Study on single and binary catalytic systems of pyridine-imine catalysts based on nickel and iron in synthesis of reactor blends and low-density polyethylene nanocomposites

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ABSTRACT: In the presence of modified methylaluminoxane as cocatalyst, the behavior of a binary catalytic system based on pyridine-imine nickel (N) and iron (F) catalysts was evaluated in order to reach a proper mixture of polyethylene (PE). A computational study along with kinetic profile suggested that the catalyst F with higher electron affinity (A) and electrophilicity (ω) in the methyl cationic active center and stronger interaction with the monomer led to high integrated monomer consumption and higher activity. In addition, the samples produced by the mixture of catalysts showed a higher value of $M_v \times 10^4$ (g (PE) mol (Fe+Ni)$^{-1}$ h$^{-1}$), melting point (127.8 °C), and crystallinity extent (41.29%) than the samples produced by the single catalysts. The addition of multiwalled carbon nanotubes (MWCNT) into the polymerization media reduced the activity of catalysts [from 7.50 × 10^4 to 0.66 × 10^4 g (PE) mol (Fe+Ni)$^{-1}$ h$^{-1}$] and the thermal properties of the low-density polyethylene nanocomposite samples. However, the sample containing 2.33% MWCNT20-30 improved the total thermal stability of the neat polyethylene blend up to 400 °C. Scanning electron microscope images of the samples demonstrated irregular to virtually uniform morphologies were obtained through the in situ and solution-mixing techniques. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2019, 136, 47376.

KEYWORDS: catalysts; composites; polyolefins

INTRODUCTION

Polyethylene (PE) is a low-cost, multipurpose thermoplastic with high production volume that shows good mechanical properties and high chemical resistance. For PE, blending is primarily applied to control the balance between processability and the mechanical properties of the raw materials.1,2 Basically, polyolefin blends are obtained by four methods: mixing by an extruder under determined conditions, polymerization in multistage reactors, utilization of operating conditions,3–5 and obtaining favored microstructures of polyethylene blends by a specific combination of different catalysts. Up to now, various types of catalyst combinations, including Ziegler–Natta/ metallocene, Ziegler–Natta/late transition metals (LTM), metallocene/metallocene, metallocene/LTM, and finally LTM/LTM have been studied in (co)polymerization of different types of monomers to produce ideal reactor polymer blends.3,4,6–12 Nowadays, regarding choosing a type of catalyst for polymerization of ethylene leading to a polymer with a specific microstructure, using a binary catalytic system is vast and interestingly, based on the features and applications of resultant blends, it could be diverse. Hence, it is obvious that the appropriate conditions for polymerization of ethylene in addition to specific features of additives play key roles in the engineering of nanocomposite/polyolefin blends.13,14 Various types of additives as well as different sizes of particles can be used to prepare the composites. Carbon nanotubes (CNTs) as effective additives have attracted much interest from academics and industries because of their outstanding mechanical, thermal, and electrical properties. The CNTs tend to form clusters and bundles due to van der Waals forces and strong π–π interactions between the tubes, which can be used to improve the
interfacial adhesion between polyolefin matrixes. Applications of these materials are being studied in a wide range of areas, from construction to automotive and aerospace engineering, alternative energy production, and medicine. Much attention has been paid to CNT-based nanocomposites for the preparation of high-performance materials that exhibit improved or unusual mechanical and physical properties, even at very low nanofiller loading. In this field, many studies have focused on using specific methods to produce polymer nanocomposites. Three methods are mainly used to incorporate CNTs into polymer composites: (1) Polymerization-filling technology (PFT), which is a promising approach for the preparation of polyolefin nanocomposites that includes the growth of chains directly on the surface of the catalyst that are attached to the fillers. Therefore, in situ polymerization can make nanocomposites with a much more uniform filler dispersion and strong interfacial adhesion without damaging filler structures (such as CNTs and graphene). The product may be used directly as a master batch for future nanocomposites. The method is relatively difficult to achieve. Therefore, a key factor to achieve appropriate products consists of breaking down the native bundles of the CNTs to reach a high level of nanofiller dissociation and establish a strong CNT–polymer interfacial adhesion for a good load transfer. Here, we report the synthesis and characterization of pyridine-imine catalysts based on nickel and iron, and we study single and binary catalyst systems in the polymerization of ethylene to reach an ideal blend at the desired conditions. The effects of composition and type of catalysts on the microstructure of the product were evaluated. Furthermore, we investigated the mutual effect of catalyst and CNTs in regard to the catalytic system used and CNT size through the in situ polymerization method. Moreover, the solution-mixing method was employed for comparison. Therefore, the influence of type and content of CNTs, the method applied on catalyst behavior, and the low-density polyethylene (LDPE)/multilwall carbon nanotube (MWCNT) nanocomposite properties (thermal, physical, and morphological) are further discussed in detail.

**EXPERIMENTAL**

**Materials and Methods**

All procedures that included air- or moisture-sensitive compounds were performed under an inert and dry atmosphere in a glove box or under ultrapure argon protection. The equipment and solvents (supplied by Merck Chemicals (Darmstadt, Germany)) were dried before use. Toluene (Iran, Petrochemical Co.), diethyl ether (DEE), and tetrahydrofuran (THF) were dried over Na/benzophenone and distilled. Similar equipment was employed in the purification of dichloromethane (DCM), and CaH2 was used as a drying agent for n-hexane. Methanol was dried by refluxing in the presence of Mg/iodine (drying agent), distilled, and kept on an active molecular sieve type 3Å/13X. Ethylene (polymerization grade) (Iran, Petrochemical Co.) was dried by passing through an activated molecular sieve column. 2-Acetylpyridine, dimethoxyethanenickel dibromide (DME) NiBr2, anhydrous iron (II) chloride, decaline, chlorobenzene, and CaH2 were purchased from Sigma Aldrich Chemical (St. Louis, MO). MWCNT20-30 (with an outside diameter of 20–30 nm, a length of 10–30 μm, and true density of 2.1 g cm−3) and MWCNT30-50 (with an outside diameter of 30–50 nm, a length of 10–20 μm, and true density of 2.1 g cm−3) were purchased from US Research Nanomaterials (Houston, TX) and used without any further purification. Triisobutylaluminum was also supplied by Sigma-Aldrich (Steinem, Germany). Chemical and was used in the synthesis of modified methylaluminoxane (MAO) according to the literature.

**Synthesis and Characterization of Ligand and Catalysts**

**Synthesis of 2-(2,6-Diisopropylphenylimino)ethyl)pyridine (L).** The ligand (L) was prepared through a procedure similar to that reported in the literature. A mixture of the appropriate 2-acetylpyridine compound (21.5 mmol), 2,6-diisopropylphenylline (28.7 mmol), a catalytic amount of formic acid (3 drops), and sodium sulfate in methanol (30 mL) was refluxed for 7 h. After cooling to room temperature, the precipitate was removed by filtration. The residue was kept in the freezer, and after 24 h, yellowish crystals appeared. The crystals were collected and washed with cold methanol to remove unreacted reactants. The product was dried under vacuum for characterization and preparation of the catalyst.

**Formula C19H24Br2N2, MW = 498.91 g mol−1; 1H-NMR (300 MHz, CDCl3, δ, ppm): 1.17 (12H, d), 2.24 (3H, s), 2.78 (2H, m), 7.10–7.21 (3H, m), 7.42 (1H, t), 7.84 (1H, t), 8.37 (1H, d), 8.72 (1H, d), 13C-NMR (300 MHz, CDCl3, selected δ, ppm): 167.01 (C (Me)=N), 156.47, 148.62, 146.44, 136.53, 135.81, 124.84, 123.64, 123.03, 121.36, 28.29, 28.06, 23.27, 22.96, 17.38. FTIR (KBr, cm−1): 3060, 2957, 1617, 1590, 1446, 1321, 1180, 781. Elemental analysis calculation: C, 81.38%; H, 8.63%; N, 9.99; found: C, 82.79; H, 8.83; N, 9.96.

**Preparation of the Catalyst 2-(2,6-Diisopropylphenylimino)ethyl)pyridine nickel dibromide (N).** A suspension of [NiBr2(DME)] (0.31 mmol) in dichloromethane (20 mL) was treated with a solution of 2-(2,6-dibenzylidene-4-methylphenylimino)methyl)pyridine (0.31 mmol) in dichloromethane (10 mL) in a glove box. The mixture was stirred at room temperature for 24 h, filtered, and the solvent was evaporated. The crude product was washed with DEE several times and dried in vacuum. The yield of the reaction was about 90%.

**Formula C14H18Br2N2Ni, MW = 498.91 g mol−1; FTIR (KBr, cm−1): 3076, 2965, 1617, 1590, 1446, 1321, 1180, 781. Elemental analysis calculation: C, 45.74; H, 4.85; N, 5.61; found: C, 45.07; H, 4.45; N, 5.14.

**Preparation of the Catalyst 2-(2,6-Diisopropylphenylimino)ethyl)pyridine iron dichloride (F).** A suspension of anhydrous FeCl2 (0.31 mmol) in THF (20 mL) at 70 °C a solution of 2-(2,6-dibenzylidene-4-methylphenylimino)methyl)pyridine (0.31 mmol)
in THF (10 mL) was added. The resulting mixture was stirred for 2 h, filtered, and its solvent was evaporated. The crude product was washed with dry n-hexane and diethyl ether and dried under inert atmosphere in a glove box. The product was obtained as a dark red powder, and the yield of the reaction was about 73%.

Formula C_{38}H_{46}Cl_{2}Fe_{2}N_{4}, MW = 814.32 g mol^{-1}; FTIR (KBr, cm⁻¹): 3084, 2964, 1619, 1592, 1441, 1317, 1186, 782. Elemental analysis calculation: C, 56.05; H, 5.94; N, 6.88. Found: C, 55.71; H, 5.48; N, 6.52.

**General Procedure for Ethylene Polymerization**

The polymerization of ethylene was performed in a sealed glass reactor equipped with a Schlenk system, ethylene inlet, and magnetic stirrer. The reactor was degassed and filled with monomer several times to remove oxygen and moisture. The desired amount of MMAO was introduced into toluene (solvent) under the continuous pressure of ethylene. An ice bath was used in order to control the temperature at 0 °C. Afterwards, toluene and cocatalyst (MMAO) were injected into the reactor, successively. Polymerization was initiated by injecting an appropriate amount of the catalyst(s) (10 μmol) into the reactor. The reaction temperature and ethylene pressure were kept constant during the polymerization process. At the end of polymerization, the remaining monomer was vented, and the reaction was quenched by adding the acidified methanol (5% v/v). The solid polyethylene was filtered and washed with methanol and dried under reduced pressure.

**Procedures for Preparation of LDPE/MWCNT Nanocomposites**

For *in situ* polymerization, a specific amount and type of MWCNT was added to a round-bottom flask containing toluene to disperse the particles. The mixture was injected into the polymerization reactor before addition of the catalyst(s) (5–10 min). The reaction was carried out for 3 h, and the reaction was vented and then quenched by adding the acidified methanol. The product was then filtered and dried under reduced pressure (40 °C).

For solution mixing, to a clear solution of LDPE in toluene at 80 °C under vigorous stirring (1500 rpm), a prescribed amount of MWCNT was added, and the final mixture was stirred while heating with a mild heating rate up to 100 °C. The hot, homogenized mixture was quenched by pouring it into a glass dish at room temperature. After 24 h, the solvent was evaporated, and a composite film was obtained.

**Characterization**

1H-NMR and 13C-NMR mass spectra and elemental analysis were recorded using Bruker Avance III-300 (Karlsruhe, Germany) and Varian CH-7A spectrometers (Palo Alto, CA) and a Thermo Finnigan Flash 1112EA microanalyzer (Waltham, MA), respectively. The Fourier transform infrared (FTIR) spectra (resolution of 5 at 32 runs) were recorded using a Thermo Nicolet AVATAR 370 (Waltham, MA) to determine the vinyl and branching content, which were calculated according to our previous work.

The viscosity average molecular weight (Mv) of the polymer samples was determined according to the literature (n = 6.2 × 10⁻²Mv⁰.₇, where n is intrinsic viscosity, α (0.7) and k (6.2 × 10⁻⁴) are mark-houwink constants). Thermogravimetric analysis (TGA; PerkinElmer TGA-7, Waltham, MA) and differential scanning calorimeter (DSC) instruments (Mettler Toledo DSC822, Columbus, OH) with a constant rate of 10 °C/min were used for polyethylene and nanocomposite characterization. The degree of crystallinity of the samples was calculated from the heat of fusion determined by DSC. The scanning electron microscope (SEM) images were obtained using a LEO VP 1450 instrument (Zeiss, Oberkochen, Germany).

**RESULTS AND DISCUSSION**

**Computational Study**

By considering the kinetic profile of the ethylene polymerization using single and binary catalyst systems, different trends in regard to activation and monomer insertion can be observed (Figure 1). To find the effect of molecular structure on the catalyst behavior, a series of theoretical studies were carried out. The precatalyst structures were built at the ground state according to the single-crystal monostructures provided in the literature.

Methyl cationic active centers (MCC) and ethylene n–complexes (n-comp.) were optimized using the Density Functional Theory (DFT) method at the B3LYP level using a 6-31+G basis set (Figure 2) by Gaussian 09W. In the structure of the Ni catalysts (LNiX₃), bromide atoms (X=Br) show greater activity than chloride (X=Cl) according to the literature, and also for a similar comparison, the precatalyst structures were considered for both halogen atoms.

Based on the computational results, the higher activity of the bromide structure can be attributed to the lower M–X bond dissociation energy for Ni–Br (360.0 kcal/mol) than for Ni–Cl (372.3 kcal/mol). Moreover, the higher electron affinity (A), global electrophilicity (ω), and lower chemical hardness (η) in the precatalyst, the closer match of Ni–Br bond dissociation energy to Al–C (267.7 kcal/mol), and the greater stability of the ethylene n–complex (stronger interaction of Ni and ethylene monomer) can lead to faster activation and a steep slope at the beginning of the kinetic profile (Table I). However, total activity of the catalyst F was higher than that of catalyst N due to higher mentioned theoretical parameters (A and ω), along with the Mulliken charge on the metal center in the n–complex affording a higher monomer uptake during the propagation reaction. More efficient
shielding of the axial sites in the coordination planes (xy, xz, yz) of the catalyst \( F \) containing an Fe cationic center, on the other hand, is another reason for the higher stability and performance of the catalyst \( F \) (Figures 3 and 4). As can be observed, the electron density around the Fe active center, especially in the planes xz and yz (axial sites), is higher than for Ni. The kinetic profile for each molar ratio of the catalysts is consistent with this explanation.

**Thermal and Structural Analysis**

Our previous studies have demonstrated that pyridine-imine catalysts are active for producing low-density polyethylene. In addition, using the single catalytic system of each one only yields a low-molecular-weight polyethylene, which dramatically depends on the polymerization parameters (the results for both catalysts are tabulated in the Supporting Information). In the present work, initially, polyethylene reactor blends were prepared using a binary system of the catalysts at different ratios of the complexes, and the results as well as the reaction conditions are tabulated in Table II. As can be observed, both catalysts had high activity in the single system at 0 °C. However, at the same polymerization conditions, the catalyst system N/MMAO showed a lower catalytic activity and \( M_v \) of the PE in comparison to F/MMAO (entries 1 and 5, Table II). The obtained results indicated that not only the polymerization activities but also the \( M_v \), melting temperature, crystallinity extent, and branching density of the polyethylene blends varied with the change in molar fraction of catalyst \( F \) \( (X_F) \) used in the reaction. Therefore, the catalytic activity using the binary system decreased linearly with increasing molar fraction of the catalyst \( N \) \( (X_N) \) [from 33.33 to 3.50 \( \times 10^3 \) g (PE) mol \((\text{Ni+Fe})^{-1} \text{h}^{-1}\)]. This observation can be attributed to the minimum interaction of catalysts \( N \) and \( F \) regarding the activity and selective activation of the metallic centers in the applied catalyst system during the ethylene polymerization (Table II). The \( M_v \) values of the polyethylene blends obtained at a fixed \([\text{Al}]/[\text{Ni+Fe}] \) ratio for each run had much
higher values than that of the polyethylene samples produced with the N and F catalysts individually. This might be due to the synergistic effect of the active centers, hindering $\beta$-hydrogen transfer, and a higher propagation/termination rate.\textsuperscript{49} As shown in Table II, $M_v$ of the resultant polyethylene blends increased to $19.4 \times 10^4$ (entry 4, Table II) by increasing the molar fraction of

Figure 3. Three-dimensional structure of Ni-MCC and electron density graphs in each plane ($xy$, $xz$, and $yz$) containing a Ni center. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 4. Three-dimensional structure of Fe-MCC and electron density graphs in each plane ($xy$, $xz$, and $yz$) containing an Fe center. [Color figure can be viewed at wileyonlinelibrary.com]
catalyst F in the catalyst combination. Figure 5 shows the broadened melting area of the polymers obtained with the N/F/MMAO system. It also shows an increase in the branching content of the polyethylene sample synthesized by catalyst F, which led to a shift in the melting and crystallization peaks toward lower temperatures and a broadening compared to those in polyethylene obtained by catalyst N.7 Furthermore, the melting temperature of the polymers obtained from the N/F/MMAO systems increased as the [Fe]/[Ni] ratio increased. Therefore, by increasing the X_F from 30% to 70% in the catalyst combination, virtually two separate melting points are observed. The two melting peaks of the samples implied a melting-recrystallization mechanism; such behavior has also been observed and discussed in similar systems.40,49,50

However, the highest and lowest melting point areas as well as degree of crystallinity of the polymers produced using different catalyst combinations were assigned to the samples produced at fixed 50:50 and 30:70 [Ni]/[Fe] proportions (entries 3 and 4, Table II), respectively. It seems that the polyethylene blend prepared using 50% X_F is an appropriate composition for the desired reactor blend in regard to polymer processing. Among all the obtained products, this sample showed the lowest branching (see Table II) and vinyl end content (35.9 methyl branches/1000 carbon atoms and 1.87 vinyl groups/1000 carbon atoms, respectively). As shown in Table II, the lowest degree of branching and the highest vinyl end content among the resultant samples (4.94 vinyl groups/1000 carbon atoms) belonged to the sample produced by the catalyst F (9.2 methyl branches/1000 carbon atoms), which can attributed to the lower tendency of Fe for chain walking and reinsertion of macromonomer, leading to a higher linearity in the polyolefin.51

### Morphology of the Polyethylene Blends

The SEM images were used to monitor the influence of different catalyst combinations on the structural morphology of the resultant products. The images are depicted in Figure 6. As can be

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**Figure 5.** DSC thermograms of polyethylene obtained using the N/F/MMAO binary system at 0 °C: the effect of X_N on polymer melting behavior. [Color figure can be viewed at wileyonlinelibrary.com]

**Table II.** Results of Ethylene Polymerization Using the Binary Catalytic Systems

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat N:Cat F</th>
<th>Activity^a</th>
<th>M_v</th>
<th>T_m (°C)^c</th>
<th>X_C (%)^c</th>
<th>VC^d</th>
<th>BD^e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100:0 (10 μmol Ni)</td>
<td>3.50</td>
<td>0.90</td>
<td>91.60, 70</td>
<td>2.05, 2.30</td>
<td>3.93</td>
<td>115.4</td>
</tr>
<tr>
<td>2</td>
<td>70:30 (7 μmol Ni: 3 μmol Fe)</td>
<td>5.05</td>
<td>12.5</td>
<td>91.20</td>
<td>2.37</td>
<td>3.17</td>
<td>104.0</td>
</tr>
<tr>
<td>3</td>
<td>50:50 (5 μmol Ni: 5 μmol Fe)</td>
<td>7.50</td>
<td>4.4</td>
<td>127.80, 105.40</td>
<td>3.20, 41.29</td>
<td>1.87</td>
<td>35.9</td>
</tr>
<tr>
<td>4</td>
<td>30:70 (3 μmol Ni: 7 μmol Fe)</td>
<td>12.60</td>
<td>19.4</td>
<td>113.40, 99.10</td>
<td>8.80, 16.77</td>
<td>2.75</td>
<td>83.3</td>
</tr>
<tr>
<td>5</td>
<td>0:100 (10 μmol Fe)</td>
<td>33.33</td>
<td>1.2</td>
<td>105.10</td>
<td>28.55</td>
<td>4.94</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Conditions: toluene = 100 mL, polymerization temperature = 0 °C, ethylene pressure = 1.2 bar, polymerization time = 2 h, MMAO as cocatalyst, [Al]/[M] = 1200.  
^a Activity × 10^4 g (PE) mol (Ni+Fe)^−1 h^−1.  
^b Viscosity average molecular weight, ×10^4.  
^c Determined by DSC.47  
^d Vinyl content: determined by FTIR, number of vinyl groups/1000 carbon atoms.  
^e Branching density: determined by FTIR, methyl branches/1000 carbon atoms.
seen, a uniform morphology is observed for the samples obtained using the catalysts N and F individually. The morphologies observed for the samples were cauliflower [Figure 6(e)] and amorphous [Figure 6(a)]. However, by increasing the molar fraction of catalyst F in the catalyst combination, the uniform morphology disappeared as the amorphous phase in the total structure of the resultant polyethylene blends increased. The DSC thermograms showed two dominant crystal peaks of the polyethylene, corresponding to the distinct polymerization process from the active centers as well as the existence of two distinct phases in the SEM images (Figures 5 and 6). However, it is not possible to distinguish the presence of two polymer phases in the SEM images of the polyethylene blend obtained using the 50:50 [Ni]/[Fe] molar fraction in the catalyst combination, which can be attributed to the different interaction and good miscibility between the polyethylene phases produced [Figure 6(c)].

**Thermal and Structural Analysis of LDPE/Nanocomposites**

The binary catalyst system based on the pyridine-imine nickel and iron catalysts (N:F) was used to produce nanocomposites. The influence of type and content of MWCNT on the catalytic activity was investigated. The polymerization was carried out in the presence of the binary system (5 mmol F and 5 mmol N) at 0 °C and 2 bar of monomer for 3 h. The nanocomposite samples were analyzed, and the details are gathered in Table III.

The catalytic activity slightly decreased with low amounts of both sizes of MWCNTs, consistent with previous results. These values were in the range of 0.66 × 10⁴ to 4.00 × 10⁴ g (PE) mol (Fe+Ni)⁻¹ h⁻¹. This observation might be attributed to the deactivation of active polymerization sites by the naturally occurring functional groups on the surface of the CNTs. However, the presence of impurity as an obstacle for ethylene monomer diffusion and reaching the active center cannot be ignored. In contrast, the MWCNTs with larger diameter (30–50 nm) led to a frustrating effect on catalyst productivity in the polymerization of ethylene (entries 4 and 5, Table III).

As shown in Figure 7, the prepared LDPE/nanocomposites exhibited a lower degree of crystallinity and melting point than the neat polyethylene blend (entries 3 and 4, Table III), and these numerous differences in the LDPE/nanocomposites containing structure of the resultant polyethylene blends increased. The DSC thermograms showed two dominant crystal peaks of the polyethylene, corresponding to the distinct polymerization process from the active centers as well as the existence of two distinct phases in the SEM images (Figures 5 and 6). However, it is not possible to distinguish the presence of two polymer phases in the SEM images of the polyethylene blend obtained using the 50:50 [Ni]/[Fe] molar fraction in the catalyst combination, which can be attributed to the different interaction and good miscibility between the polyethylene phases produced [Figure 6(c)].

![Figure 6. SEM images of polyethylene prepared with different nickel molar fractions (X_N) in the N/F/MMAO binary system: (a) 0, (b) 0.3, (c) 0.5, (d) 0.7, (e) 1. [Color figure can be viewed at wileyonlinelibrary.com]](image)

**Table III. In Situ Polymerization Results for Production of LDPE/Nanocomposites Using a Combination of Pyridine-imine Catalysts Based on Nickel (N) and Iron (F)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>wt %a</th>
<th>MWCNT type</th>
<th>Content (mg)</th>
<th>Time (min)</th>
<th>PE (g)</th>
<th>Activityb</th>
<th>T_m [°C]c</th>
<th>X_C (%)d</th>
<th>VCd</th>
<th>BDd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>—</td>
<td>0</td>
<td>120</td>
<td>1.51</td>
<td>7.50</td>
<td>127.80, 105.40</td>
<td>3.20, 41.30</td>
<td>1.87</td>
<td>35.9</td>
</tr>
<tr>
<td>2</td>
<td>2.33</td>
<td>20–30 nm</td>
<td>7</td>
<td>180</td>
<td>0.30</td>
<td>1.00</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.93</td>
<td>50.1</td>
</tr>
<tr>
<td>3</td>
<td>1.80</td>
<td>20–30 nm</td>
<td>21</td>
<td>180</td>
<td>1.17</td>
<td>4.00</td>
<td>121.90, 102.70</td>
<td>0.83, 4.53</td>
<td>0.12</td>
<td>34.7</td>
</tr>
<tr>
<td>4</td>
<td>0.87</td>
<td>30–50 nm</td>
<td>7</td>
<td>180</td>
<td>0.80</td>
<td>2.70</td>
<td>87.60, 52.20</td>
<td>2.30, 0.40</td>
<td>4.17</td>
<td>70.8</td>
</tr>
<tr>
<td>5</td>
<td>10.50</td>
<td>30–50 nm</td>
<td>21</td>
<td>180</td>
<td>0.20</td>
<td>0.66</td>
<td>n.d.</td>
<td>n.d.</td>
<td>5.30</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Conditions: toluene = 100 mL, polymerization temperature = 0 °C, ethylene pressure = 1.2 bar, catalyst N = 5 μmol, catalyst F = 5 μmol [50:50], MMAO as cocatalyst, [Al]/[M] = 1200.

a wt % of CNT in polymer matrix.
b Activity ×10⁴ g (PE) mol (Ni+Fe)⁻¹ h⁻¹.
c Determined by DSC.
d Vinyl content: determined by FTIR, number of vinyl groups/1000 carbon atoms.
d Branching density: determined by FTIR, methyl branches/1000 carbon atoms.
MWCNT_{30-50} can be ascribed to a high degree of branching (70.8 methyl branch/1000 carbon atoms; entry 1, Table III). In fact, the nanofiller (such as CNTs) could increase the chain transfer reaction and β-hydrogen elimination due to an electronic effect that consequently increases the branching content. As exhibited in Figure 8 and Table III (Entries 2–5), the values for LDPE/nanocomposite samples varied between 11.5 and 70.8 methyl branches/1000 carbon atoms. Furthermore, nanocomposite samples containing MWCNT_{20-30} showed the lowest vinyl content (0.12 vinyl groups/1000 carbon atoms) among all the samples. However, the addition of MWCNT_{30-50} into the polymerization media led to a greater vinyl content in the products, up to 5.30 vinyl groups/1000 carbon atoms.

In order to better understand the effect of MWCNTs on the final properties of LDPE/nanocomposites, the polymerization of ethylene using a single Ni catalyst and MWCNT was carried out, and the results are gathered in Table IV.

The activity of the catalyst N in polymerization, as well as the melting point and crystallinity of the resultant sample, dropped as the MWCNT_{20-30} was added into the polymerization reactor. However, the branching and vinyl content trends in these
samples are not the same as in the sample produced by the dual catalyst system under the same conditions. The result is consistent with the fact that the catalyst $F$ is more dominant than catalyst $N$ in relation to the sample properties (entries 2 and 3, Tables III and IV). As shown in Figure 7(b), the sample obtained using the in situ polymerization technique indicated a lower melting temperature as well as crystallinity than found for the corresponding nanocomposite obtained via solution mixing (entries 2 and 4, Table IV). This behavior can be explained by the higher degree of branching and weaker intermolecular forces in the resultant sample as compared to the sample obtained by solution mixing and the possible interaction of MWCNTs during in situ polymerization.$^{10,28}$

### Morphology of LDPE/Nanocomposites

SEM images were used to investigate the influence of the different type and content of MWCNTs as well as different preparation techniques on the morphology of the final products.
Therefore, the samples along with their dispersity are depicted in Figures 9 and 10. In Figure 9(b), a uniform morphology is not seen for the sample obtained in the presence of MWCNT$_{20,30}$ (entry 3, Table III); however, virtually a single fraction of the crystalline phase in DSC traces was observed for the sample containing MWCNT$_{30,50}$ [entry 5, Table III, and Figure 7(a)], in which the presence of nanotubes is obvious in the polymer matrix [Figure 9(c)].

In Figure 10(b), a soft, uniform morphology without any specific shape can be observed for the sample prepared via the solution-mixing technique, and a broad single peak is obtained in the DSC thermogram [Figure 7(b)]. In contrast, two melting peaks are more distinguishable and different crystalline phases in the DSC trace [Figure 7(b)] were recorded for the sample with a uniform morphology prepared by the in situ polymerization technique [Figure 9(a)].

**Thermogravimetric Analysis**

TGA is a useful tool for evaluating the thermal stability of the nanocomposite samples. The resulting thermogravimetric studies are shown in Figure 11 and Table V. The thermal stability of the nanocomposite samples strongly depends on the type and content of CNTs. At the same conditions, the lowest and highest half-lives of the nanocomposites were attributed to those products, respectively, in the presence of 1.80 wt % MWCNT$_{20,30}$ (entry 2, Table V) and 10.50 wt % MWCNT$_{30,50}$ (entry 4, Table V). The differential curve analysis of the resultant samples (Table V) showed that the sample with a high content of...
MWCNT$_{30:50}$ (10.50 wt %) has the highest onset and end point of degradation temperature (entry 4, Table V). However, the greatest weight loss in this sample occurred at 10.66% of the degradation time (entry 4, Table V). Furthermore, a single peak is also obtained for the nanocomposite in the presence of MWCNT$_{20:30}$ (2.33 wt %), which had a higher combustion temperature (647.7 °C) than the neat polyethylene blend [Figure 11 (b)]. In fact, with decreasing MWCNT$_{20:30}$ content (from 2.33 to 1.80 wt %), the thermal stability of the obtained nanocomposites slightly increased, which can be attributed to the increasing amount of crystallinity and decrease in branching content in the prepared sample.\(^5\)

**CONCLUSIONS**

Reactor blends containing linear and highly branched polyethylene were prepared in the presence of modified methylaluminoxane using a binary system based on pyridine-imine nickel (N) and iron (F) catalysts. As a result, introducing different ratios of the catalysts at the same conditions can enhance the properties of the obtained products such as $M_v$ as well as the thermal properties [up to $19.4 \times 10^3$ g (PE) mol $\left(\text{Fe}+\text{Ni}\right)$\(^{-1}\) h\(^{-1}\) and 127.8 °C]. The DSC and SEM results indicate that the combination of linear PE with less branched PE through the binary catalyst system can achieve a better polymer miscibility when polymerization is conducted at a fixed 50:50 [Ni]/[Fe] molar ratio of the catalysts. LDPE/nanocomposite samples containing different types and content of MWCNTs were successfully prepared via in situ polymerization. By increasing the content of MWCNT$_{20:30}$, the activity of the catalysts was improved, which can be attributed to adsorption of catalyst on the CNT surface, but overall the performance of the catalyst mixture decreased in the presence of MWCNTs. The LDPE/nanocomposites with lower melting point and degree of crystallinity compared to the neat polyethylene blend implied higher chain walking, degree of branching, and vinyl content. Moreover, the sample containing MWCNT$_{20:30}$ exhibited contrary results in regard to the unsaturation content. The melting point and crystallinity extent of the samples obtained via the in situ process exhibited lower values as well as a distinct morphology compared to the corresponding sample prepared by the solution-mixing technique. The addition of MWCNT$_{20:30}$ caused an increase in the thermal stability, due to a better and uniform dispersion of the nanofillers in the LDPE matrix.

**ACKNOWLEDGMENTS**

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**REFERENCES**


**Table V.** Differential Thermogravimetric Results for LDPE/Nanocomposites Prepared by in Situ Polymerization

<table>
<thead>
<tr>
<th>Entry</th>
<th>wt %$^a$</th>
<th>Content of CNT (mg)</th>
<th>Diameter of CNT (nm)</th>
<th>Degradation data</th>
<th>Time (s)</th>
<th>Temperature (°C)</th>
<th>Half-life (s)</th>
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<td>3045</td>
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</table>

$^a$ wt % of MWCNT in polymer matrix.
47. Mogheiseh, M.; Zohuri, G. H.; Yazdanbakhsh, M. Presented at the 1st Iranian Applied Chemistry Seminar (IACS), Tabriz, Iran, August 2016.