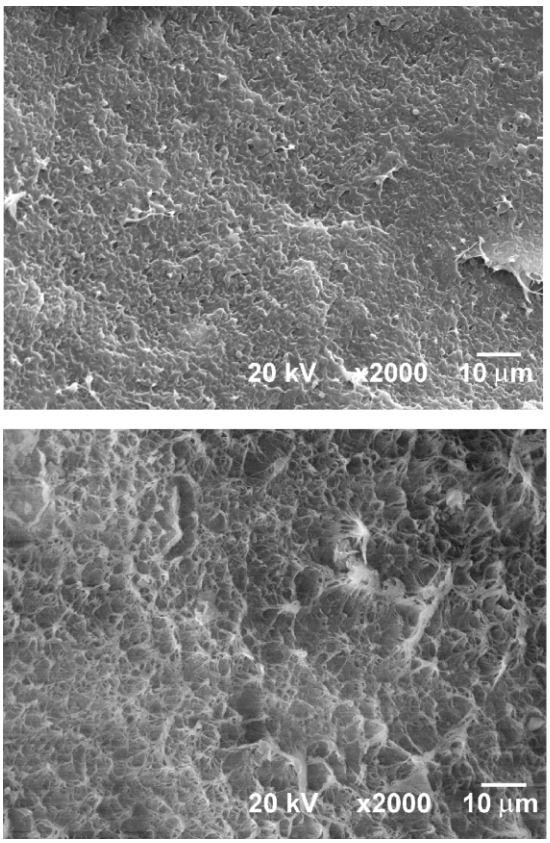


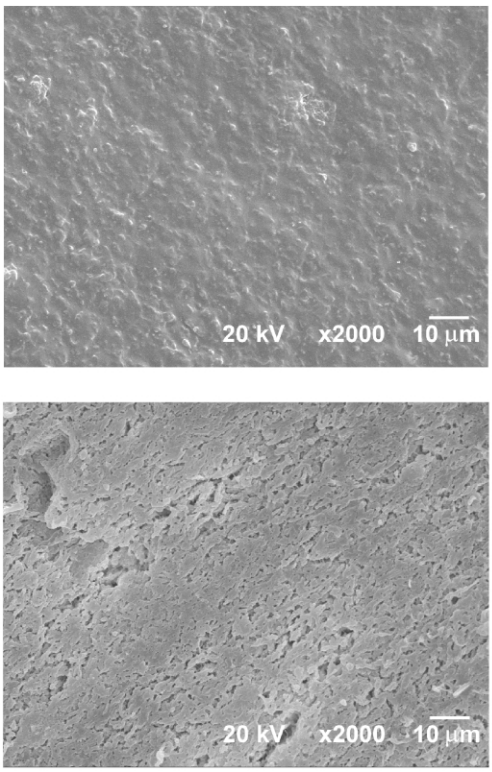
Fig. 4. DMTA of the polyethylenes produced at 30 °C using a combination of catalytic precursors **1** and **2**.



(a)

(b)

Fig. 5. SEM micrographs of BPE/HDPE blends cryo-fractured surfaces produced at 30 °C: (a) $x_{Zr} = 0.25$; (b) $x_{Zr} = 0.25$ after etched with *o*-xylene.



(a)

(b)

Fig. 6. SEM micrographs of BPE/HDPE blends cryo-fractured surfaces produced at 30 °C: (a) $x_{Zr} = 0.75$; (b) $x_{Zr} = 0.75$ after etched with *o*-xylene.

3.4. Morphology of the PE blends

SEM micrographs made on cryo-fractured surfaces of the polyethylene blend samples produced at 30 °C using $x_{Zr} = 0.25$ and 0.75 are shown in Figs. 5 and 6. Comparing the SEM micrographs of the blend samples it was observed that lower amount of catalyst precursor **2** in the binary catalyst system ($x_{Zr} = 0.25$) determine the formation of LPE/BPE blend showing two phase components (Fig. 5(a)) well dispersed. Increasing the amount of **2**, there was the production of a LPE/BPE blend which also shows a double morphology but in that case it was observed the presence of very small particles of BPE dispersed in the LPE matrix (Fig. 6(a)). In order to evaluate the distribution of the PE phases in the matrix, cryo-fractured surfaces were etched with hot *o*-xylene and studied by SEM. Fig. 5(b) shows the formation of a 'cobweb structure' as a consequence of the extraction of the highly branched PE produced by **1**. In Fig. 6(b) the formation of holes uniformly distributed on LPE matrix was observed. The dissimilarity between the structures produced after etched with hot *o*-xylene can be rationalized in terms of major molar fraction of the catalyst precursor **1** present in the binary catalyst system ($x_{Zr} = 0.25$) determining the production of large amount of BPE. Furthermore, the formation of these structures is an indication of the incompatibility of the polyethylene phases that may be related to the large difference in the molecular structure and molecular weight.

3.5. Fractionalized precipitation of the PE blend components

Data of the PEs obtained by fractionalized precipitation of the blends produced at 30 °C using the binary catalyst system ($x_{Zr} = 0.25–0.75$) are presented in Table 2. The fractionalized precipitation results have demonstrated that the amount of BPE (*o*-xylene-soluble fraction at 80 °C) decreases substantially as the zirconium molar fraction increases from $x_{Zr} = 0.25$ to 0.75 (compare entries 17–19). This observation is in accord with the SEM data previously discussed. It is worth noting that the amounts of *o*-xylene-insoluble (attributed to the linear PE) and -soluble fraction (attributed to the branched PE) existing in the PE blend matched very well with the predicted quantities calculated assuming that each catalyst precursor was working independently. For instance, the amount of LPE produced for $x_{Zr} = 0.25$ and 0.75 (27.0 and 80.0 wt%, respectively) are slightly higher than the calculated values (22.4 and 72.2 wt%). These results are in agreement with the productivity data suggesting that at this polymerization temperature (30 °C) the catalyst precursors polymerize ethylene independently.

The higher T_m values (134–136 °C) observed for the LPE (*o*-xylene-insoluble fractions) indicate, as discussed previously (Section 3.2) that the presence of BPE in the polyethylene blend interfere in the LPE crystallization.

Table 2
Composition and properties of the polyethylenes obtained by fractionalized precipitation of the PE blends

Entry	x_{Zr}	Soluble fraction (wt%)[a]	Insoluble fraction (wt%)[b]	T_m (°C)	χ (%)	M_w ($\times 10^{-3}$)	M_w/M_n
		73 (77.6)		–	–	220	1.8
17	0.25		27.0 (22.4)	136	29	250	1.9
		60 (53.6)		–	–	240	2.1
18	0.50		40.0 (46.4)	134	27	230	2.3
		20 (27.8)		–	–	280	2.0
19	0.75		80.0 (72.2)	134	34	250	2.1

Polymerization reactions carried out at 30 °C. Predicted quantity calculated assuming that each catalyst precursor was working independently are shown in parentheses.

[a] *o*-xylene-soluble fraction at 80 °C.

[b] *o*-xylene-insoluble fraction at 80 °C.

The molecular weight of the PEs obtained from *o*-xylene-soluble and -insoluble fractions are in the expected range ($220-280 \times 10^3$ g mol^{-1}) when compared to the GPC data obtained for the polymer blends (compare entries 17–19 with 6, 8 and, 10). Furthermore, a monomodal molecular weight distribution were observed for all case (MWD = 1.8–2.3).

The comparable M_w values obtained between the PEs generated by fractionalized precipitation and those ones produced by **1** and **2** separately suggest strongly that these catalyst precursors work independently during the ethylene polymerization as mentioned previously. In addition, similar branching contents have been found for the *o*-xylene-soluble fraction (entry 18, $x_{Zr} = 0.50$) (93 branches/1000 backbone chain carbon atoms 1000C) and BPE produced by **1** (107 branches/1000 backbone chain carbon atoms) [19].

4. Conclusion

The use of a binary catalyst system **1/2** in the ethylene polymerization enables the production different grades of polyethylene, depending on the polymerization temperature and x_{Zr}. Higher productivities were obtained at 50 °C. The GPC results showed the production of polyethylenes with monomodal molecular weight distribution and narrow polydispersities. The storage moduli (E') and mechanical damping (tan δ) of the BPE/HDPE blends are strongly influenced by x_{Zr}. For the polymer blends produced at 30 °C the intensity of the β-transition decreased as x_{Zr} increased in the polymerization milieu. The surface morphology of the blends revealed a low miscibility between the PE phases resulting in the formation of a 'cobweb structure' (for $x_{Zr} = 0.25$). By increasing the zirconium molar fraction ($x_{Zr} = 0.75$) it was observed that the formation of holes were uniformly distributed on the LPE matrix. The dissimilarity between the structures is attributed to the presence of different amounts of catalyst precursor **1** in the binary catalyst system. Finally, the distinct behavior of the productivities as well as polymer properties of the LPE/BPE blends produced in hexane with respect to those ones obtained in toluene [12] showed that the choice of solvent in the polymerization reaction is a key feature for the production of polymeric materials with desired combination of properties.

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[16] x_{Zr} is defined as the zirconium mole fraction calculated from [Zr]/([Zr] + [Ni]).
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