



CHAPTER IV

RESULTS AND DISCUSSIONS

In this present study, results and discussion were divided into three parts. In the first portion, the study of the activities and characteristics of LLDPE/nanocomposite with using various ratios of $[Al]_{d-MMAO}/[Zr]$. The second portion was based on the study of first portion, but ratios of $[Al]_{d-MMAO}/[Zr]$ was fixed at 1135 with various amount of nano- Al_2O_3 . Thus, the amount of filler effect was then reported. The third portion, the study of the activities and characteristics of LLDPE/nanocomposites with using various types of nano-inorganic materials when the ratio of $[Al]_{d-MMAO}/[Zr]$ was fixed at 3405 was also reported in this study.

4.1 Nanopowder alumina as a filler of LLDPE- Al_2O_3 nanocomposite synthesized via *in situ* polymerization with various $[Al]_{d-MMAO}/[Zr]_{cat}$ ratios.

4.1.1 Characterization of fillers and catalyst precursors with X-ray diffraction (XRD).

The XRD patterns of the Al_2O_3 nanofiller before and after impregnation with d-MMAO are shown in Figure 4.1 indicating the similar patterns. It can be observed the XRD peaks at 33.2, 37.3, 39.5, 41.4, 43.3, 45.8, 60.1 and 67.4°, assigned to alumina in the gamma (γ) form. However, after impregnation with d-MMAO, the similar XRD patterns were still observed. This was suggested that the d-MMAO present on the Al_2O_3 nanofiller was in the well dispersed form.

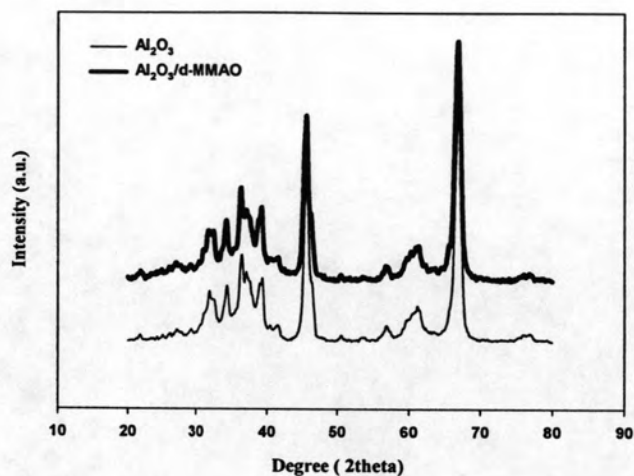


Figure 4.1 XRD patterns of the Al_2O_3 nanofiller before and after impregnation with d-MMAO

4.1.2 Characterization of fillers and catalyst precursors with Transmission electron microscope (TEM)

In addition, the TEM micrographs of the Al_2O_3 nanofiller before and after impregnation with d-MMAO were also illustrated in Figure 4.2a and 4.2b, respectively. It revealed that the Al_2O_3 particles exhibited agglomeration and being present as a group of the secondary particles. There was also no significant change upon the particle morphology after impregnation with d-MMAO. Apparently, the crystallite size of the primary particle by means of TEM measurement was below 100 nm as seen from Figure 4.2.

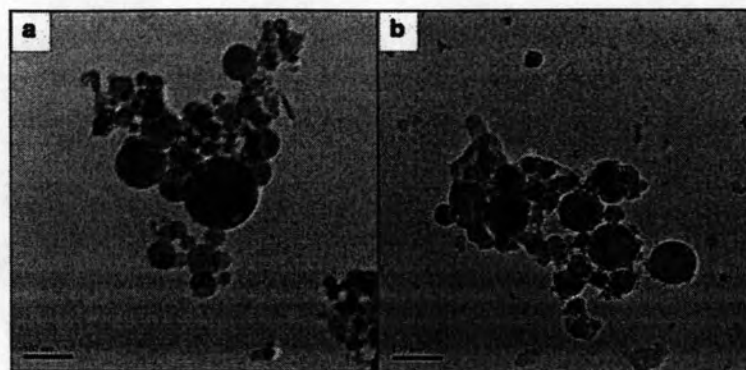


Figure 4.2 TEM micrographs of the Al_2O_3 nanofiller a) before and b) after impregnation with d-MMAO.

4.1.3 Effect of nano-Alumina with various $[\text{Al}]_{\text{d-MMAO}}/[\text{Zr}]_{\text{cat}}$ ratios on activity and characteristics of LLDPE.

Table 4.1 Activity of LLDPE- Al_2O_3 nanocomposites

nano-Alumina filler (g)	$[\text{Al}]_{\text{d-MMAO}}/[\text{Zr}]_{\text{cat}}$	time ^a (s)	Polymer yield ^b (g)	% Al_2O_3 content	Catalytic activity ^c	1-Hexene insertion ^d (%)
No filler	1135	208	0.61	0	14188	43.2
0.1	1135	315	0.50	9.1	7631	19.5
0.2	2270	302	0.52	16.1	8296	23.6
0.3	3405	288	0.59	20.1	9959	35.6

^a A period of time used for the total 0.018 mol of ethylene was consumed.

^b Measured at polymerization temperature of 70 °C, $[\text{Ethylene}] = 0.018$ mol, $[\text{Al}]_{\text{TMA}}/[\text{Zr}]_{\text{cat}} = 2500$, in toluene with total volume = 30 ml, and $[\text{Zr}]_{\text{cat}} = 5 \times 10^{-5}$ M.

^c Activities (kg of polymer/ mol of Zr.h)

^d 1-hexene insertion or incorporation was calculated based on ^{13}C NMR

In order to produce the LLDPE/Al₂O₃ nanocomposites, copolymerization of ethylene/1-hexene was performed with the presence of d-MMAO/Al₂O₃ using the zirconocene catalyst. In fact, the amounts of d-MMAO/Al₂O₃ were ranged from 0.1, 0.2 and 0.3 g corresponding to the [Al]_{d-MMAO}/[Zr]_{cat} ratios of 1135, 2270, and 3405, respectively. For a comparative study, copolymerization of ethylene/1-hexene with the absence of d-MMAO/Al₂O₃ (homogeneous catalytic system) was also conducted. The catalytic activities for each run are listed in Table 4.1. It can be observed that upon the presence of the Al₂O₃ nanofiller, the activities increased with increasing the [Al]_{d-MMAO}/[Zr]_{cat} ratios. This indicated that the greater amounts of d-MMAO resulted in more active species being present during polymerization. It was proposed that d-MMAO possibly had many functions, such as an alkylating agent, a stabilizer for a cationic metallocene alkyl and/or counterion, an ionizing and/or reducing agent for the transition element, and a scavenger for the metallocene catalytic system. However, one of the most important roles of this alkylaluminumoxane is apparently to prevent the formation of ZrCH₂CH₂Zr species, which is formed via a bimolecular process [70]. Considering copolymerization of ethylene/1-hexene in the absence of d-MMAO/Al₂O₃, it was found that the obtained activity was much higher compared with when the d-MMAO/Al₂O₃ was added. This was due to more steric hindrance and strong interaction between d-MMAO and the Al₂O₃ nanofiller resulting in much lower activity when d-MMAO/Al₂O₃ was employed. The Al₂O₃ nanofiller contents were in the range of 9-20 wt% corresponding to the amounts of it added.

Table 4.2 Characteristics of LLDPE nanocomposites

nano-filler (g)	% crystallinity	DSC		GPC analysis		
		T _m (°C)	T _c (°C)	M _w	M _n	MWD
No filler	5.26	67.5	61.5	12,500	6,200	2.0
0.1	23.50	100.0	87.9	25,400	11,700	2.2
0.2	21.22	90.6	79.0	25,400	11,100	2.3
0.3	10.80	87.9	74.0	27,700	12,500	2.2

The DSC was used to measure the melting (T_m) and crystallization temperature (T_c). The DSC results are shown in Table 4.2. It can be observed that with the addition of Al_2O_3 nanofiller, both T_m and T_c increased substantially. This was suggested that the crystallinity of LLDPE could be enhanced by the addition of the Al_2O_3 nanofiller. However, increased the amounts of the Al_2O_3 nanofiller added apparently resulted in decreased T_m and T_c indicating less crystallinity of LLDPE with larger amounts of the filler. It is known that decreased crystallinity of LLDPE can be attributed to the higher degree of 1-olefin insertion. This was suggested that the addition of the Al_2O_3 nanofiller presumably inhibited the insertion of 1-hexene into the polymer backbone leading to the increased crystallinity of LLDPE/ Al_2O_3 nanocomposite. It should be addressed that the larger amounts of the Al_2O_3 nanofiller added could result in lesser degree of crystallinity. It was reported that the particles in polymer matrix can act as nucleating agents. Consequently, they increase the crystallinity of polymer. However, when the large amounts of particle are employed, they may locate themselves in the interlamellar spaces, which leave a little room for additional crystallization. So, the presence of large amounts of these particles may even inhibit crystallization as seen in Table 4.2.

The GPC was performed in order to determine the M_w , M_n and MWD of LLDPE/ Al_2O_3 nanocomposite. The GPC results are also shown in Table 4.2. It indicated that all samples exhibited only the unimodal molecular weight distribution. Obviously, the addition of the Al_2O_3 nanofiller trended to increase the M_w and M_n of the LLDPE/ Al_2O_3 nanocomposite about 2 times without a significant change in MWD. In particular, increase in M_w and M_n can be attributed to the inhibition of chain transfer reaction with the presence of the Al_2O_3 nanofiller. In addition, the narrow MWD was also observed for both in the absence and presence of the Al_2O_3 nanofiller indicating the conventional single catalytic site present.

4.1.4 Characterization of LLDPE-nanocomposites with nuclear magnetic resonance (NMR)

Among a bunch of important aspects of making a polymer composite, one should mention how the filler affects the molecular structure of polymer produced. Then, ^{13}C NMR is one of the most powerful techniques to identify the polymer microstructure,

especially polyolefins. The resulted ^{13}C NMR spectra (shown in appendix B) for all samples were assigned typically to the LLDPE obtained from copolymerization of ethylene/1-hexene. The triad distribution was identified based on the method described by Randall [73]. It can be observed that the LLDPE $-\text{Al}_2\text{O}_3$ exhibited similar ^{13}C NMR patterns indicating similar molecular structure of polymer. Based on calculations described by Galland et al. [74], the triad distribution of monomer is listed in Table 4.3. It indicated that all LLDPE samples were random copolymer with the difference in 1-hexene insertion.

This result was also similar with what we found in previous works without the addition of nano- Al_2O_3 [75-78]. According to the triad distribution shown in Table 4.3, the 1-hexene insertion can be calculated based on ref. [74]. The 1-hexene insertion in LLDPE/nano- Al_2O_3 is shown in Table 4.2. It can be observed that 1-Hexene insertion (%) were increasing with increased $[\text{Al}]_{\text{d-MMAO}}/[\text{Zr}]_{\text{cat}}$ due to less steric hindrance as also described by Figure 4.3. Hence, the large molecule of 1-hexene can insert more. The melting temperature (T_m) as also shown in Table 4.2 trended to decrease with more insertion of 1-hexene due to decreased crytallinity.

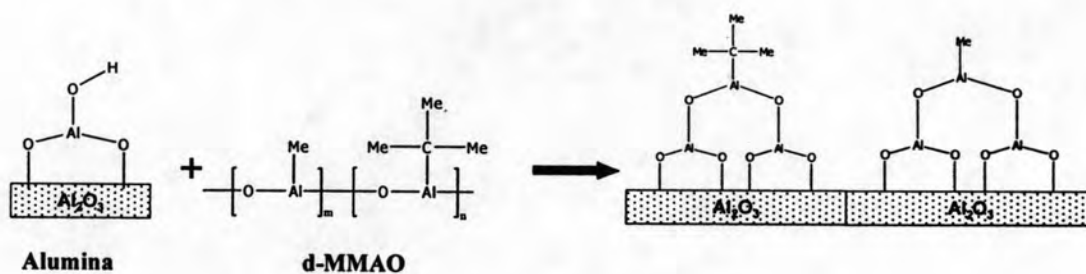


Figure 4.3 Conceptual model for immobilization of d-MMAO on Al_2O_3 nanofiller

Table 4.3 Triad distribution obtained from ^{13}C NMR of LLDPE- Al_2O_3 nanocomposites.

Filler	Weight (g)	EEE	EEH + HEE	HEH	EHE	EHH + HHE	HHH
Homogeneous	-	0.364	0.118	0.086	0.064	0.368	0.000
Nano- Al_2O_3	0.1	0.685	0.081	0.039	0.039	0.156	0.000
	0.2	0.639	0.085	0.040	0.044	0.192	0.000
	0.3	0.462	0.112	0.070	0.059	0.298	0.000

4.1.5 The effect of nano-alumina on the morphologies of LLDPE-nanocomposites.

In order to study the morphology of the LLDPE/ Al_2O_3 nanocomposite, SEM was performed. The SEM micrographs are shown in Figure 4.4. It can be observed that there was no significant change upon increased amounts of the Al_2O_3 nanofiller added.

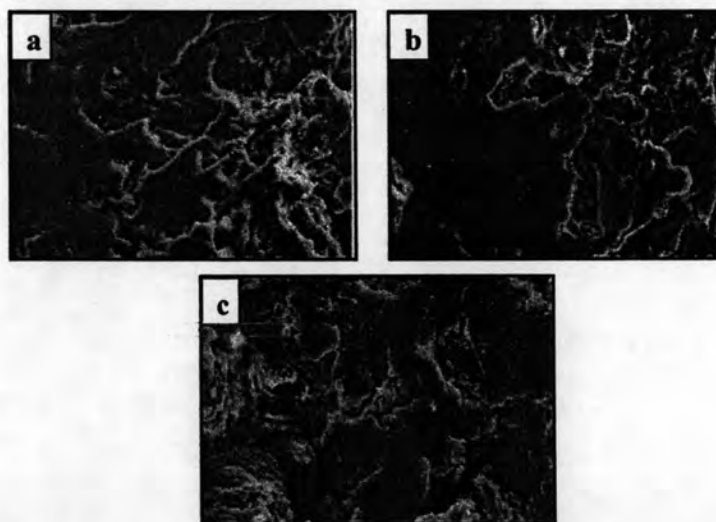


Figure 4.4 Morphologies of (a) nano- Al_2O_3 -filled LLDPE composite (0.1 g of filler), (b) nano- Al_2O_3 -filled LLDPE composite (0.2 g of filler) and (c) nano- Al_2O_3 -filled LLDPE composite (0.3 g of filler)

4.1.6 The distribution of nano- Al_2O_3 in LLDPE-nanocomposites.

The SEM micrographs and EDX mapping for O and Al are shown in Figure 4.5. It can be observed that there was no significant change upon increased amounts of the Al_2O_3 nanofiller added. Besides, based on the EDX mapping, the Al_2O_3 nanofiller represented as the white spots was well distributed over the polymer matrix corresponding to its content.

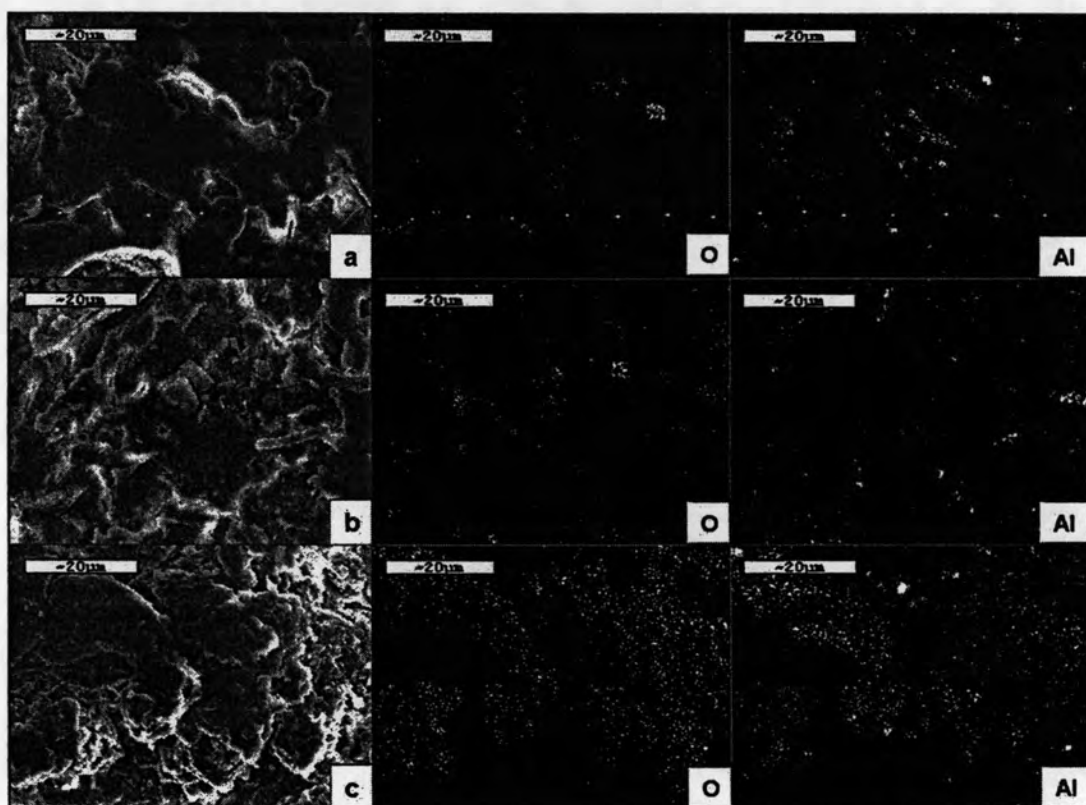


Figure 4.5 SEM micrographs and EDX mapping of (a) nano- Al_2O_3 -filled LLDPE composite (0.1 g of filler), (b) nano- Al_2O_3 -filled LLDPE composite (0.2 g of filler) and (c) nano- Al_2O_3 -filled LLDPE composite (0.3 g of filler)

4.1.7 Characterization of LLDPE-nanocomposites with transmission electron microscope (TEM)

As known, the images from high-resolution transmission electron microscopy (TEM) are an essential component of nanoscience and nanotechnology, therefore, TEM was performed in order to determine the dispersion of the Al_2O_3 nanofiller. The TEM micrographs for the Al_2O_3 nanofiller and the LLDPE/ Al_2O_3 nanocomposites having different amounts of the Al_2O_3 nanofiller are shown in Figure 4.6a, 4.6b, 4.6c and 4.6d, respectively. As seen from all images, the Al_2O_3 nanofillers appeared as a group of spherical-like particles indicating the agglomeration of the primary particles. Thus, it indicated that the Al_2O_3 nanofiller was well distributed inside the polymer matrix (based on EDX), but somehow was poorly dispersed (based on TEM) due to the agglomeration.

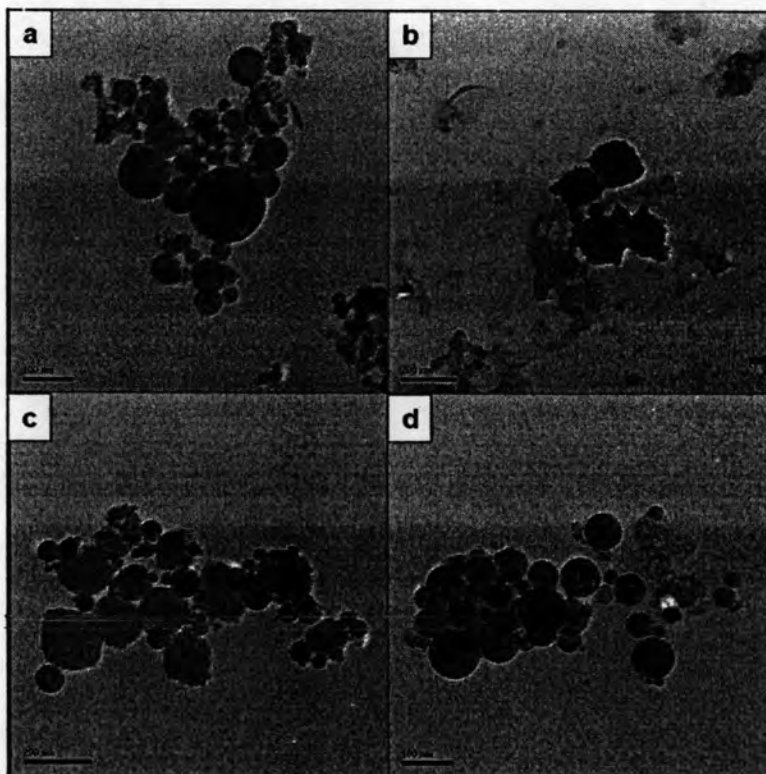


Figure 4.6 TEM micrographs of (a) nano- Al_2O_3 filler (b) nano- Al_2O_3 -filled LLDPE composite (0.1 g of filler), (c) nano- Al_2O_3 -filled LLDPE composite (0.2 g of filler) and (d) nano- Al_2O_3 -filled LLDPE composite (0.3 g of filler)

4.2 Effect of the amount of nano-Al₂O₃ on properties of LLDPE.

In the first part, the ratios of $[Al]_{d-MMAO}/[Zr]$ were varied with the amounts of nano-Al₂O₃ used. This was because the amounts of d-MMAO being present in 1 g of nano-Al₂O₃ were the same during d-MMAO impregnation. Hence, larger amounts of nano-Al₂O₃ meant higher ratios of $[Al]_{MAO}/[Zr]$. In this part, the ratio of $[Al]_{MAO}/[Zr]$ was kept constantly at 1135 by changing the catalyst concentrations, $[Zr]$. Thus, the amounts of nano-Al₂O₃ can be varied without changing the $[Al]_{d-MMAO}/[Zr]$ ratio.

4.2.1 Effect of the amount of nano-Al₂O₃ on activity and characteristics of LLDPE-Al₂O₃ nanocomposites.

Using the similar ways as mentioned in 3.1, activities and characteristics of LLDPE/nano-Al₂O₃ composite were obtained as shown in Table 4.4.

Table 4.4 Activity and characteristics of LLDPE-Al₂O₃ nanocomposites at $[Al]_{d-MMAO}/[Zr] = 1135$

nano-filler (g)	time ^a (s)	Polymer yield ^b (g)	% Al ₂ O ₃ content	Catalytic activity (kg polymer/ mol Zr.h)	% 1-Hexene insertion ^c
0.1	315	0.50	9.1	7631	19.5
0.2	252	0.66	14.4	6284	23.0
0.3	190	0.54	25.7	4546	26.0

^a A period of time used for the total 0.018 mol of ethylene was consumed.

^b Measured at polymerization temperature of 343 K, $[Ethylene] = 0.018$ mol, $[Al]_{TMA}/[Zr]_{cat} = 2500$, in toluene with total volume = 30 ml, and $[Zr]_{cat} = 5 \times 10^{-5}$ M.

^c 1-hexene insertion or incorporation was calculated based on ¹³C NMR

It was found that at the specified condition the activity went to a maximum with the certain amount of nano-Al₂O₃ (0.1 g), then went down with increased amount of nano-Al₂O₃ (0.3 g). Decreased activity with increasing the amount of nano-Al₂O₃

can be attributed to decreased distribution of d-MMAO. Consequently, this also resulted in increased 1-hexene insertion as also shown in Table 4.4. However, increased amounts of nano- Al_2O_3 more resulted in decreased activity. This was probably due to stronger interaction between particles.

The DSC was used to measure the melting (T_m) and crystallization temperature (T_c). The DSC results are shown in Table 4.5. It can be observed that with the addition of Al_2O_3 nanofiller, T_m increased substantially. This was suggested that the crystallinity of LLDPE could be enhanced by the addition of the Al_2O_3 nanofiller. However, increased the amounts of the Al_2O_3 nanofiller added apparently resulted in decreased T_m indicating less crystallinity of LLDPE with larger amounts of the filler.

The GPC results are also shown in Table 4.5. It indicated that the molecular weight of polymer decreased with increasing the amounts of fillers. This was due to increased rate of chain transfer reaction arising from the fillers. In addition, the broader MWD obtained by increased amounts of fillers suggested the deviation from single site nature.

Table 4.5 Characteristics of LLDPE nanocomposites at $[\text{Al}]_{\text{d-MMAO}}/[\text{Zr}] = 1135$

nano-filler (g)	% crystallinity	DSC		GPC analysis		
		T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	M_w	M_n	MWD
0.1	23.50	100.0	87.9	25,400	11,700	2.2
0.2	19.92	98.71	90.88	8900	2700	3.3
0.3	19.93	92.89	85.86	6800	2000	3.4

4.2.2 Characterization of LLDPE-nanocomposites (fixed ratio of $[\text{Al}]_{\text{d-MMAO}}/[\text{Zr}] = 1135$) with Nuclear Magnetic Resonance (NMR)

The triad distribution of monomer is listed in Table 4.5. It indicated that all LLDPE samples were random copolymer with the difference in 1-hexene insertion.

Table 4.6 Triad distribution obtained from ^{13}C NMR of LLDPE- Al_2O_3 nanocomposites.

Filler	Weight (g)	EEE	EEH + HEE	HEH	EHE	EHH + HHE	HHH
Nano- Al_2O_3	0.1	0.685	0.081	0.039	0.039	0.156	0.000
	0.2	0.652	0.077	0.040	0.038	0.192	0.000
	0.3	0.586	0.099	0.055	0.048	0.202	0.009

4.2.3 The effect of nano-Alumina on the morphologies of LLDPE-nanocomposites (fixed ratio of $[\text{Al}]_{\text{d-MMAO}}/[\text{Zr}] = 1135$)

In order to study the morphology of the LLDPE/ Al_2O_3 nanocomposite, SEM was performed. The SEM micrographs are shown in Figure 4.6. It can be observed that there was no significant change upon increased amounts of the Al_2O_3 nanofiller added

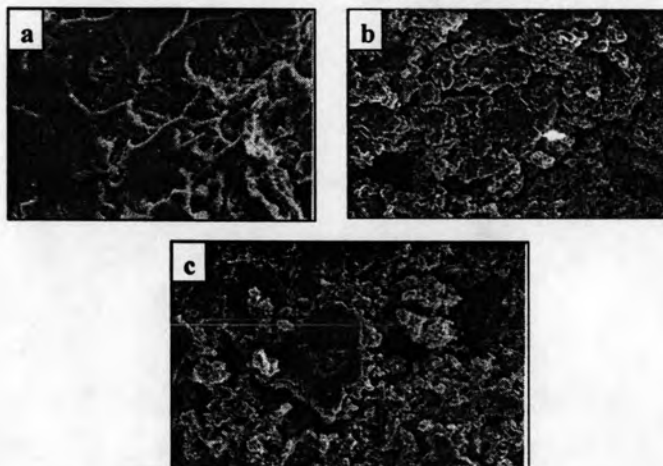


Figure 4.7 Morphologies of (a) nano- Al_2O_3 -filled LLDPE composite (0.1 g of filler), (b) nano- Al_2O_3 -filled LLDPE composite (0.2 g of filler) and (c) nano- Al_2O_3 -filled LLDPE composite (0.3 g of filler) (fixed ratio of $[\text{Al}]_{\text{d-MMAO}}/[\text{Zr}] = 1135$)

4.3 LLDPE/nanocomposites with various types of nano inorganic materials

This section, the study of the activities and characteristics of LLDPE/nanocomposites with using various types of nano inorganic materials when the ratio of $[Al]_{d-MMAO}/[Zr]$ was fixed at 3405 was also reported in this study.

4.3.1 Effect of types of nano inorganic materials on activity and characteristics of LLDPE nanocomposites. (fixed ratio of $[Al]_{d-MMAO}/[Zr] = 3405$)

In order to produce the LLDPE/ nanocomposites, copolymerization of ethylene/1-hexene was performed with the presence of d-MMAO/ nano-inorganic materials using the zirconocene catalyst. In fact, the amount of d-MMAO/ nano-inorganic materials was fixed at 0.3 g corresponding to the $[Al]_{d-MMAO}/[Zr]_{cat}$ ratio of 3405. For a comparative study, copolymerization of ethylene/1-hexene with the various types of filler was also conducted. The catalytic activities for each run are listed in Table 4.7. It can be observed that upon the types of the nanofillers employed, the activities with using nano- Al_2O_3 as filler exhibited the highest activity and decreased in the following order of $SiO_2 > TiO_2 > ZnO$. This indicated that the nano- Al_2O_3 was good to use as fillers based on activity. However, its activity was still lower than the homogeneous system.

The DSC results are shown in Table 4.8. It can be observed that with the addition of Al_2O_3 nanofiller, the polymer showed lower T_m and T_c than that of SiO_2 nanofiller, but somehow higher than those of TiO_2 and ZnO . This was suggested that the crystallinity of LLDPE could be enhanced by the addition of the Al_2O_3 nanofiller. It is known that decreased T_m and T_c of LLDPE can be attributed to the higher degree of 1-olefin insertion. This was suggested that the addition of the Al_2O_3 nanofiller presumably inhibited the insertion of 1-hexene into the polymer backbone leading to the increased crystallinity of LLDPE/ Al_2O_3 nanocomposite. It should be addressed that the larger amounts of the Al_2O_3 nanofiller added could result in lesser degree of crystallinity. It was reported that the particles in polymer matrix can act as nucleating agents. Consequently, they increase the crystallinity of polymer. However, when the large amounts of particle are employed, they may locate themselves in the terlamellar

spaces, which leave a little room for additional crystallization. So, the presence of large amounts of these particles may even inhibit crystallization.

Table 4.7 Activity and characteristics of LLDPE-nanocomposites at $[Al]_{d-MMAO}/[Zr] = 3405$

Type of fillers	time ^a (s)	Polymer yield ^b (g)	Catalytic activity (kg polymer/ mol Zr.h)	1-Hexene insertion ^c (%)
Al ₂ O ₃	288	0.60	9959	35.6
SiO ₂	311	0.53	8178	27.7
ZnO	376	0.54	6891	47.3
TiO ₂	348	0.59	8135	42.3

^a A period of time used for the total 0.018 mol of ethylene was consumed.

^b Measured at polymerization temperature of 343 K, [Ethylene] = 0.018 mol, $[Al]_{TMA}/[Zr]_{cat} = 2500$, in toluene with total volume = 30 ml, and $[Zr]_{cat} = 5 \times 10^{-5}$ M.

^c 1-hexene insertion or incorporation was calculated based on ¹³C NMR.

Table 4.8 Characteristics of LLDPE-nanocomposites at $[Al]_{d-MMAO}/[Zr] = 3405$

Type of fillers	T_m ($^{\circ}C$)	T_c ($^{\circ}C$)	% crystallinity
Al_2O_3	87.9	74.0	10.80
SiO_2	91.36	80.57	12.59
ZnO	46.24	40.02	0.41
TiO_2	66.92	49.74	1.75

4.3.2 Characterization of LLDPE-nanocomposites using various types of nano inorganic materials with Nuclear Magnetic Resonance (NMR)

The triad distribution of monomer is listed in Table 4.9. It indicated that all LLDPE samples were random copolymer with the difference in 1-hexene insertion.

Table 4.9 Triad distribution^a obtained from ^{13}C NMR of LLDPE-nanocomposites

Filler	Weight (g)	EEE	EEH + HEE	HEH	EHE	EHH + HHE	HHH
Al_2O_3	0.3	0.462	0.112	0.070	0.059	0.298	0.000
SiO_2	0.3	0.563	0.107	0.053	0.045	0.232	0.000
ZnO	0.3	0.281	0.126	0.119	0.073	0.251	0.149
TiO_2	0.3	0.332	0.137	0.108	0.078	0.211	0.134

4.3.3 The effect of types of nano-material on the morphologies of LLDPE-nanocomposites

From the SEM results, it can be seen that the texture of LLDPE with TiO_2 and ZnO was apparently homogeneous whereas one obtained from Al_2O_3 and SiO_2 was not. This was suggested that TiO_2 and ZnO essentially mix well with the LLDPE.

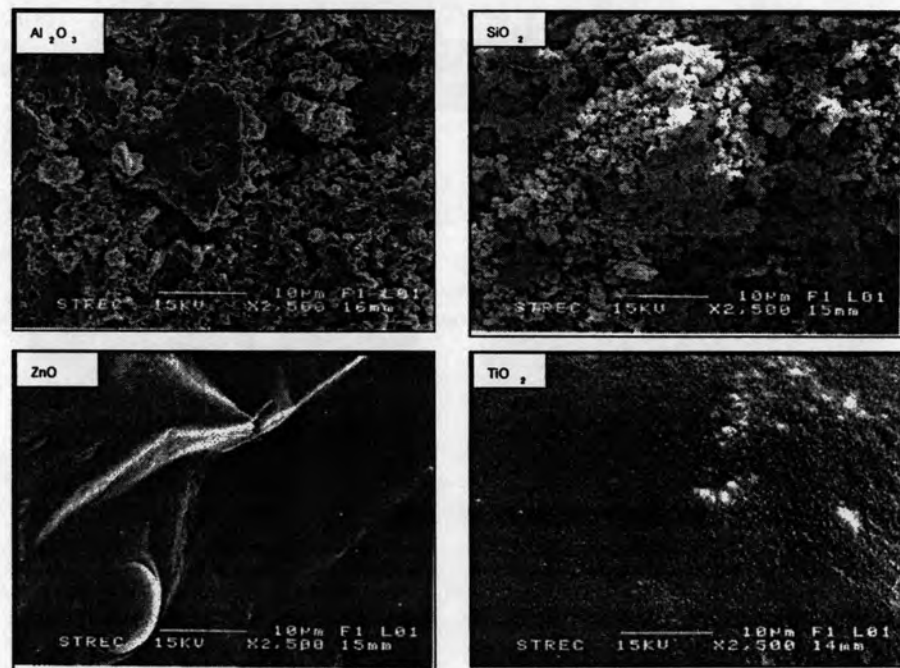


Figure 4.8 Morphologies of LLDPE/nano composites with various type of fillers.

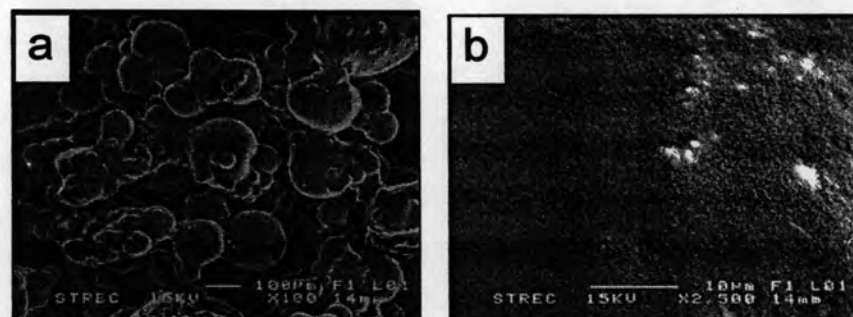


Figure 4.9 Morphologies of LLDPE/ nanocomposites with 0.3 g of nano-Titania

a) $\times 100$ b) $\times 2500$

