

Dual Catalyst System Composed by Nickel and Vanadium Complexes Containing Nitrogen Ligands for Ethylene Polymerization

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Blendas de polietileno ramificado/polietileno de alta densidade (BPE/HDPE) foram preparadas usando uma combinação de catalisadores $[\text{NiCl}_2(\text{diimina-}\alpha)]$ (**1**) (diimina- α = 1,4-bis(2,6-diisopropilfenila)-acenafeteno) e $[\text{Tp}^{\text{Ms}^*}\text{VCl}_2(\text{N}^i\text{Bu})]$ (**2**) (Tp^{Ms^*} = hidridobis(3-mesitilpirazol-1-il)(5-mesitilpirazol-1-il)). As reações de polimerização foram realizadas em hexano ou tolueno em três diferentes temperaturas (0, 30 e 50 °C), utilizando várias razões molares de níquel (x_{Ni}), na presença de metilaluminoxano (MAO) como cocatalisador. Em todas as temperaturas, as atividades mostraram uma correlação aproximadamente linear com x_{Ni} , indicando o não aparecimento de um efeito sinérgico entre as espécies de níquel e vanádio. Altas atividades foram obtidas a 0 °C. As temperaturas de fusão (T_m) das blendas de polietileno produzidas a 0 °C diminuem conforme a x_{Ni} aumenta no meio reacional, indicando uma boa miscibilidade entre as fases de polietileno produzidas por ambos catalisadores. A morfologia da superfície das blendas de BPE/HDPE estudadas por microscopia eletrônica de varredura (MEV) revelou uma baixa miscibilidade entre as fases de PE, principalmente no caso das blendas poliméricas produzidas a alta temperatura (50 °C).

Branched polyethylene/high-density polyethylene blends (BPE/HDPE) were prepared using the combined $[\text{NiCl}_2(\alpha\text{-diimine})]$ (**1**) (α -diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) and $[\text{Tp}^{\text{Ms}^*}\text{VCl}_2(\text{N}^i\text{Bu})]$ (**2**) (Tp^{Ms^*} = hydridobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)) catalysts. The polymerization reactions were performed in hexane or toluene at three different polymerization temperatures (0, 30 and 50 °C) and several nickel molar fractions (x_{Ni}), using MAO as cocatalyst. At all temperatures, the activities show an approximate linear correlation with x_{Ni} , indicating a non-synergistic effect between the nickel and the vanadium species. Higher activities were found in toluene at 0 °C. The melting temperatures for the polyethylene blends produced at 0 °C decrease as x_{Ni} increases in the medium indicating good miscibility between the polyethylene phases made by both catalysts. The surface morphology of the BPE/HDPE blends studied by scanning electron microscopy (SEM) revealed low miscibility between the PE phases mainly in the case of the polymer blends produced at high temperature (50 °C).

Keywords: BPE/HDPE blends, ethylene polymerization, homogeneous binary catalyst system, Nickel and Vanadium catalysts

Introduction

A large range of polyolefinic materials with interesting properties have been disclosed in the last decades as a result of the development of new classes of olefin polymerization catalysts¹ as well as of blending existing polymers.² Furthermore, a new approach has been introduced that is based on catalyst systems that combine, in a single reactor, two or more types of catalysts that produce polymers with different and controlled molecular weight averages (M_w) and molecular weight distributions (MWD).³ This method

has been successfully used to produce linear low density PE (LLDPE),⁴ branched polyethylenes,⁵ polyethylenes with long chain branches (LCB-PE),⁶ ethylene/1-hexene copolymers,⁷ and polyethylene blends.⁸

In the last few years we have developed homogeneous binary catalyst systems for the production of polyethylene blends,⁹ and LLDPE.¹⁰ Our studies demonstrated that the variation of polymerization parameters such as solvent, cocatalyst, temperature of polymerization as well as metal mole fraction strongly influences the activity and polymer properties. Particularly, for the binary catalytic system composed of $[\text{NiCl}_2(\alpha\text{-diimine})]$ (α -diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine)/ $[\text{Tp}^{\text{Ms}^*}\text{TiCl}_3]$

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system **1**/MAO exhibited higher activities than **2**/MAO for all temperatures and solvents employed in the polymerization runs as can be seen in Figures 1 and 2. The catalytic system **1**/MAO reached a maximum activity in toluene at 0 °C (2248 Kg of PE mol[Ni]⁻¹ h⁻¹, entry 20) while a highest activity for system **2**/MAO was obtained in hexane at 30 °C (456 Kg of PE mol[V]⁻¹ h⁻¹, entry 6).

Comparing the performance of both catalytic systems it was observed that the nickel catalyst was more sensitive to temperature, than the vanadium catalyst decreasing the activity with increasing polymerization temperature. Furthermore, the difference between the activities obtained for the systems **1**/MAO and **2**/MAO decreases as the

polymerization temperature increases, this effect being more pronounced in hexane. For instance, at 50 °C this activity difference was 1.2 fold and reaches 3.9 fold at 0 °C (compare entries 1 and 5, and 11 and 15).

Polymerization runs carried out when varying x_{Ni} and temperature, with constant amount of MAO, showed that the activities are strongly dependent on these parameters as can be seen in Figures 1 and 2. At low temperature (0 °C) apparently the solvent does not promote any significant influence on the activity. In that case, the activities increase linearly with x_{Ni} indicating that each catalyst precursor work independently. At higher polymerization temperatures (30 and 50 °C) the influence of the solvent on the activity is

Table 1. Ethylene polymerization using homogeneous binary catalyst system composed of [NiCl₂(α -diimine)] (**1**) and [Tp^{Ms}*VCl₂(N^tBu)] (**2**) in hexane under atmospheric ethylene pressure^a

Entry	x_{Ni} ^b	T(°C)	Polymer yield(g)	Activity ^c	T _m (°C)	χ (%)	MFI ^d (g/10 min)
1	0.00	0	1.07	428	144	20	< 0.001
2	0.25	0	1.84	736	142	18	< 0.001
3	0.50	0	2.22	888	135	17	0.010
4	0.75	0	2.85	1140	124	16	0.010
5	1.00	0	4.20	1680	121	14	0.020
6	0.00	30	1.14	456	144	23	< 0.001
7	0.25	30	0.72	288	139	14	0.140
8	0.50	30	0.47	188	138	5	1.790
9	0.75	30	0.84	336	135	3	1.900
10	1.00	30	2.06	824	–	–	13.10
11	0.00	50	1.07	428	143	29	< 0.001
12	0.25	50	0.90	360	142	20	< 0.001
13	0.50 ^e	50	0.10	204	142	25	< 0.001
			0.41		–	–	142.00
14	0.75 ^e	50	0.09	180	139	17	0.180
			0.36		–	–	147.00
15	1.00	50	1.37	548	–	–	156.00

^aPolymerization conditions: Glass Reactor (1L); hexane = 300 mL. [Al]/[M] = 500; MAO as activator; ^b x_{Ni} = [Ni]/([Ni] + [V]); ^ckg of PE mol[M]⁻¹ h⁻¹;

^dMelt flow indexes (MFI) were determined at 190°C using a 21.6 kg standard charge; ^eThe reaction showed spontaneous separation of the PE phases.

Table 2. Ethylene polymerization using homogeneous binary catalyst system composed of [NiCl₂(α -diimine)] (**1**) and [Tp^{Ms}*VCl₂(N^tBu)] (**2**) in toluene under atmospheric ethylene pressure^a

Entry	x_{Ni} ^b	T(°C)	Polymer yield(g)	Activity ^c	T _m (°C)	χ (%)	MFI ^d (g/10 min)
16	0.00	0	0.44	176	146	27	< 0.001
17	0.25	0	1.99	796	141	16	< 0.001
18	0.50	0	2.53	1012	126	12	< 0.001
19	0.75	0	5.23	2092	122	12	< 0.001
20	1.00	0	5.62	2248	118	15	< 0.001
21	0.00	30	0.85	340	143	19	< 0.001
22	0.25	30	1.04	416	141	19	< 0.001
23	0.50	30	1.48	592	135	2	0.560
24	0.75	30	2.23	892	137	4	1.820
25	1.00	30	3.73	1492	–	–	0.420
26	0.00	50	0.58	232	143	19	< 0.001
27	0.25	50	0.41	164	139	13	< 0.001
28	0.50	50	1.09	436	137	1	19.16
29	0.75	50	1.36	544	138	1	27.96
30	1.00	50	1.72	688	–	–	95.10

^aPolymerization conditions: Glass Reactor (1L); toluene = 300 mL. [Al]/[M] = 500; MAO as activator; ^b x_{Ni} = [Ni]/([Ni] + [V]); ^ckg of PE-mol[M]⁻¹ h⁻¹; ^dMelt flow indexes (MFI) were determined at 190 °C using a 21.6 kg standard charge.

more clearly presented. For the polymerization reactions performed in toluene the dependence of the activity with respect to the x_{Ni} was roughly linear.

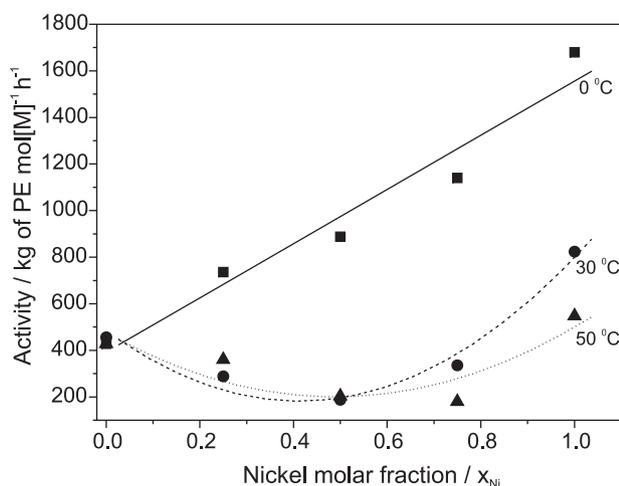


Figure 1. Influence of the polymerization temperature on the activity varying x_{Ni} for the polymerization reactions performed in hexane.

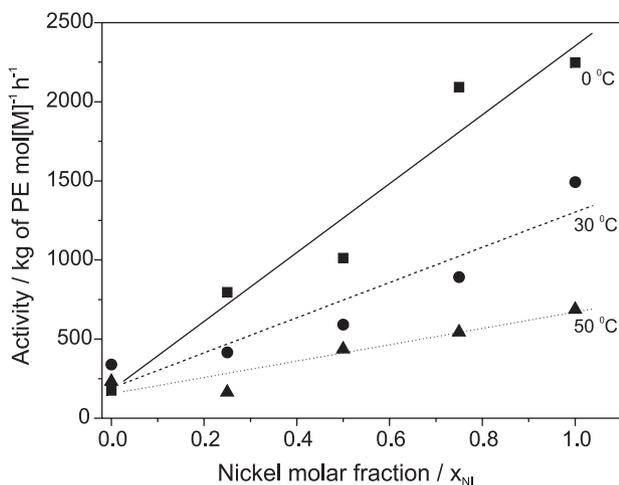


Figure 2. Influence of the polymerization temperature on the activity varying x_{Ni} for the polymerization reactions performed in toluene.

On the other hand, the use of hexane instead toluene determined a clearly non-linear correlation between the nickel molar fraction ($x_{Ni} = 0.25, 0.50$ and 0.75) and the activity, suggesting that the combination of **1** and **2** in this solvent can be promoting a partial deactivation of these catalyst precursors. For instance, the activities found for $x_{Ni} = 0.50$ (30 °C , $188\text{ kg of PE mol[M]}^{-1}\text{ h}^{-1}$; 50 °C , $204\text{ kg of PE mol[M]}^{-1}\text{ h}^{-1}$) are 3.4 and 2.4 times respectively lower than the predicted ones (30 °C , $640\text{ kg of PE mol[M]}^{-1}\text{ h}^{-1}$; 50 °C , $488\text{ kg of PE mol[M]}^{-1}\text{ h}^{-1}$).¹⁴

Influence of x_{Ni} and polymerization temperature on the polymer properties

The influences of x_{Ni} , solvent and polymerization temperature on polyethylene microstructure have been evaluated by means of differential scanning calorimetry (DSC), and melt flow index (MFI). The results are summarized in Tables 1 and 2.

The melting temperature (T_m) of the polymers produced by **1** or **2** is not extensively affected by changing the solvent. As expected, the branched polyethylenes (BPE) produced by **1** ($x_{Ni} = 1.00$) have T_m of 118 °C (toluene) and 121 °C (hexane) while the high-density polyethylenes (HDPE) produced by **2** ($x_{Ni} = 0.00$) show T_m around 145 °C .

In contrast to the thermal behavior of the PE blends produced at 0 °C using the homogeneous binary catalyst system $[\text{NiCl}_2(\alpha\text{-diimine})]/[\text{rac-ethylenebis(IndH}_4\text{)ZrCl}_2]^9$, broad single melting and crystallization peaks were observed in the PE blends produced by **1/2/MAO** catalyst system, indicating good miscibility between the branched and high-density PE phases (Figures 3 and 4). It is significant to note that the T_m is strongly influenced by the nickel molar fraction whatever the solvent used in the polymerization reaction. For instance, the T_m values for the polyethylene blends produced in hexane varied from 122 °C ($x_{Ni} = 0.75$) to 141 °C ($x_{Ni} = 0.25$).

At higher polymerization temperatures (30 and 50 °C) only a slight decrease of T_m was observed. At these temperatures, the polyethylenes formed by **1** are totally amorphous due to the higher branch content¹⁵ and apparently they do not interfere in the crystallization process of the high-density polyethylenes due to a higher level of phase segregation. This phenomenon could be better visualized in the polymerization reactions carried out in hexane at 50 °C where two polymers (BPE and HDPE) separated spontaneously and thus allowed the analysis of both phases (entries 13 and 14).

A comparison of the DSC results of the polymer samples produced in toluene at $0, 30$, and 50 °C (Figure 5), shows higher dependence of the T_m values with respect to the x_{Ni} for the polyethylene blends produced at 0 °C than at 30 or 50 °C . T_m values decrease as the polymerization temperature increases indicating that at lower polymerization temperatures the miscibility between the PE phases is more effective. It is worth noting that nickel- α -diimine complexes show ability to promote the displacement of the metal along the growing polymer chain so-called chain walking mechanism.¹⁶ This process determines the number of branches in the polymer backbone. Therefore the extent of branching in the PE is sensitive to polymerization temperature, decreasing with decreasing polymerization temperature. At 0

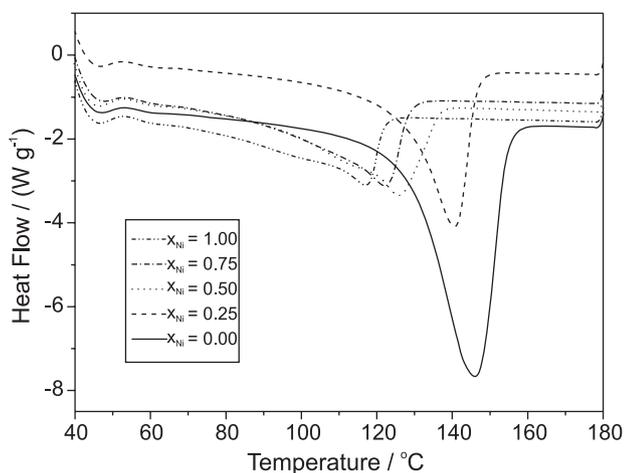


Figure 3. DSC curves of the PE blends produced in toluene at 0 °C.

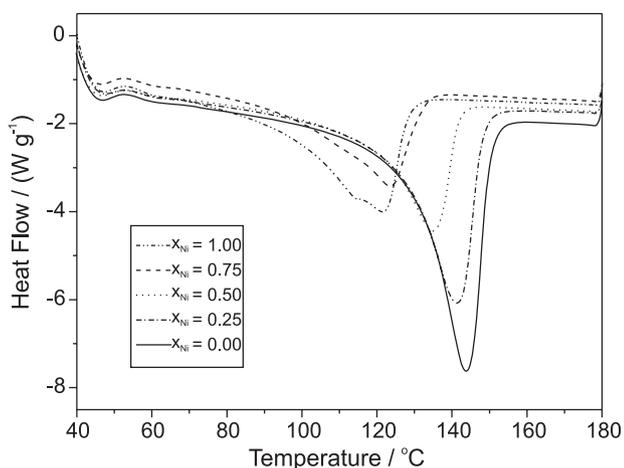


Figure 4. DSC curves of the PE blends produced in hexane at 0 °C.

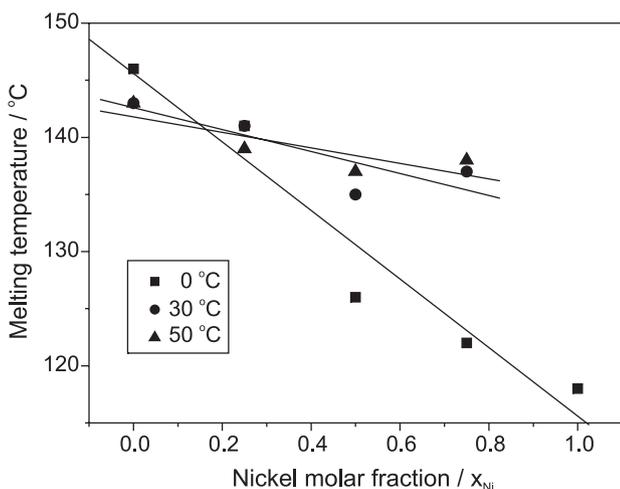


Figure 5. Dependence of the melting temperature (T_m) on x_{Ni} for polymerization of ethylene in toluene.

°C, **1** produces PE with lower degree of branching and thus, its miscibility with the PE produced by **2** is more pronounced.

As expected, the polyethylenes produced by **1** showed higher melt flow indexes (MFI) compared to those obtained using **2**, since catalyst **2** produces ultra-high molecular weight PE.¹³ The MFI data for the polymer blends produced at 0 °C indicate the formation of polymer with high molecular weight. These very low MFI values can be associated to the production of high molecular weight polyethylene by **1** at this polymerization temperature.^{17,9} In general, at higher polymerization temperatures (30 and 50 °C) the MFI values increase as the x_{Ni} increases in the medium, this behavior being attributed to the formation of more branched and lower molecular weight polyethylenes produced mainly by **1**.¹⁵

Morphology of the PE blends

The morphology of the polymer blends was investigated using scanning electron microscopy (SEM). SEM micrographs made on cryo-fractured surfaces of the polyethylene blend samples produced at 30 and 50 °C using $x_{Ni} = 0.25$ are shown in Figures 6 and 7. The SEM micrograph of the blend samples produced at 30 °C showed two phase components (Figure 6a) well dispersed. Increasing the polymerization temperature (50 °C) there occurred the production of a BPE/HDPE blend which also shows a double morphology, but in this case the presence of very small particles of BPE dispersed in the HDPE matrix was observed (Figure 7a). 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. Figure 6b shows the formation of large holes and defects distributed on HDPE matrix as a consequence of the extraction of the branched PE produced by **1**. The non-uniform distribution of these holes and defects on the HDPE surface indicates the high incompatibility degree of these two phase components, considering mainly the large difference between the molecular weight of the PE produced by **1** and that produced by **2**, which is responsible for the formation of ultra-high molecular weight PE. The extraction of the highly branched PE from the PE blend produced at 50 °C generated a “sandwich structure” (Figure 7b) similarly found for homogeneous binary catalyst system composed by $[NiCl_2(a\text{-diimine})]$ and $[Tp^{Ms*}TiCl_3]$.⁹

Conclusions

We have shown that the combination of precursor catalysts **1** and **2** in the presence of MAO generates an effective binary catalyst system for ethylene polymerization. Different types of polyethylene blends can be produced depending on the

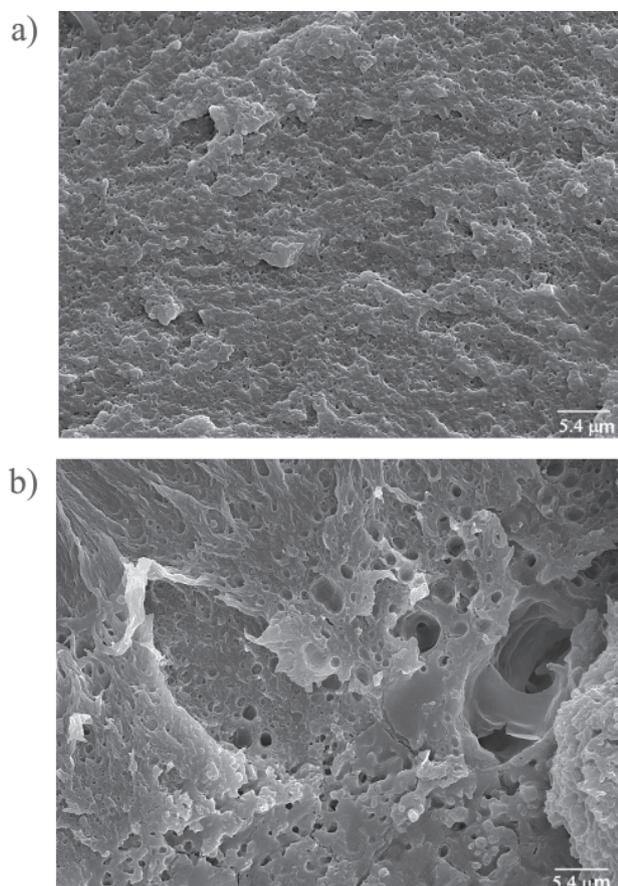


Figure 6. SEM micrographs of BPE/HDPE blends crio-fractured surfaces produced at 30 °C in hexane: (a) $x_{Ni} = 0.25$ (x 2000); (b) $x_{Ni} = 0.25$ (x 2000) after etching with *o*-xylene.

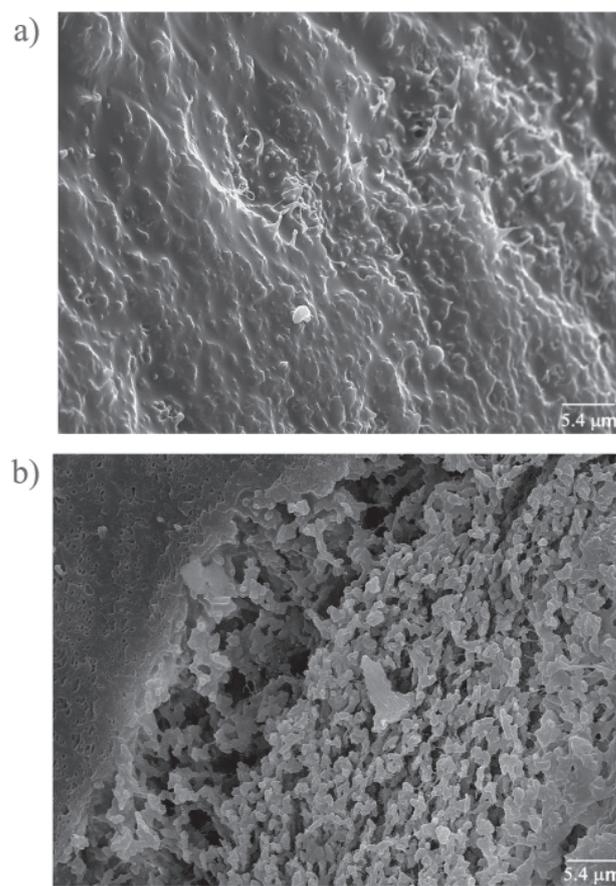


Figure 7. SEM micrographs of BPE/HDPE blends crio-fractured surfaces produced at 50 °C in hexane: (a) $x_{Ni} = 0.25$; (b) $x_{Ni} = 0.25$ after etching with *o*-xylene.

polymerization temperature, solvent, and x_{Ni} . Higher activities have been found using toluene as solvent at 0 °C as a consequence of better stability of **1** at this polymerization conditions. The surface morphology of the blends revealed very low miscibility between the PE phases, resulting in the formation of big holes and defects distributed on the HDPE matrix. This behavior is associated mainly to the large difference of the PE properties produced by **1** and **2** that has led to spontaneous phase separation during ethylene polymerization carried out in hexane at 50 °C.

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