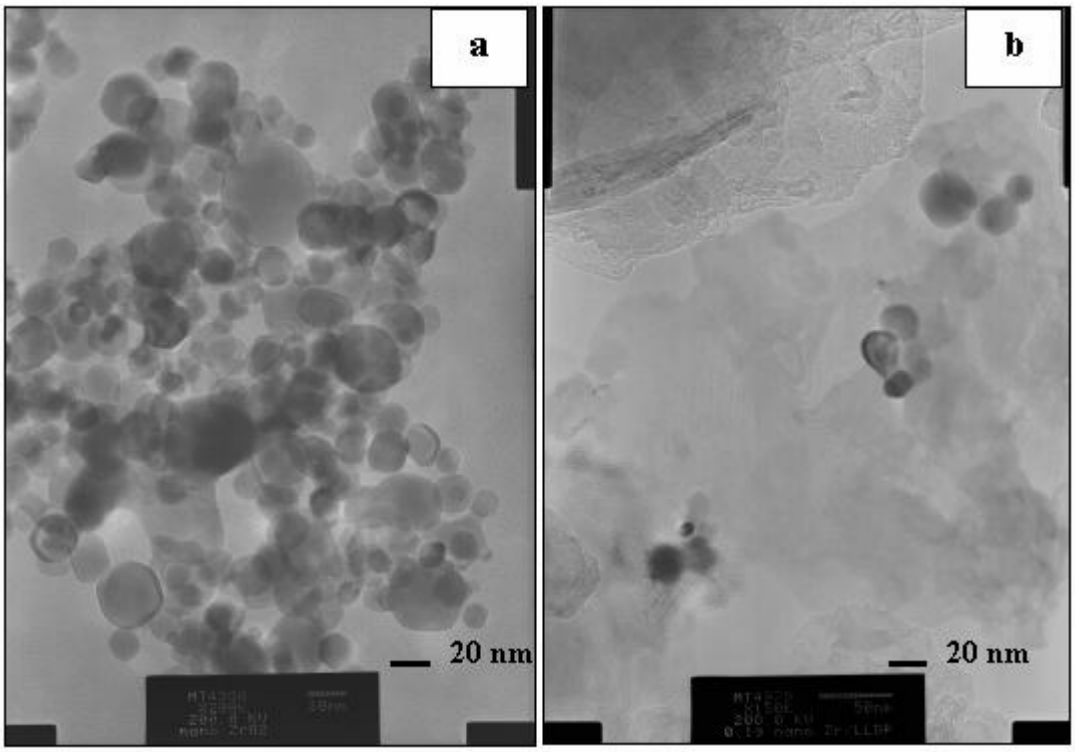


Figure 2

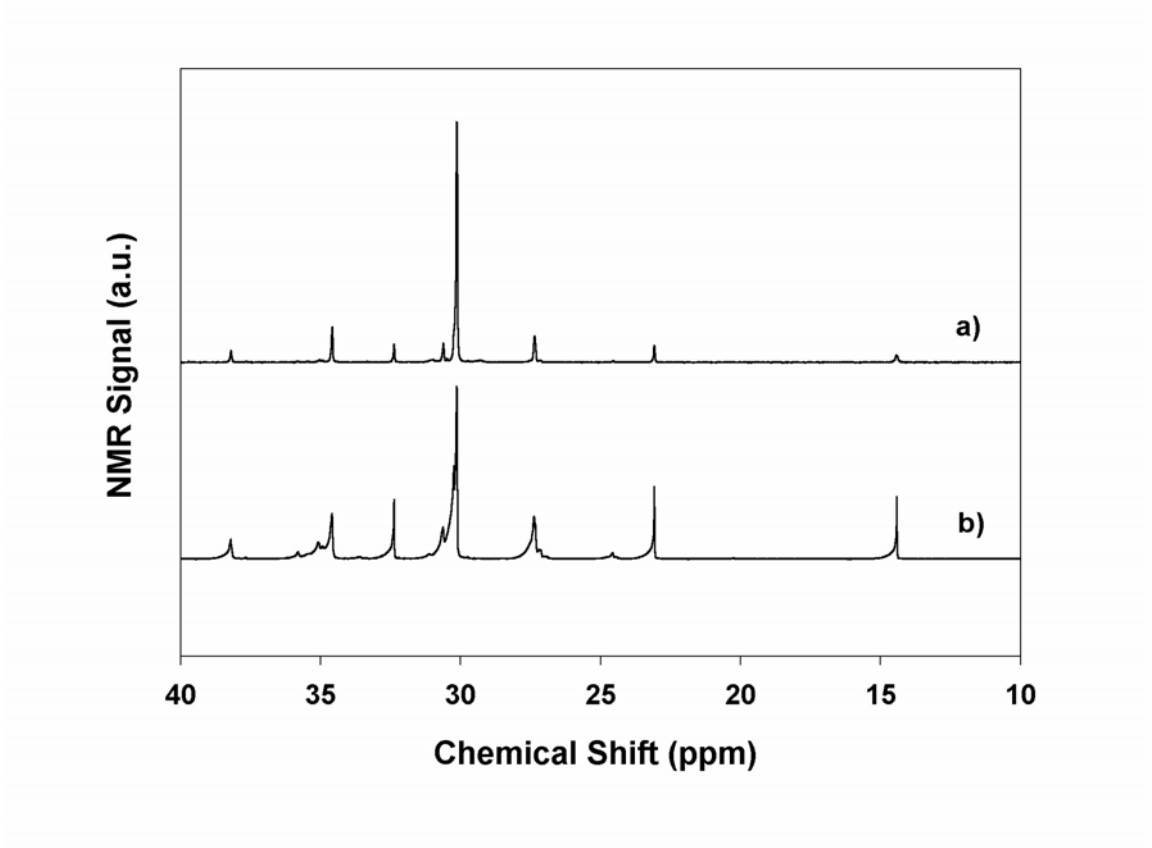


Figure 3

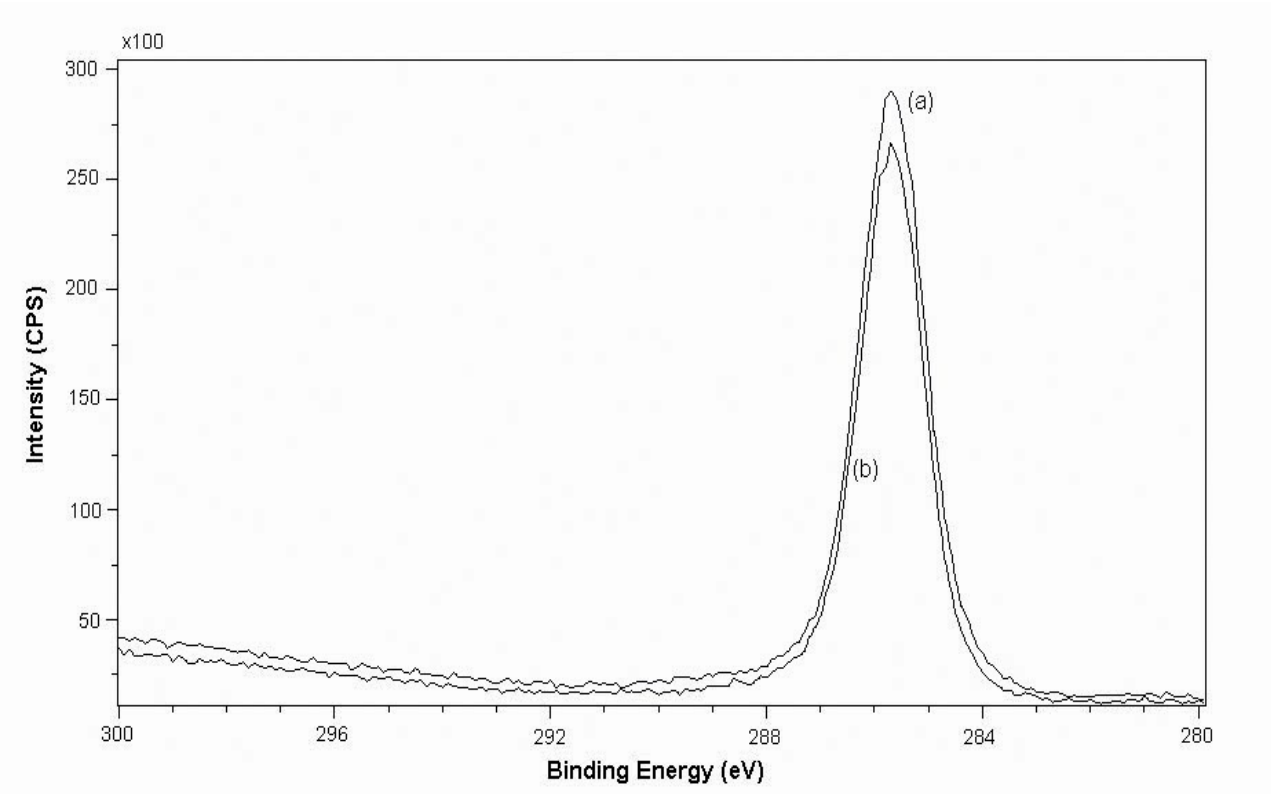
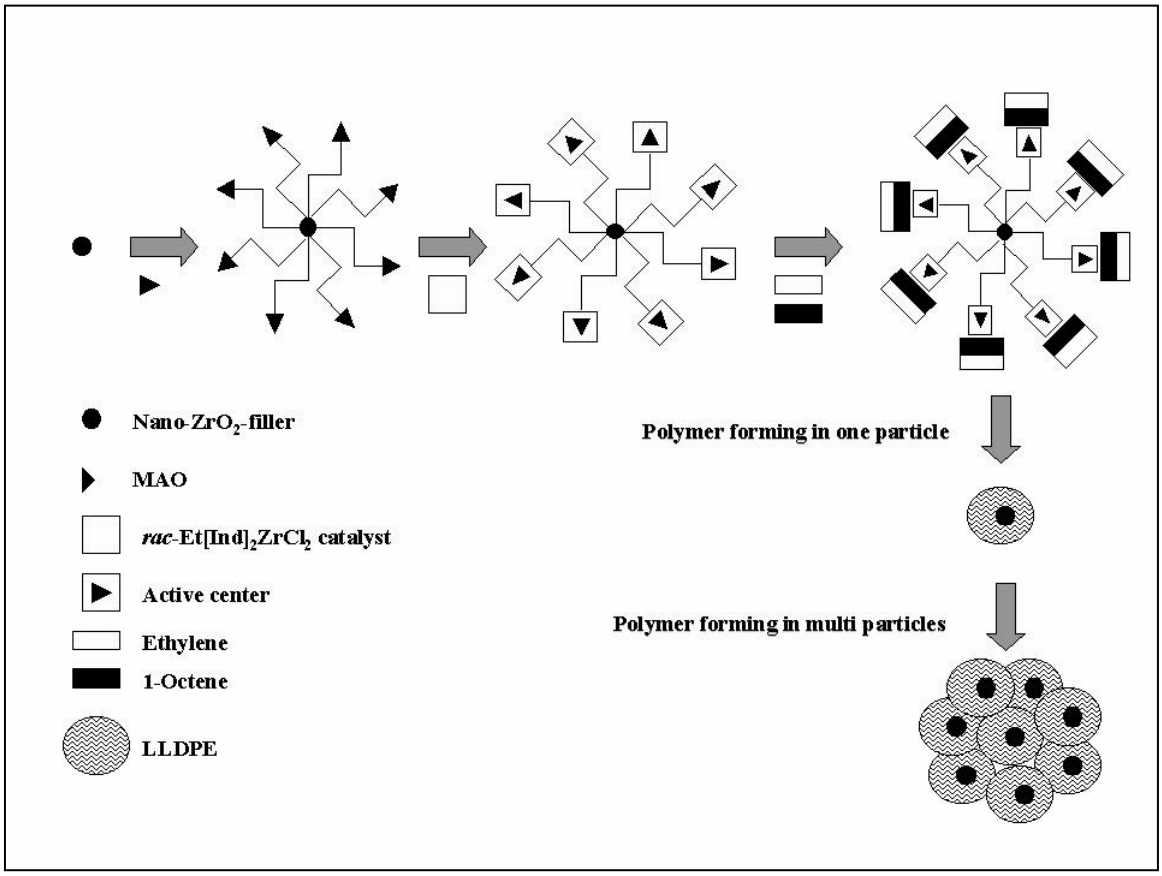

x100
300
250
200
150
100
50
Intensity (CPS)
(a)
(b)
300
296
292
288
284
280
Binding Energy (eV)

Figure 4


Nano-ZrO_2-filler
MAO
rac-Et[Ind]$_2$$ZrCl_2$ catalyst
Active center
Ethylene
1-Octene
LLDPE
Polymer forming in one particle
Polymer forming in multi particles

Scheme 1

ภาคผนวก C

บทความวิจัยที่ได้รับการตีพิมพ์ในวารสารระดับนานาชาติ

1. **Bunjerd Jongsomjit**[*], Sutti Ngamposri and Piyasan Praserthdam, *"Application of Silica/Titania Mixed Oxide-Supported Zirconocene Catalyst for Synthesis of Linear Low-Density Polyethylene"*, ***Industrial & Engineering Chemistry Research*** **44**, PP. 9059-9063 (2005). [Impact factor =1.504 (2005)]

2. **Bunjerd Jongsomjit**[*], Joongjai Panpranot, Mitsuhiro Okada, Takeshi Shiono, and Piyasan Praserthdam, *"Characteristics of LLDPE/ZrO_2 Nanocomposite Synthesized by In-situ Polymerization using a Zirconocene/MAO Catalyst"*, ***Iranian Polymer Journal*** **15**, PP431-437 (2006). [Impact factor = 0.316 (2006)]

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Application of Silica/Titania Mixed Oxide-Supported Zirconocene Catalyst for Synthesis of Linear Low-Density Polyethylene

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The present study focused on the application of mixed TiO_2−SiO_2-supported methylaluminoxane (MAO) with a zirconocene catalyst on the linear low-density polyethylene (LLDPE) production. At low concentrations of TiO_2 present in the mixed supports, it revealed that TiO_2 was decorated on the SiO_2 surface and acted as a spacer to anchor MAO to the SiO_2 surface resulting in less steric hindrance and less interaction. As a result, catalytic activities via ethylene/1-olefin copolymerization apparently increased with the presence of TiO_2. Besides increased activities, the presence of TiO_2 in the mixed supports can result in a slightly lower molecular weight (MW) of polymers, suggesting a higher chain transfer rate.

1. Introduction

For years, metallocene catalysts have brought much attention to research in olefin polymerization. As a matter of fact, it has led to an extensive effort for utilizing metallocene catalysts more efficiently. It is known that the copolymerization of ethylene with higher 1-olefins is a commercial importance for productions of elastomer and linear low-density polyethylene (LLDPE). Metallocene catalysts with methylaluminoxane (MAO) have been studied for such a copolymerization. In particular, zirconocene catalysts along with MAO have been reported for a potential use to polymerize ethylene with 1-olefins.[1−2]

Nevertheless, it was found that a homogeneous metallocene catalytic system has two major disadvantages: the lack of morphology control of polymers produced and reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports can provide a promising way to overcome these drawbacks. It has been reported that many inorganic supports such as SiO_2, Al_2O_3, and $MgCl_2$ have been extensively studied.[3−13] It has been mentioned that silica is perhaps the most widely used support for metallocene catalysts so far. Unfortunately, due to the support effect, it is found that the catalytic activity of catalysts in the heterogeneous system is usually lower than the homogeneous one. Therefore, a modification of the support properties is required in order to maintain high activity as in the homogeneous system or even closer. TiO_2−SiO_2 mixed oxide has been considered to be very attractive as catalysts and supports, which have brought much attention in recent years. It was reported that TiO_2−SiO_2 mixed materials have been used as catalysts and supports for various reactions.[14] This TiO_2−SiO_2 mixed oxide would lead to robust catalytic supports of metallocene catalysts for olefin polymerization.

In the present study, the application of mixed TiO_2−SiO_2-supported MAO for LLDPE production was investigated. The weight percent of TiO_2/SiO_2 used was varied. The mixed TiO_2−SiO_2-supported MAO were prepared, characterized, and tested for ethylene/1-olefin copolymerization. The characteristics of the polymers obtained were also identified.

2. Experimental Section

All chemicals [TiO_2 (anatase, Ishihara), SiO_2 (Cariact P-10), toluene, *rac*-ethylenebis (indenyl) zirconium dichloride [*rac*-Et(Ind)$_2$ZrCl$_2$], methylaluminoxane (MAO), trimethylaluminum (TMA), and 1-olefins such as 1-hexene, 1-octene, and 1-decene] were manipulated under an inert atmosphere using a vacuum glovebox and/or Schelenk techniques. The mixed TiO_2−SiO_2 supports [surface areas of SiO_2 = 300 m^2/g and TiO_2 (anatase form) = 70 m^2/g] for MAO were prepared by the physical mixing of 1 g of a designed weight ratio of TiO_2−SiO_2 in 20 mL of toluene. The mixture was stirred for 30 min, filtered, and then dried under vacuum. The TiO_2:SiO_2 weight percents were varied as follows: 0:100, 20:80, 40:60, 60:40, 80:20, and 100:0. The supports were heated under vacuum at 400 °C for 6 h. To prepare the TiO_2−SiO_2 mixed oxides-supported MAO, 1 g of the mixed TiO_2−SiO_2 support was reacted with the desired amount of MAO at room temperature and stirred for 30 min. The solvent was then removed from the mixture. About 20 mL of toluene was added into the obtained precipitate, the mixture was stirred for 5 min, and then the solvent was removed. This procedure was done 5 times to ensure the removal of impurities. Then, the solid part was dried under vacuum at room temperature to obtain the white powder of mixed TiO_2−SiO_2-supported MAO.

To study polymerization, the ethylene/1-octene (EO) [the ethylene/1-hexene (EH) and ethylene/1-decene (ED) copolymerization were also performed separately] copolymerization reaction was carried out in a 100 mL semibatch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 0.1 g of the supported MAO ($[Al]_{MAO}/[Zr]$ = 1135) and 0.018 mol of 1-octene along with toluene (to make the total volume of 30 mL) were put into the reactor. The desired amount of *rac*-Et(Ind)$_2$ZrCl$_2$ (5×10^{-5} M) and TMA ($[Al]_{TMA}/[Zr]$ = 2500) was mixed and stirred for 5-min aging at room temperature, separately, and then was injected into the reactor. The reactor was frozen in liquid nitrogen to stop the reaction for 15 min, and then the reactor was

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10.1021/ie050806d CCC: $30.25
Published on Web 10/27/2005

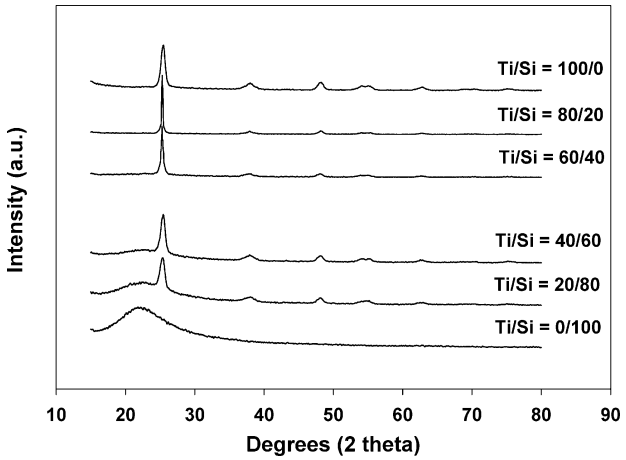


Figure 1. XRD patterns various mixed TiO_2-SiO_2 supports.

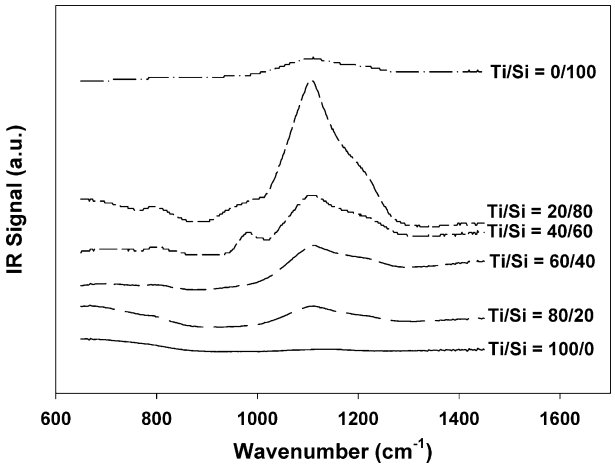


Figure 2. IR spectra of various mixed TiO_2-SiO_2 supports.

evacuated to remove argon. The reactor was heated to polymerization temperature (70 °C). By feeding the fixed amount of ethylene (0.018 mol, ~6 psi) into the reaction mixtures, the ethylene consumption can be observed corresponding to the ethylene pressure drop. The polymerization reaction was stopped, and the reaction time used was recorded when all ethylene (0.018 mol) was totally consumed. After all the ethylene was consumed, the reaction was terminated by addition of acidic methanol (0.1% HCl in methanol) and stirred for 30 min. After filtration, the obtained copolymer (white powder) was washed with methanol and dried at room temperature.

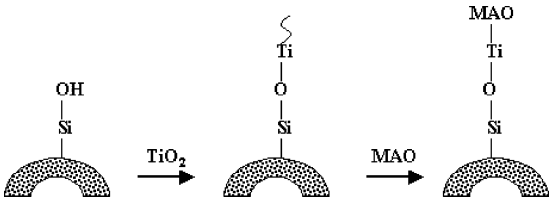
Characterization of supports and catalyst precursors was performed using (i) X-ray diffraction (XRD), SIEMENS D-5000 X-ray diffractometer with Cu Kα (λ = 1.54439 Å), (ii) scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM and EDX), JEOL mode JSM-5800LV, and (iii) FTIR spectroscopy, Perkin-Elmer series 2000 instruments.

Characterization of polymer was conducted using (i) SEM as mentioned above, (ii) gel permeation chromatography (GPC), Waters 150-C, (iii) differential scanning calorimetry (DSC), NETZSCH DSC 200, and (iv) carbon-13 nuclear magnetic resonance (^{13}C NMR), JEOL JMR-A500. The triad distribution was calculated on the basis of reference 15.

3. Results and Discussion

3.1. Characteristics of the Mixed Supports. The XRD patterns of the supports before impregnation with MAO are shown in Figure 1. It was observed that the pure silica exhibited a broad XRD peak assigning to the conventional amorphous SiO_2. Similar to the pure SiO_2, the XRD patterns of the pure TiO_2 indicated only the characteristic peaks of anatase TiO_2 at 25 (major), 37, 48, 55, 56, 62, 71, and 75°. The XRD patterns of mixed TiO_2-SiO_2 supports containing various weight percent of TiO_2/SiO_2 exhibited the combination of mixed TiO_2/SiO_2 supports. However, it seemed there was not a linear proportionality between the area and weight percent of TiO_2. This discrepancy could be associated to a no perfect uniform distribution of TiO_2 in the SiO_2. This could be attributed to the particle size distribution of TiO_2 used. After impregnation with MAO, the various supports were also identified with XRD in order to determine any changes when the MAO was added. It was found that XRD patterns for the supports after impregnation with MAO were identical with those before impregnation, indicating a highly dispersed form of MAO species in the supports.

Scheme 1. Conceptual Model for the Connection of MAO to the Mixed Supports



To determine the morphologies and elemental distributions of the supports before and after impregnation, SEM and EDX were performed, respectively. The SEM micrographs (not shown) of the supports before and after impregnation with MAO essentially indicated that the SiO_2 was appeared in larger particles than the TiO_2. There was no significant change in the morphologies of supports upon the MAO impregnation as well. Moreover, it was also found that, at the low contents of TiO_2 ranging between 20 and 60 wt %, TiO_2 was apparently decorated on the outer SiO_2 surface. However, at high contents of TiO_2, the isolation of TiO_2 from the SiO_2 surface can be observed because the adsorption ability of SiO_2 itself was limited by the large amounts of TiO_2 added. To determine the interaction between TiO_2 and SiO_2, including the chemical species present, IR spectroscopy on the mixed TiO_2/SiO_2 supports was performed. The IR spectra of various supports are shown in Figure 2. It indicated that, at low concentrations of TiO_2, the IR band at ca. 980 cm^{-1} assigned to Si−O−Ti connectivity was observed as also reported by Dutoit et al.[16] The strong IR bands were also seen at ca. 1100 cm^{-1}, assigned to asymmetric Si−O−Si stretching vibration. Based on the SEM and IR results, the connection of MAO to the mixed supports could be drawn as shown in Scheme 1.

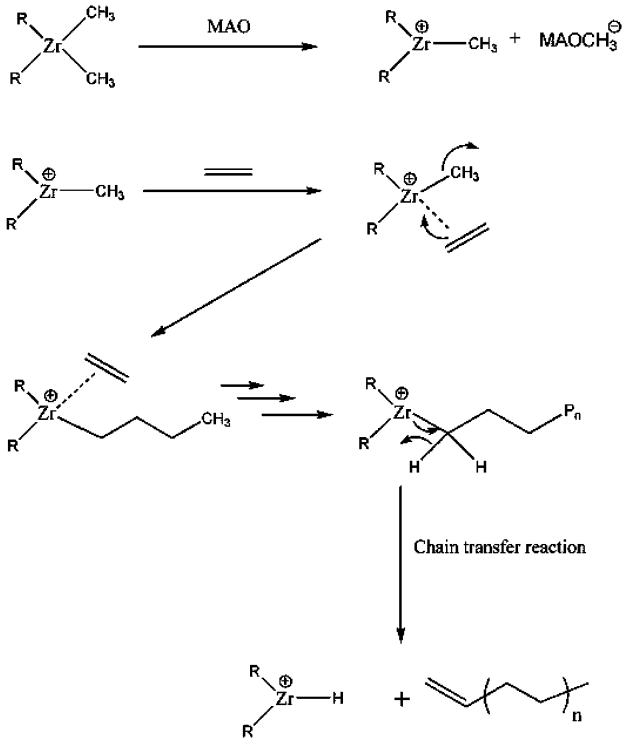
3.2. Polymerization Activity. In general, the typical polymerization mechanism using a zirconocene/MAO catalyst was proposed as shown in Scheme 2. To study the effect of the mixed TiO_2-SiO_2-supported MAO with the *rac*-Et[Ind]$_2ZrCl_2$ catalyst on copolymerization of ethylene/1-olefins, such copolymerization was performed with EO. The resulting reaction study is shown in Table 1. It was found that activities of the supported system were much lower than the homogeneous one as expected

Table 1. Catalytic Activities during Ethylene/1-Octene (EO) Copolymerization via Mixed TiO_2−SiO_2-Supported MAO with *rac*-Et[Ind]$_2$$ZrCl_2$ Catalyst

TiO_2−SiO_2 wt %	wt % of TiO_2 in mixed support	polym yield (g)	polymerization time (s)	catalytic activity[a] ($\times 10^{-4}$ kg of polym/(mol of Zr·h))
homogeneous	0	1.13	87	3.1
0/100	0	1.19	152	1.9
20/80	20	1.14	116	2.4
40/60	40	1.19	132	2.2
60/40	60	1.18	149	1.9
80/20	80	1.17	157	1.8
100/0	100	1.13	161	1.7

[a] Activities were measured at polymerization temperature of 70 °C, [ethylene] = 0.018 mol, [1-octene] = 0.018 mol, $[Al]_{MAO}/[Zr]$ = 1135, and $[Al]_{TMA}/[Zr]$ = 2500, in toluene with total volume = 30 mL and $[Zr] = 5 \times 10^{-5}$ M.

Scheme 2. Mechanism of LLDPE Synthesis via a Zirconocene/MAO Catalyst



due to the supporting effect. However, considering only the supported system, it revealed that activities apparently increased with increasing amounts of TiO_2 up to 60 wt % in the mixed supports compared with those for the pure SiO_2 one. The maximum activity can be obtained with the presence of 20 wt % TiO_2 in the mixed support, as also seen in Table 1. However, with an increase in the amounts of TiO_2 more than 60 wt %, the decreased activities were observed. It was also found that the activity for the pure TiO_2 was the lowest since the strong support interaction[17] between MAO and TiO_2 was more pronounced. Thus, the role of TiO_2 in the mixed TiO_2−SiO_2 supports can be proposed on the basis of the resulting activities. It should be noted that when the heterogeneous system was conducted, activities decreased significantly compared to the homogeneous one, as also seen in this study. This is due to a loss of active species by support interaction and/or the steric hindrance arising from the support. On the basis of the resulting activities from the present study, catalytic activities via the mixed TiO_2−SiO_2-supported MAO can be categorized into three levels. The first level was referred to the low activities obtained from the pure TiO_2 support itself, including supports with the presence

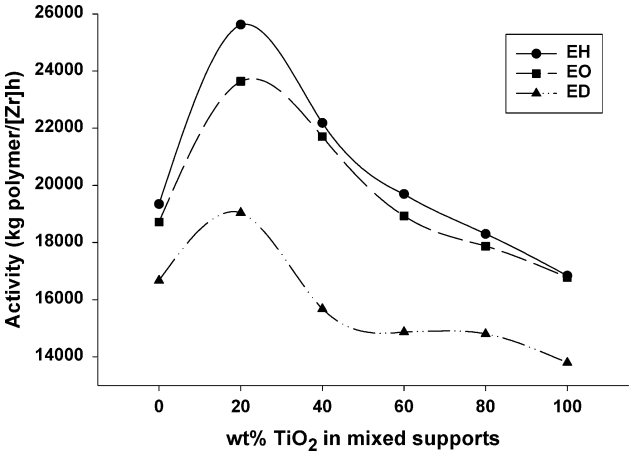


Figure 3. Activities of various TiO_2−SiO_2-supported MAO with *rac*-Et[Ind]$_2$$ZrCl_2$ catalyst.

of TiO_2 more than 60 wt %. The moderate activity can be considered as the second level where only pure SiO_2 itself was used as a support for MAO. The third level was recognized as the high activities, which can be observed with the presence of TiO_2 in the mixed supports up to 60 wt %. It showed that the presence of TiO_2 up to 60 wt % apparently enhanced the catalytic activities. The contribution of TiO_2 can be drawn as the MAO anchored on SiO_2 with TiO_2 as a spacer group. Thus, activities increased about 15−25% with the presence of TiO_2 at 20 and 60 wt % in the mixed supports compared with those of SiO_2 solely. It should be mentioned that increased activities with the presence of TiO_2 as a spacer were observed because of less steric hindrance and less interaction on the support surface when TiO_2 was introduced. Thus, this was suggested to be a more homogeneous-like system. Investigation of a spacer such as silane ($SiCl_4$) in copolymerization of ethylene/1-olefins was also reported[18,19] in our previous work.

In addition, to further investigate the effect of various mixed TiO_2−SiO_2 supports on other 1-olefin comonomers, the copolymerization of ethylene/1-hexene (EH) and ethylene/1-decene (ED) was also conducted separately. The resulting catalytic activities via the mixed TiO_2−SiO_2 supports of EH, EO, and ED were plotted in Figure 3. It was found that the catalytic activities of EH and ED via the mixed TiO_2−SiO_2 supports exhibited a trend similar to those of EO. Activities of EH were the highest, whereas those of ED were the lowest corresponding to the chain length of each comonomer as reported before. However, when comparing the present results with those from our previous work[19] with silane ($SiCl_4$) modification of the SiO_2 support, we found that the modification of silane pronouncedly enhanced

Table 2. MW and MWD of Copolymers (EO) Obtained via Mixed TiO_2−SiO_2-Supported MAO with *rac*-Et[Ind]$_2$$ZrCl_2$ Catalyst

TiO_2−SiO_2 wt %	wt % of TiO_2 in mixed support	M_w[a] ($\times10^{-4}$ g/ mol)	M_n[a] ($\times10^{-4}$ g/ mol)	MWD[a]
0/100	0	3.61	1.06	3.4
20/80	20	3.42	1.08	3.2
40/60	40	2.91	1.13	2.6
60/40	60	2.60	0.96	2.7
80/20	80	2.65	0.93	2.8
100/0	100	2.41	0.59	4.1

[a] Obtained from GPC, and MWD was calculated from M_w/M_n.

Table 3. Triad Distribution Obtained from ^{13}C NMR of Copolymers (EO) Obtained from Various Mixed TiO_2−SiO_2-Supported MAO with *rac*-Et[Ind]$_2$$ZrCl_2$ Catalyst[a]

TiO_2/SiO_2 wt %	EEE	OEE + EEO	EOE
0/100	0.63	0.18	0.19
20/80	0.69	0.15	0.16
40/60	0.72	0.14	0.14
60/40	0.79	0.10	0.11

[a] E refers to ethylene, and O refers to 1-octene. No evidence for OEO, OOE + EOO, and OOO was found.

activities for EH only, but had less effects on EO and ED. The present study revealed that the modification of SiO_2 with the TiO_2 could result in enhanced activities regardless of the comonomer chain length. Besides the effect of mixed TiO_2−SiO_2 supports on the catalytic activities, it would be also interesting to investigate how the mixed supports alter the characteristics of the copolymers produced or not. Thus, the microstructure, morphologies, and thermal properties of copolymers obtained were further investigated with different characterization techniques.

3.3. Characteristics of Polymer. The molecular weight (MW) and molecular weight distribution (MWD) of copolymers (EO) produced are shown in Table 2. It can be observed that MW of the copolymers slightly decreased with the presence of TiO_2 in the mixed supports. The decreased MW was more pronounced when pure TiO_2 was applied, suggesting a higher degree of chain-transfer reaction. Since titania was the first support where strong metal support interaction was observed, therefore its role on promoting the chain-transfer reaction should be attributed to the strong metal support interaction. On the other hand, it is difficult for the living chain to attach to the strongly interacted catalytic site. As a result, the active site becomes idle. In addition, it was proposed that most likely β-hydrogen elimination is more prevalent when the support surface was treated with silane.[18] However, it should be noted that the degree of chain transfer obtained from silane modification was higher compared with that from the mixed TiO_2−SiO_2 supports. Considering the MWD of copolymers, it can be seen that the narrower MWD was observed with the presence of TiO_2 in the mixed supports, indicating more single catalytic sites present on this system. However, broader MWD was observed when only the pure TiO_2 was used.

The characteristics of ^{13}C NMR spectra (not shown) for the copolymers (EO) were similar. The triad distribution obtained from ^{13}C NMR is shown in Table 3. Although ethylene incorporation in all systems gave copolymers with similar triad distribution, the incorporation of the comonomer was slightly different. It indicated that the presence of TiO_2 in the mixed support can result in less incorporation of the comonomer in the polymer chain. As seen in Table 3, the incorporation of 1-octene referred to as EOE decreased from 19% (pure SiO_2) to 11% (TiO_2/SiO_2 = 60/40). Also shown was little probability to produce the blocks of OO, which is the characteristic of this zirconocene catalyst in a homogeneous system.[13,18−20] Only random copolymers can be produced with this mixed TiO_2−SiO_2 system regardless of the amounts of TiO_2 present.

Table 4. Melting Temperatures (T_m) Obtained from DSC of EH, EO, and ED Produced via Various Mixed TiO_2–SiO_2-Supported MAO with *rac*-Et[Ind]$_2$$ZrCl_2$ Catalyst

	T_m (°C)		
TiO_2−SiO_2 wt %	EH	EO	ED
0/100	89	86	89
20/80	89	88	89
40/60	91	91	91
60/40	94	92	94
80/20	95	89	95
100/0	100	99	100

Differential scanning calorimetry (DSC) was used to determine the melting temperatures (T_m) of copolymers produced in all system. The resulted melting temperatures are shown in Table 4. It indicated that the increased T_m of copolymers was found with the presence of TiO_2 in the mixed supports. The similar trend can be also observed even with different comomers used. There was no sginificant change in morphologies of copolymers upon the presence of TiO_2 in the mixed TiO_2−SiO_2 supports.

4. Summary

The presence of TiO_2 in the mixed TiO_2−SiO_2-supported MAO with the *rac*-Et[Ind]$_2$$ZrCl_2$ catalyst can enhance the catalytic activities by 15−25% for ethylene/1-olefin polymerization. It was proposed that with the presence of TiO_2 up to 60 wt % in the mixed supports, TiO_2 acted as a spacer to anchor MAO to the silica support, resulting in less steric hindrance and less interaction on the support surface. A slight chain-transfer effect was observed with the presence of TiO_2 in the mixed TiO_2−SiO_2 supports resulting in a slight decrease in MW. However, the narrower MWD can be observed when TiO_2 was present indicating more single catalytic site. The microstructure of copolymers produced was not affected by the mixed TiO_2−SiO_2 supports indicating only random copolymers produced. The presence of TiO_2 resulted in a slight increase in melting temperature (T_m). On the basis of this present study, it can be concluded that the presence of TiO_2 in the mixed TiO_2−SiO_2 supports has somehow brought the SiO_2 support system into a more homogeneous-like system.

Acknowledgment

The authors thank the Thailand Research Fund (TRF) and Thailand−Japan Technology Transfer Project (TJTTP-JBIC) for the financial support of this work.

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Received for review July 8, 2005
Revised manuscript received August 22, 2005
Accepted September 29, 2005

IE050806D

Iranian Polymer Journal
15 (5), 2006, 431-437

Available online at: http://journal.ippi.ac.ir

Characteristics of LLDPE/ZrO_2 Nanocomposite Synthesized by In-situ Polymerization using a Zirconocene/MAO Catalyst

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Received 7 March 2006; accepted 6 May 2006

A B S T R A C T

In the present study, the linear low-density polyethylene (LLDPE)/ZrO_2 nanocomposites were synthesized via in-situ polymerization with *rac*-Et(Ind)$_2$$ZrCl_2$/MAO catalyst. First, the nano-ZrO_2 filler was impregnated with the desired amount of MAO. Then, copolymerization of ethylene/1-octene was performed in the presence of nano-ZrO_2/MAO filler to produce the LLDPE/ZrO_2 nanocomposites. The amounts of nano-ZrO_2 filler employed were varied at 0.1 and 0.3 g corresponding to $[Al]_{MAO}$/[Zr] ratios=1135 and 3405, respectively. It can be observed that the polymer yield increased with increasing the ratios of $[Al]_{MAO}$/[Zr]. However, the observed polymer yields were much lower (about 5-30 times) compared to the yield with no filler addition. The filler contents in polymer were in the range of 23-25 wt%. The characteristics of LLDPE/ZrO_2 nanocomposites obtained were determined by means of DSC, SEM/EDX, TEM, ^{13}C NMR, and XPS. It was observed that the LLDPE/ZrO_2 nanocmposites exhibited slightly lower melting temperature (T_m) and crystallization temperature (T_c). SEM Micrographs demonstrate the homogeneous matrix of the samples. In addition, with EDX mapping technique, it was also revealed that the nano-ZrO_2 filler was well distributed over the polymer matrix. Based on the TEM result, it was also revealed that the smaller and more uniform particles can be observed after polymerization. These observations suggested that the fragmentation of nano-ZrO_2 particles or segregation of the secondary particles could occur resulting in good dispersion of the particles. The distribution of comonomer was studied by ^{13}C NMR. It was shown to be random as seen in the similar catalytic system without filler addition. The binding energy (BE) for C 1s obtained from XPS to be 285.7 eV indicating no significant change in the polymer microstructure with the addition of nano-ZrO_2 filler.

Key Words:

polyolefins;
metallocene catalysts;
nanocomposites;
NMR;
TEM.

INTRODUCTION

It is known that blending the polymers with inorganic materials as fillers can be recognized as a way to produce filled polymers or polymer composites. However, upon some significant developments of nanoscience and nanotechnology in recent years, nanofillers such as silica, alumina, titania, and so on have brought much attraction to research in filled polymers. As known, polymer composites filled with nanofillers are so-called polymer nanocomposites.

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Apparently, with an introduction of nanofillers into polymers, robust materials can potentially be produced due to the synergetic effects arising from the blending process. In general, there are technically three methods used to produce a filled polymer; (i) melt mixing [1-5], (ii) solution blending [6] and (iii) in-situ polymerization [7]. Due to the direct synthesis via polymerization along with the presence of fillers, the in-situ polymerization is perhaps considered the most promising technique to produce polymer nanocomposites with homogeneous dispersion of nanofillers inside the polymer matrix. Based on the commercial interest of using metallocene catalysts for olefin polymerization, an extensive effort has been made for efficient utilization of metallocene catalysts [8-12]. With a combination of knowledge in nanotechnology, polymerization, and metallocene catalysis, a promising way to synthesize the polymer nanocomposites using a metallocene catalyst is captivating. Therefore, the main objective of this present study was to investigate, for the first time, the feasibility for making polymer nanocomposites and their characteristics via the in-situ polymerization with a metallocene catalyst.

EXPERIMENTAL

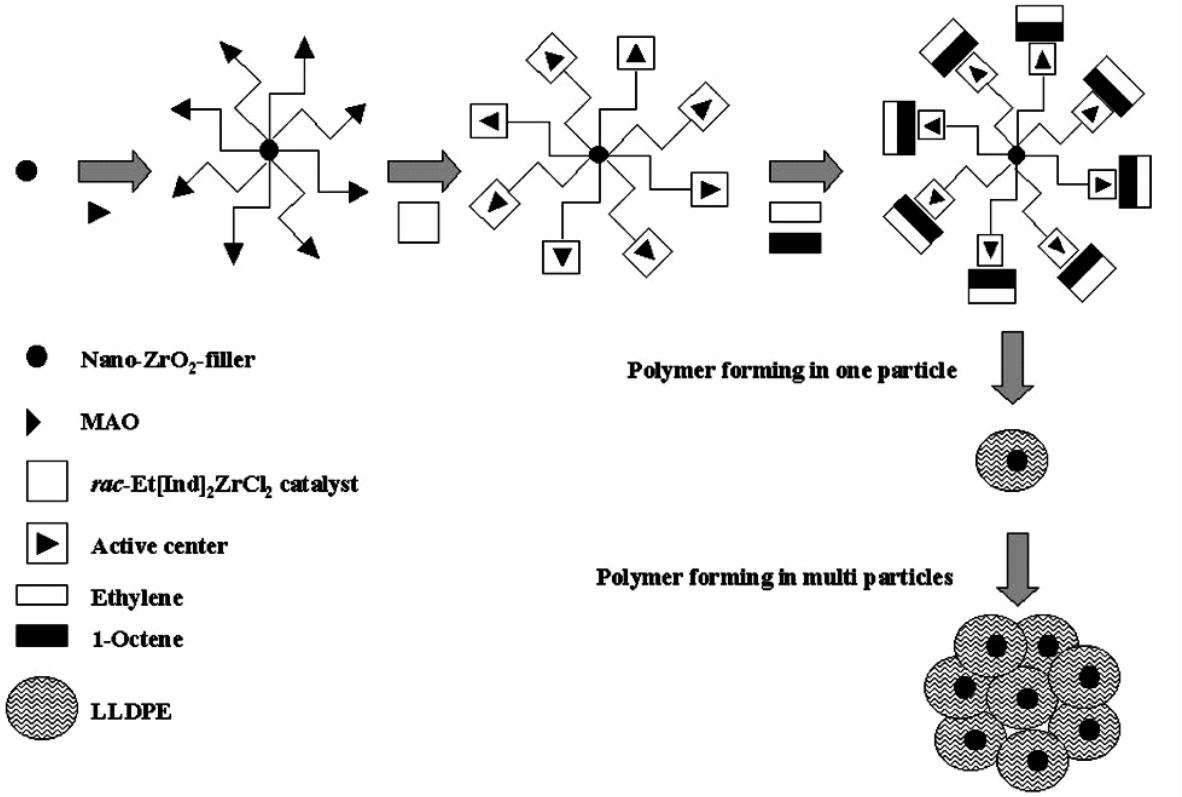
All chemicals (ethylene, toluene, *rac*-ethylenebis (indenyl) zirconium dichloride [*rac*-$Et(Ind)_2ZrCl_2$], methylaluminoxane (MAO), trimethylaluminium (TMA), 1-octene and nano-ZrO_2 filler) were manipulated under an inert atmosphere using a vacuum glove box and/or the Schlenk techniques.

The nano-ZrO_2 filler was synthesized by flame spray pyrolysis (FSP) as described by Mueller et al. [13]. The primary particle size of ZrO_2 was in the range of 6-35 nm. The crystal structure consisted of the tetragonal/monoclinic phase (95/5 by mol%). First, 1 g of the filler was reacted with a desired amount of MAO in toluene at room temperature and stirred for 30 min. The solvent was then removed from the mixture. About 20 mL of toluene was added into the obtained precipitate, the mixture was stirred for 5 min, and then the solvent was removed. This procedure was performed 5 times to ensure the removal of impurities. The white powder of nano-ZrO_2 filler-impregnated MAO was obtained. The ethylene/1-octene copolymerization reaction on the filler-impregnated MAO was carried out in a 100 mL semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 0.1 and 0.3 g of the filler ($[Al]_{MAO}/[Zr]$=1135 and 3405, respectively) and 0.018 mol of 1-octene along with toluene (to make a total volume of 30 mL) were put into the reactor. The desired amount of *rac*-$Et(Ind)_2ZrCl_2$ (5×10^{-5} M) and TMA ($[Al]_{TMA}/[Zr]$=2500) was mixed and stirred for 5 min aging at room temperature, and then it was injected into the reactor. The reactor was heated up to polymerization temperature at 70ºC. To start reaction, 0.018 mol of ethylene was fed into the reactor. After the full consumption of all ethylene, the reaction was terminated by addition of acidic methanol. After filtration, it was washed with methanol and dried at room temperature and a white powder of nano-ZrO_2-filled polymer was obtained.

The polymer sample was then characterized using the differential scanning calorimetry, DSC (NETZSCH DSC 200), scanning electron microscopy, SEM (Jeol-JSM-5800LV), energy dispersive X-ray spectroscopy, EDX (Link Isis series 300), transmission electron spectroscopy, TEM (Jeol-TEM 200CX), X-ray photoelectron spectroscopy, XPS (Shimadzu AMICUS with Vision 2 control software), and ^{13}C NMR (Jeol JMR-A500).

RESULTS AND DISCUSSION

In the present study, the nano-ZrO_2-filled linear low-density polyethylene (LLDPE) was synthesized via copolymerization of ethylene/1-octene using *rac*-$Et(Ind)_2ZrCl_2$/MAO metallocene catalyst. It is known that the copolymerization of ethylene with higher 1-olefins is of commercial importance for production of LLDPE. In this study the nano-ZrO_2 particle, synthesized by flame spray pyrolysis (FSP) [13], was used as a filler due to its narrow particle size distribution, weak agglomeration of single crystal, high thermal resistance, high mechanical resistance and high corrosive resistance. Thus, the physical properties of LLDPE can be escalated with the addition of nano-ZrO_2 filler. In order to synthesize the nano-ZrO_2-filled LLDPE, first, the filler was impregnated



Scheme I. Conceptual model for polymer forming on the nano-ZrO_2-filler via in-situ polymerization by a metallocene catalyst.

Table 1. Results of the amount of polymer obtained, filler content, yield, melting temperature (T_m) and crystallization temperature (T_c) of samples.

Nano-filler (g)	Polymer obtained[a](g)	Filler content (wt%)	Polymerization time[b] (s)	Yield[c] (kg Pol./mol Zr.h)	T_m[d] (^oC)	T_C[d] (^oC)
No filler	1.1	0	87	31.000	104	86
0.1	0.3	25	605	1.209	93	85
0.3	1.0	23	352	6.924	94	79

(a) Weight excluding the filler; (b) a period of time used for the total 0.018 mol of ethylene was totally consumed; (c) measured at polymerization temperature of 70^{o}C, [ethylene]=0.018 mol, [1-octene]=0.018 mol, $[Al]_{MAO}/[Zr]$=1135, $[Al]_{TMA}/[Zr]$=2500, in toluene with total volume=30 mL, and [Zr] of Et$[Ind]_2ZrCl_2$=5x10^{-5} M; (d) measurement error ±1^{o}C.

with MAO (as a cocatalyst). Then, the in-situ polymerization was conducted while the filler-impregnated MAO was present. It was proposed that polymer was formed at the surface of filler-impregnated MAO as shown in Scheme I suggesting that highly dispersed filler inside the polymer matrix could be achieved. The yield, filler content, melting temperature (T_m) and crystallization temperature (T_c) are shown in Table 1. It can be observed that the polymer yield increases with increasing the amount of filler from 0.1 to 0.3 g. This was due to an increase in the $[Al]_{MAO}/[Zr]$ ratio from 1135 to 3405. It should be noted that the filler contents in the obtained polymer nanocomposites were found to be within the range of

23-25 wt%. However, considering the yield without any filler added, the yield was substantially higher (~5-30 times) than that with the filler added. It was proposed that the low yield as a result of the filler addition could be due to more steric hindrance arising from the nanoparticles. Thus, in order to improve the yield, the modification of nanofiller requires further work. DSC Analysis was performed in order to determine the thermal properties of samples. The temperature range of -10 to 120ºC at the heating rate of 20ºC/min was employed. The heating cycle was twice operated. In the first scan, the sample was heated up to 120ºC, then cooled down to the ambient temperature. In the second scan, the sample was reheated at the same condition. The melting temperatures at the second scan were reported whereas the crystallization temperatures were obtained during the cooling process. Based on DSC results, it is shown that DSC patterns for all samples were similar. The T_m and T_c of samples obtained are also shown in Table 1. The results indicate that the nano-ZrO_2-filled LLDPE exhibits slightly lower T_m and T_c than those of pure LLDPE. It was suggested that addition of nano-ZrO_2 filler rendered lower crystallinity in the LLDPE/ZrO_2 nanocomposites.

In order to identify the morphologies of samples, SEM was performed. It can be observed that the polymer formed has covered the filler as noticed by SEM (Figure 1). As shown in Figure 1a, prior to polymerization, the nano-ZrO_2 filler appeared in white powder as flat sheets of secondary particles. However, after polymerization, the nano-ZrO_2-filled LLDPE was obtained as shown in Figure 1b indicating a homogeneous matrix of filled polymer (not PE particles). In order to determine the location of ZrO_2 in the polymer matrix, EDX mapping technique was also performed (not shown due to low resolution). However, it was suggested that the filler apparently exhibited good distributions inside the polymer matrix. As mentioned, an image from the high-resolution transmission electron microscopy (TEM) is an essential component of nanoscience and nanotechnology. Therefore, TEM was performed in order to determine how the nanofiller behaved before and after the in-situ polymerization. TEM Images of the nano-ZrO_2 filler before and after polymerization are shown in Figures 2a and 2b, respectively. As seen in Figure 2a,

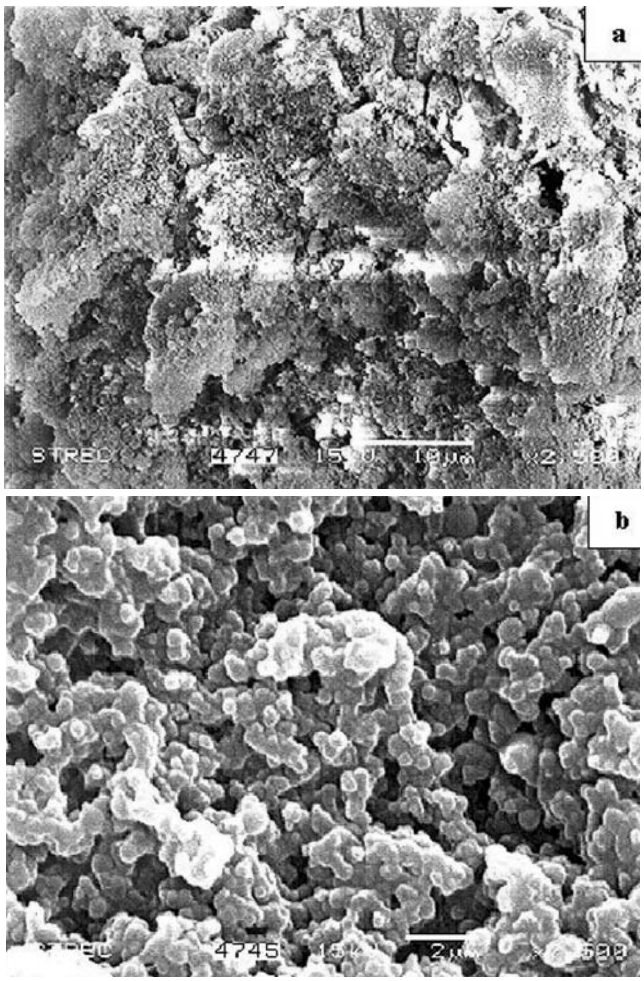


Figure 1. SEM Micrographs of (a) nano-ZrO_2 filler at x 2,500 magnification and (b) nano-ZrO_2-filled LLDPE composite at x 2,500 magnification.

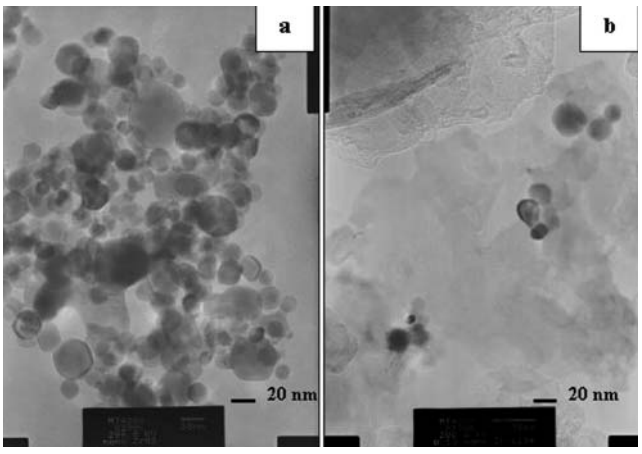


Figure 2. TEM Images of (a) nano-ZrO_2 filler at 200,000 magnification and (b) nano-ZrO_2-filled LLDPE composite (0.1 g of filler) at 150,000 magnification.

prior to polymerization, the nano-ZrO_2 filler appeared in a bunch of spherical-like particles indicating the agglomeration of primary particles. The primary particle size of nano-ZrO_2 filler was in the range of ca. 6-35 nm. However, after polymerization was done on the filler, it can be observed from Figure 2b that the nano-ZrO_2 filler was well dispersed inside the polymer matrix. Apparently, the smaller and more uniform particles were noticed after polymerization. It was suggested that the fragmentation of nanofiller probably occurred as also reported by Fink et al. [14-17]. They found that the fragmentation of a particle such as microsilica, used as a metallocene catalyst support or a carrier, occurred essentially under some specific conditions. In particular, the hydraulic forces of the growing polymer, which may be observed in the case of nano-ZrO_2 filler, induced such a fragmentation of filler as well. However, the segregation of secondary particles from the primary particles was also the case for the nanofiller.

Among various important aspects for making a polymer nanocomposite, one should also mention how the microstructure of polymer is altered with the addition of nanofiller. Technically, the filler added should not affect the polymer microstructure, but only change the physical properties based on macroscopic points of view. It is known that ^{13}C NMR is one of the most powerful techniques used to identify the microstructure of polymer, especially, polyolefins. ^{13}C NMR Spectra obtained from the nano-ZrO_2-filled LLDPE samples (0.1 and 0.3 g of filler) are shown in Figure 3a,b, respectively. ^{13}C NMR Spectra were assigned to the typical LLDPE obtained from the copolymerization of ethylene/1-octene. Based on calculation described by Galland et al. [18], the distribution of comonomer was considered random and similar to what we found in our previous work without any filler added [10]. Since XPS is one of the most powerful surface analysis techniques, so it is also interesting to use the XPS to identify the microstructure of the polymer nanocomposites. A plot of the binding energy (BE) for C 1s obtained from XPS for both nano-ZrO_2-filled LLDPE samples with 0.1 and 0.3 g of filler are shown in Figure 4a,b, respectively. The binding energy for both samples was found to be 285.7 eV. It is suggested that the microstructure has not changed upon the presence of nanofiller. Besides

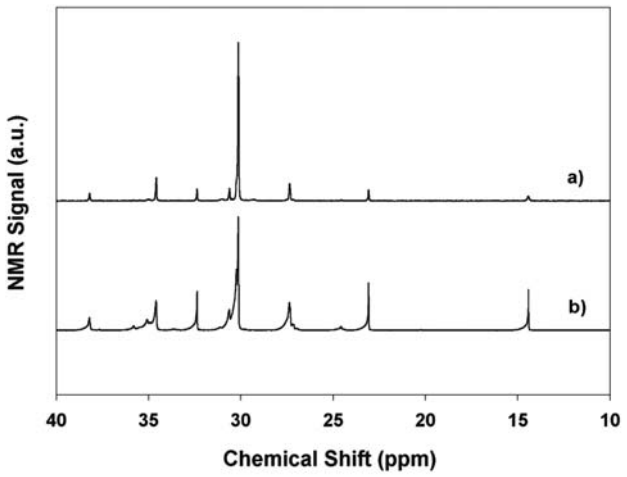


Figure 3. Typical ^{13}C NMR spectra of ethylene/1-octene copolymer obtained with the nano-ZrO_2-filled LLDPE samples: (a) 0.1 g of filler and (b) 0.3 g of filler.

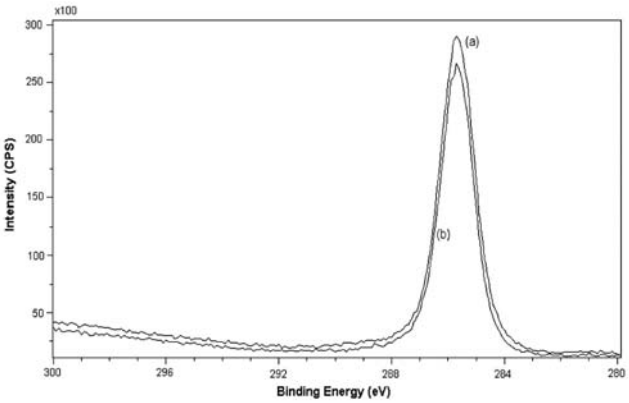


Figure 4. A plot of binding energy for C 1s obtained by XPS of the nano-ZrO_2-filled LLDPE samples: (a) 0.1 g of filler and (b) 0.3 g of filler.

the binding energy for C 1s, the amounts of Zr atomic concentration at surface (the depth for XPS analysis is ca. 5 nm) was also determined by XPS and only 0.02% of Zr was found at the surface for both samples. This could be an indication that the ZrO_2 filler deeply penetrated into the polymer matrix resulting in the highly dispersed nanofiller as examined by TEM. Therefore, based on the ^{13}C NMR and XPS data, it can be concluded that the addition of nano-ZrO_2-filler has not changed the microstructure of LLDPE significantly.

CONCLUSION

In summary, the nano-ZrO_2-filled LLDPE can be synthesized via the in-situ polymerization using *rac*-Et[Ind]$_2$$ZrCl_2$/MAO catalyst. In particular, the nano-ZrO_2 filler exhibited good distribution and dispersion inside the polymer matrix as observed by TEM. No significant change in the microstructure of polymer was observed by means of XPS and ^{13}C NMR. However, the melting temperature (T_m) and crystallization temperature (T_c) were found to decrease slightly with the addition of nano-ZrO_2 filler due to decreased crystallinity. Besides the characteristics of LLDPE nanocomposite produced, it should be mentioned that a decreased yield was more pronounced when the nanofiller was added compared to when nanofiller was absent. Therefore, in order to elevate the polymer yield, some developments of process and modification of the nanofiller need to be further investigated. In addition, a rheological characterization would be very useful for explaining the very large reduction in productivity in the future research consideration.

ACKNOWLEDGEMENT

We thank the Thailand Research Fund (TRF), the National Science and Technology Development Agency (NSTDA) and Thailand-Japan Technology Transfer Project (TJTTP-OECF) for the financial supports of this project. We also thank Dr. Okorn Mekasuwandumrong for providing the nano-ZrO_2 filler used in this study.

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