# CHARPTER IV
RESULT AND DISCUSSION

All the experimental results are briefly concluded first, followed by the detailed results and discussion. In the preparation procedure, magnesium ethyl carbonate was prepared from the reaction of magnesium ethoxide with carbon dioxide in ethanol (see equation 4.1). The experimental result shows that ethanol effected on solubility of magnesium ethyl carbonate. Next, the magnesium ethyl carbonate was precipitated from the solution to active $MgCl_2$ by adding chlorinating agent which is selected from $TiCl_4$, $AlEt_2Cl$ or $Al_2Et_3Cl_3$. In this step, particle size of supported catalyst could be controlled by adjusting agitation speed.

$$Mg(OEt)_2 + nCO_2 \xrightarrow{ethanol/toluene} Mg(OEt)_{2-n}(OCOOEt)_n \quad n = 1,2 \qquad eq. 4.1$$
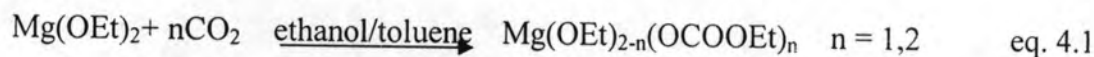
Finally, Ziegler-Natta catalysts were prepared by reacting the active magnesium ethyl carbonate synthesized from eq.4.1 with $TiCl_4$ under different reaction conditions. Each of catalytic systems so obtained was tested in ethylene polymerization.

The parameters influencing the synthesis of the catalyst were investigated and the results are described as follows:

4.1. Effect of EtOH:Mg(OEt)₂ molar ratio

Ethanol was used in this work because it can dissolve magnesium ethyl carbonate. The effect of $EtOH:Mg(OEt)_2$ molar ratio on properties of magnesium ethyl carbonate was studied and the result is demonstrated in Table 4.1.

Table 4.1. Effect of EtOH:Mg(OEt)$_2$ molar ratio on appearance of magnesium ethyl carbonate

EtOH:Mg(OEt)$_2$ Molar ratio	Appearance
1	coarse particle
2	viscous soluble and a coarse particle
3	clear solution
4	clear solution

When EtOH:Mg(OEt)$_2$ molar ratio was lower than 2, coarse particles were formed. When EtOH:Mg(OEt)$_2$ molar ratio was 3 and higher, a clear solution was observed. In order to use a minimum amount of EtOH, thus EtOH:Mg(OEt)$_2$ ratio = 3 was chosen for further experiments. EtOH was chosen as a solvent in this work because it prevents undesirable transesterification reaction due to its ethoxide group which is as same as the ethoxide group of magnesium compound. In the literature, various patents have reported methods for preparing magnesium ethyl carbonate [18, 20, 26]. Several types of medium were selected from polar solvents such as alcohol, tetrahydrofuran, and xylene. In some work, large excess of EtOH was used which causes difficulty in removing EtOH [10, 18]. In our work, time for removing ethanol was short.

In this work, it should be mentioned that toluene was introduced to the reaction as a dispersing agent.

The obtained magnesium ethyl carbonate solid after removing ethanol was analyzed by FT-IR (Fig. 4.1). Strong bands belonging to carbonyl (C=O) and C-O peak of ester group were observed at 1646 and 1326 cm^{-1}. Band of ethoxy group of -OEt appeared at 1449 cm^{-1}[10].
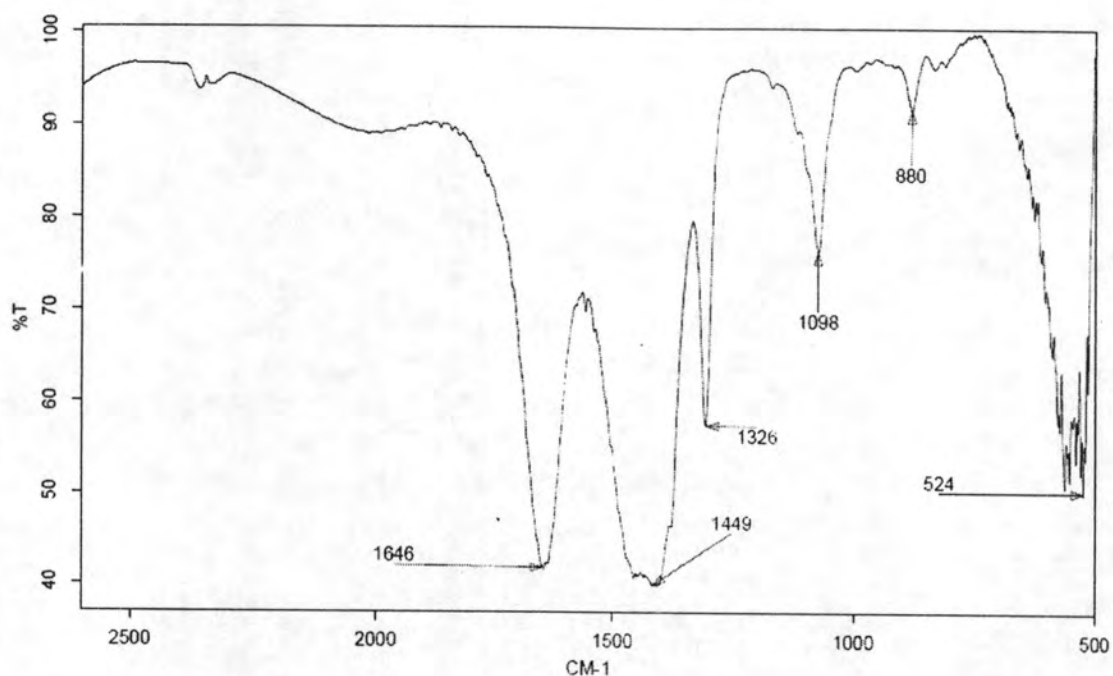
Fig. 4.1 FT-IR spectrum of magnesium ethyl carbonate.

Differential TGA curves of magnesium ethoxide and magnesium ethyl carbonate are shown in Fig. 4.2. Magnesium ethoxide was decomposed into MgO at about 400°C while magnesium ethyl carbonate exhibited decomposition of carbonate with weight loss in a range of 100-150°C and 400°C. The amount of CO_2 was calculated from integral weight loss at about 100-150°C, about 30 %, corresponding to 1 mol of CO_2 lost from magnesium ethyl carbonate [10, 19, 24].
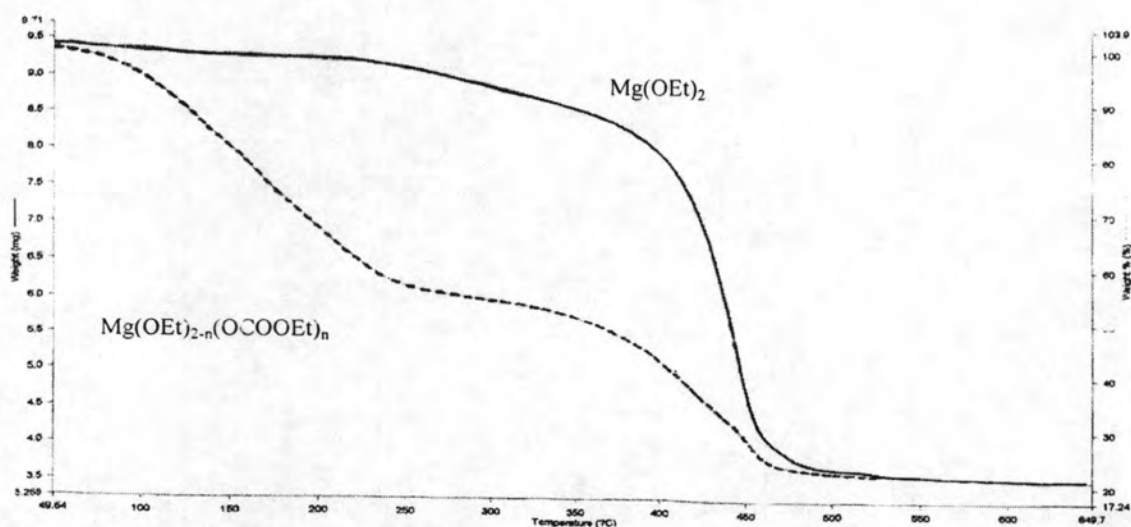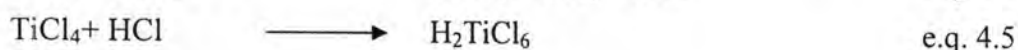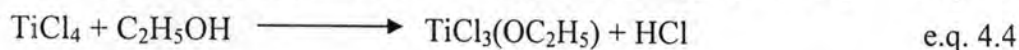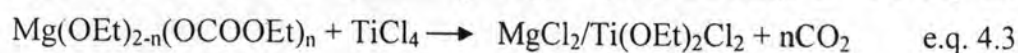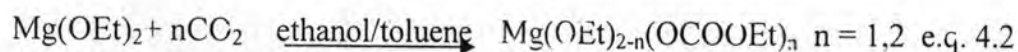

Fig. 4.2 Differential TGA of magnesium ethoxide (continuous line) and magnesium ethyl carbonate support (dot line).

4.2 Effect of chlorinating agent types on supports

The obtained magnesium ethyl carbonate was treated with chlorinating agent in order to precipitate the $MgCl_2$ support. Several types of chlorinating agent were selected from titanium tetrachloride ($TiCl_4$), diethyl aluminium chloride ($AlEt_2Cl$), and ethylaluminium sesquichloride ($Al_2Et_3Cl_3$). The molar ratio of chlorinating agent to $Mg(OEt)_2$ was fixed at 0.5.

Reaction of magnesium ethoxide with CO_2 resulted in formation of $Mg(OEt)_{2-n}(OCOOEt)_n$ (in equation 4.2), which further reacted with $TiCl_4$ to $MgCl_2/Ti(OEt)_2Cl_2 + nCO_2$ (in equation 4.3). Side reactions also occurred, excess of EtOH added can react with $TiCl_4$ to produce HCl gas (equation 4.4) This HCl reacted with $TiCl_4$ to produce titanium complex, H_2TiCl_6, which was reported to be inactive for ethylene polymerization.

$$Mg(OEt)_2 + nCO_2 \xrightarrow{ethanol/toluene} Mg(OEt)_{2-n}(OCOOEt)_n \quad n = 1,2 \quad \text{e.q. } 4.2$$

$$Mg(OEt)_{2-n}(OCOOEt)_n + TiCl_4 \longrightarrow MgCl_2/Ti(OEt)_2Cl_2 + nCO_2 \quad \text{e.q. } 4.3$$

$$TiCl_4 + C_2H_5OH \longrightarrow TiCl_3(OC_2H_5) + HCl \quad \text{e.q. } 4.4$$

$$TiCl_4 + HCl \longrightarrow H_2TiCl_6 \quad \text{e.q. } 4.5$$

When using $AlEt_2Cl$ as a chlorinating agent, the results showed that $AlEt_2Cl$ gave puffy particles. In the case of $Al_2Et_3Cl_3$, the solids were precipitated from the clear solution. The composition of magnesium chloride complex was proposed to contain a partially chlorinated magnesium compound as shown in equation 4.6.

$$Mg(OEt)_{2-n}(OCOOEt)_n + 0.5Al_2Et_3Cl_3 \longrightarrow MgCl_{2-x}(Mg(OEt)_{2-n}(OCOOEt)_n)_x$$
$$+ Al_2Et_3(OEt)_yCl_{3-z} \quad \text{e.q. } 4.6$$

As reported in the patents, the solution of magnesium ethyl carbonate was precipitated in nonpolar solvent (hexane or heptane) under extremely agitation [23] or using spray drying technique [22].

4.3 Effect of Al₂Et₃Cl₃:Mg molar ratio on properties of catalyst

The effect of $Al_2Et_3Cl_3$:Mg molar ratio on the properties of catalyst was investigated. Catalysts were prepared with constant Ti:Mg molar ratio = 3:1 and agitation speed of 400 rpm together with different $Al_2Et_3Cl_3$:Mg molar ratios (0.06-1.00) to activate the support. The suitable amount of $Al_2Et_3Cl_3$:Mg molar ratio was evaluated by polyethylene yield after *in-situ* preparation of catalyst.

The properties of catalyst are shown in Table 4.2. The Ti:Mg molar ratio in catalyst was not significantly different when $Al_2Et_3Cl_3$:Mg molar ratio was increased (0.06-0.50). However $Al_2Et_3Cl_3$:Mg molar ratio = 1.00:1 showed different Ti:Mg molar ratio due to the excess of $Al_2Et_3Cl_3$ reacted with $TiCl_4$ and the structure of catalyst same as the first generation Ziegler-Natta catalyst ($TiCl_3$ 1/3 $AlCl_3$). It has revealed that alkyl aluminium chloride is not effective for anchoring $TiCl_4$ [28]. However, $Al_2Et_3Cl_3$ has affected oxidation state of Ti active species. It was noticed that $MgCl_2$ support agglomerated when $Al_2Et_3Cl_3$:Mg was as high as 1.00:1. The prepared catalyst exhibited broad particle size distribution (PSD). It was found that by using $Al_2Et_3Cl_3$:Mg molar ratio = 0.50:1, the catalyst had the highest activity (20.1 kg PE/g catalyst). Therefore, this ratio was used for further experiments.

Table 4.2. Properties and activities of catalysts at different $Al_2Et_3Cl_3$:Mg molar ratios (Ti:Mg molar ratio = 3:1)

$Al_2Et_3Cl_3$:Mg molar ratio	Properties of catalysts			Activity (kg PE/g cat.) at 1 bar of H_2
	Ti:Mg molar ratio	APS (µm)	PSD	
0.06:1	0.11	9.3	1.4	6.7
0.12:1	0.09	10.7	3.2	9.3
0.25:1	0.07	8.8	2.6	9.1
0.50:1	0.07	7.0	2.6	20.1
1.00:1	0.39	13.6	7.1	10.2

APS = average particle size, PSD = particle size distribution

4.4 Effect of agitation speed on particle size of support

The smaller particle size of the support should have larger surface area and it is easy to incorporate with $TiCl_4$.

The $MgCl_2$ supports were prepared by chlorinating reaction using $AlEt_3Cl_3$:Mg molar ratio = 0.50 at room temperature. The agitation speed was varied from 300-700 rpm in order to control the average particle size (APS) and particle size distribution (PSD) of the supports. The APS and PSD of prepared supports are shown in Table 4.3. The APS of resultant supports decreased when the stirring speed was increased but the PSDs were not different (1.7-2.0). For next experiments, the agitation speed of 700 rpm was used because it gave the lowest APS value.

Table 4.3. The average particle size and particle size distribution of supported catalyst

Speed of agitator (rpm)	APS (μm)	PSD
300	13.1	1.80
400	12.9	1.70
600	10.6	1.82
700	9.8	2.00

4.5 The effect of Ti:Mg molar ratio on titanium content in catalyst

The preparation of the catalyst was performed by operating with a constant $Al_2Et_3Cl_3$:Mg molar ratio (0.50) and performing the titanation at different Ti:Mg molar ratio (2:1-5:1), the results are shown in Table 4.4. The Ti:Mg molar ratio on the supported catalyst increased when Ti:Mg molar ratio was increased. At Ti:Mg molar ratio = 5:1, the PSD of catalyst had the broadest value and when it was used in ethylene polymerization, it gave lower PE yield. At Ti:Mg molar ratio = 3:1 the activity was the highest therefore this ratio was chosen to use for further experiments.

It should be mentioned that Ti:Mg molar ratio used in this work was low, which was contrast to the very high ratio used in the literature (Ti:Mg molar ratio = 250-1000) [27] because the $TiCl_4$ was used for removing the excess of EtOH.

Table 4.4. Properties and activities of catalysts at different Ti:Mg molar ratios ($Al_2Et_3Cl_3$:Mg molar ratio = 0.50:1 and agitation speed of 400 rpm)

Ti:Mg molar ratio	Properties of catalysts			Activity (kg PE/g cat.) at 1 bar of H_2
	Ti:Mg molar ratio	APS (μm)	PSD	
2:1	0.04	7.4	1.8	0.3
3:1	0.07	7.0	2.6	20.1
4:1	0.09	5.0	2.5	11.5
5:1	0.10	5.6	5.8	1.5

APS = average particle size, PSD = particle size distribution

The structure of catalyst was analyzed by FT-IR (Fig. 4.3). Strong bands belonging to Mg-Cl stretching of free surface of $MgCl_2$ was observed at 1636 cm^{-1} as reported by Kang et al [10]. Observed peaks at 1852 and 2252 cm^{-1} are assigned to $MgCl_2$. Peaks at 400-600 cm^{-1} range indicate the presence of Ti-Cl [12].
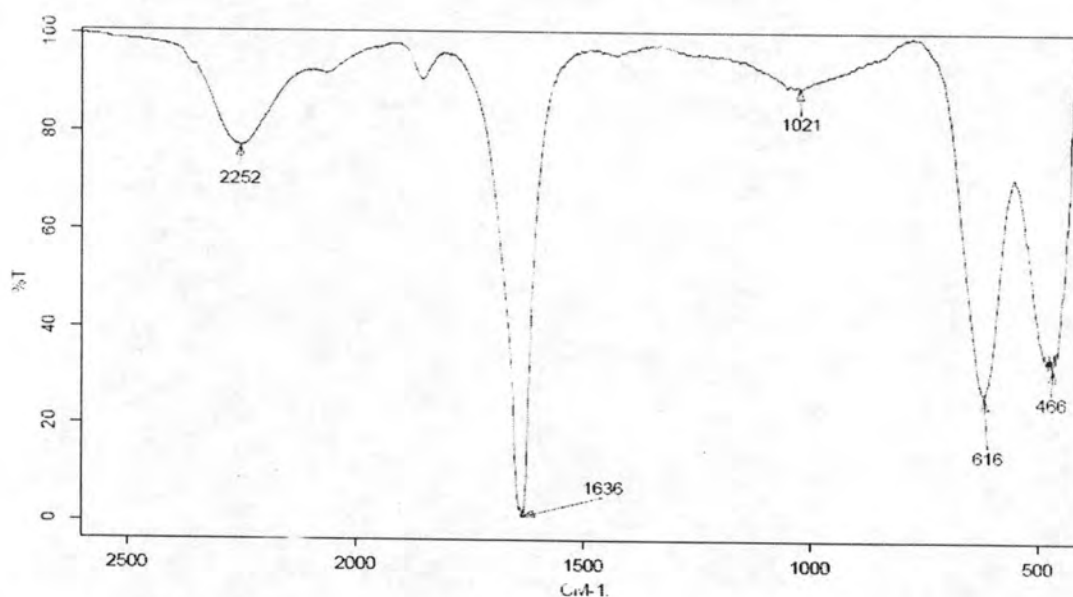
Fig. 4.3 FT-IR spectrum of catalyst.

4.6 Number of titanation

A general method to increase the active of Ti is to perform titanation many times. In the titanation step, $Al_2Et_3Cl_3$:Mg molar ratio = 0.50:1 and Ti:Mg molar ratio = 3:1 were used. The effect of numbers of titanation (1-3) was investigated. Each last number of titanation, mother liquor of catalyst was siphoned off and replaced with fresh hepane before increasing the number of titanation.

The results are shown in Table 4.5. It was found that double titanation could increase Ti:Mg molar ratio in the catalyst. However, the Ti:Mg molar ratio did not increase further after performing three-time titanation. Three-time titanation gave the lowest activity due to longer preparation and treatment time [30]. The activities of catalysts at one or two-time titanation were not different. Therefore, only one titanation step is enough.

The APS of catalysts at different numbers of titanation were in the range of 7-10 μm and PSDs were not significantly different.

Table 4.5. Properties and activities of catalysts at different number of titanation (Ti:Mg molar ratio = 3:1, $Al_2Et_3Cl_3$:Mg molar ratio = 0.50:1, and agitation speed = 400 rpm)

Number of titanation	Properties of catalysts			Activity (kg PE/g cat.) at 1 bar of H_2
	Ti:Mg molar ratio	APS (μm)	PSD	
1	0.07	7.0	2.6	20.1
2	0.15	10.0	2.5	20.5
3	0.16	10.4	2.7	9.6

4.7 The effect of reaction time of heat treatment

It has been accepted that PE with broad or bimodal MWD can reach an excellent balance between mechanical and rheological properties. Catalysts treated at high temperature and maintained for long time can produced broad MWD in

single-reactor [34]. However, broad MWD polymer can be produced by modified polymerization reactors or two-stage polymerization in order to produce bi-modal polyethylene. But the catalyst should have suitable activity and hydrogen response balance (AB) value [2].

The condition used was $Al_2Et_3Cl_3$:Mg molar ratio = 0.50:1 and Ti: Mg molar ratio = 3:1. The catalysts were treated at a constant temperature around 110°C with varying of the treatment time (2, 5 and 10). The results are shown in Table 4.6. It was found that the treated catalyst possessed higher Ti:Mg molar ratio than the untreated catalyst. It was found that the catalyst, which underwent treatment time for 2 h gave the highest PE yield.

It was also found that the heat treatment did not affect the APS of catalysts (7-21 µm), while PSDs were significantly different.

It is clear that the catalysts undergoing heat treatment produced polymer with different molecular weights. The catalyst which was treated with shorter treatment time gave low molecular weight polymer (higher MFI). This is in agreement with the literature [30]. There are two different active sites, chlorotitanate and titanoxane. When the catalyst was treated at high temperature chlorotitanate ($-Ti(OCH_2CH_3)_nCl_{4-n}$) was converted into titanoxane (Ti-O-Ti) (Fig. 4.4), which is corresponding to high molecular weight polymer.

In principles, high AB value of Ziegler-Natta catalyst results from high yield of catalyst at both low and high concentration in polymerization and high hydrogen response (high MFI). The AB value decreased when heat treatment time was increased. The untreated catalyst had the highest activity balance (AB = 4.8), but very low activity. Therefore, the 2 h treated catalyst was used for further experiments because its highest activity.

Table 4.6. Properties and activities of catalysts at different treatment times (Ti:Mg molar ratio = 3:1, $Al_2Et_3Cl_3$:Mg molar ratio = 0.50:1, and agitation speed = 400 rpm, treatment temperature = 110°C)

Heat treatment time (h)	Properties of catalysts			Activity (kg PE/g cat.) at 1 bar of H_2	$MFI_{2.16}$ (g/10 min) at 1 bar of H_2	Activity (kg PE/g cat.) at 3 bar of H_2	$MFI_{2.16}$ (g/10 min) at 3 bar of H_2	*Activity Balance (AB)
	Ti:Mg molar ratio	APS (μm)	PSD					
0	0.05	17.6	2 4	2.9	1.6	2.5	8.1	4.8
2	0.07	7.0	2.6	20.1	1.1	14.7	9.5	3.1
5	0.12	16.8	2.0	9.8	0.4	5.4	2.3	1.3
10	0.12	21.7	2.5	8.6	0.3	4.4	2.0	1.3

AB = [average CA x log[(MFI_2/MFI_2)]/|ΔCA| : where, MFI_2* = melt flow index at 3 bar of H_2 pressure, MFI_2 = melt flow index at 1 bar of H_2 pressure. CA = catalyst activity
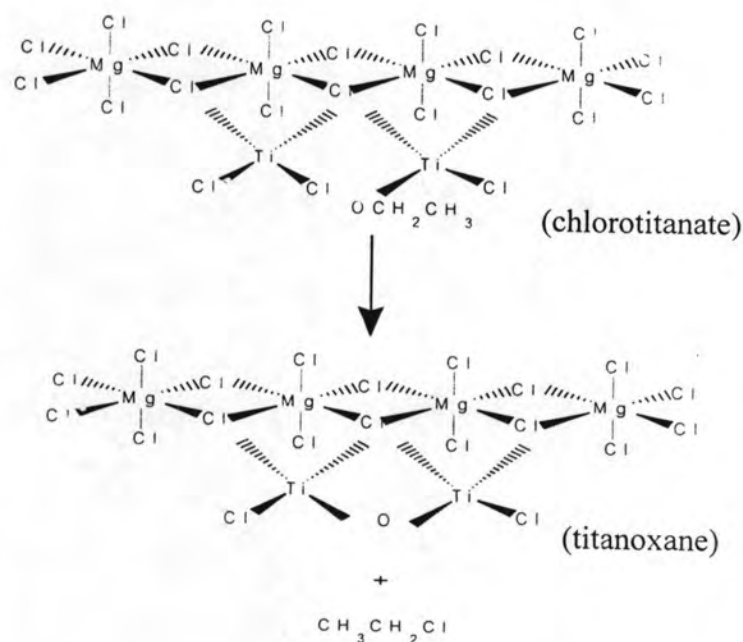
Fig. 4.4 The surface of active Ti species before and after heat treatment.

4.8 Effect of ethyl benzoate (EB) on the properties of catalyst

The effect of EB on activity and stereoregularity of polypropylene has been extensively investigated. It was found that catalyst had high activity and good hydrogen response when EB was added to supported catalyst. [2, 13].

The effect of the electron donor, ethyl benzoate (EB), on the properties and activities of the catalyst was studied. The same reaction conditions as above were used, $Al_2Et_3Cl_3$:Ti molar ratio = 0.50:1, Ti:Mg molar ratio = 3:1, treatment temperature = 110°C, and treatment time = 2 h. The amount of ethyl benzoate was varied (EB:Mg molar ratio = 0.06:1-0.25:1). The results are shown in Table 4.7.

Results showed that Ti:Mg molar ratio in the catalyst with EB addition was lower than that from the EB-free catalyst. The Ti:Mg molar ratio slightly changed when the EB:Mg molar ratio was increased. This showed that EB affected both amount and distribution of $TiCl_4$ in the catalyst. The (110) face of the catalyst was covered with EB. The possible structures of titanium complex are monomeric and dimeric forms shown in Fig. 4.5. Two oxygen atoms of EB coordinated to two magnesium and on titanium on the (110) face [31-32].

The activity of catalyst was found to decrease when EB:Mg molar ratio was increased due to the strong poisoning of the active site from the aromatic ester, especially with a large excess amount of EB, which can saturate vacant coordination sites in active centers [33].

The activity balance (AB) increased when EB:Mg molar ratio was increased. However, at EB:Mg molar ratio = 0.25 it did not increase further. The catalyst system prepared using EB:Mg molar ratio = 0.12 had the highest AB (6.1). The higher value indicated high stability of the catalyst under hydrogen pressure.

Table 4.7. Properties and activities of catalysts with ethyl benzoate (EB) addition (Ti:Mg molar ratio = 3:1, $Al_2Et_3Cl_3$:Mg molar ratio = 0.50:1, and agitation speed = 400 rpm, treatment temperature = 110°C, and treatment time = 2 h)

EB:Mg molar ratio	Properties of catalysts			Activity (kg PE/g cat.) at 1 bar of H_2	$MFI_{2.16}$ (g/10 min) at 1 bar of H_2	Activity (kg PE/g cat.) at 3 bar of H_2	$MFI_{2.16}$ (g/10 min) at 3 bar of H_2	*Activity Balance (AB)
	Ti:Mg molar ratio	APS (μm)	PSD					
0	0.07	11.9	1.7	20.1	1.05	14.7	9.5	3.1
0.06:1	0.06	13.5	1.6	11.5	1.56	9.2	10.5	3.7
0.12:1	0.05	13.1	1.8	9.5	1.86	8.3	12.3	6.1
0.25:1	0.05	12.1	1.7	4.8	2.00	1.8	20.1	1.1

AB = [average CA x log[(MFI_2/MFI_2)]]/|ΔCA| : where, MFI_2* = melt flow index at 3 bar of H_2 pressure, MFI_2 = melt flow index at 1 bar of H_2 pressure, CA = catalyst activity

(a)

(b)
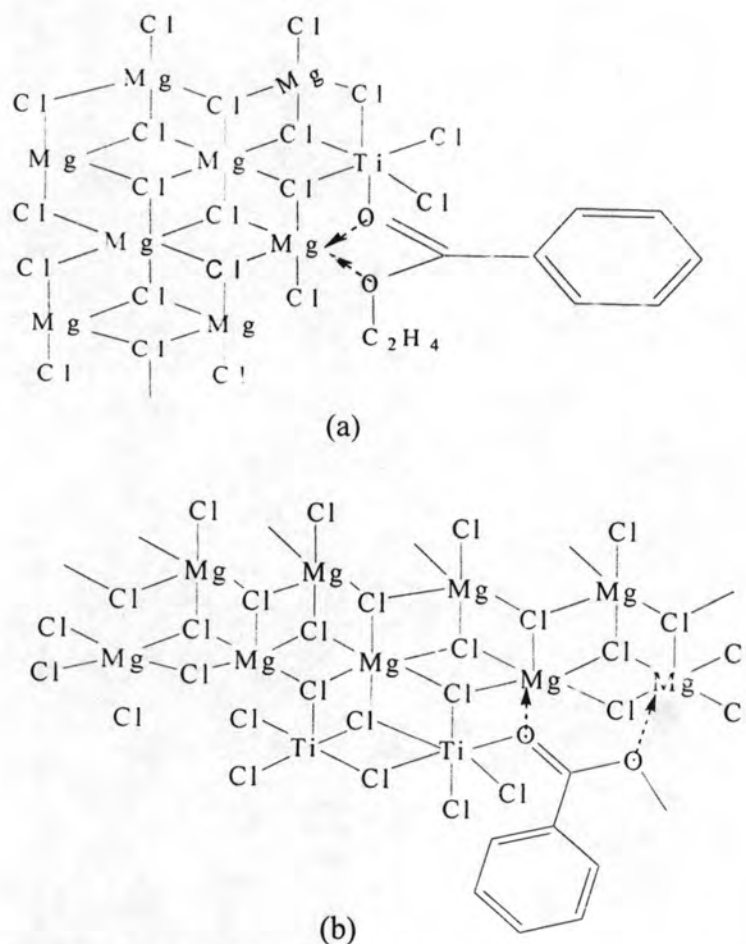
Fig. 4.5 Possible models for EB coordination on the (110) (a) and (100) (b) faces of $MgCl_2$.

The structure of catalyst with and without EB compared with EB were analyzed by FT-IR (Fig.4.6). The EB-catalyst shows strong absorption band at around 1638, 1857, and 2256 cm^{-1} which assigned to Mg-Cl stretching of MgCl$_2$, same as catalyst without EB. However, the EB incorporated catalyst containing C=O stretching belonging to ester appears at 1719 cm^{-1}. The C—O stretching belonging to ester conjugated to C=C aromatic ring appears at 1277 cm^{-1} while the peak appears at 1109-1029 cm^{-1} is assigned to carbonyl group vibration [10].
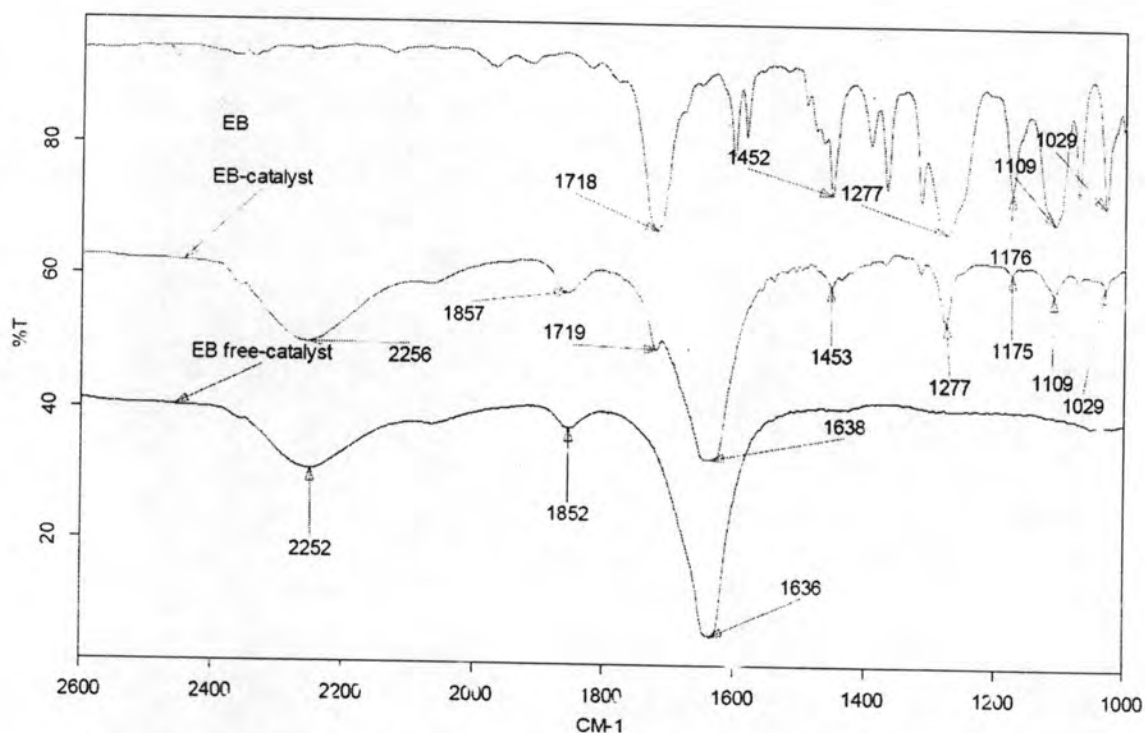

Fig. 4.6 FT-IR spectra of the EB-free and EB-catalysts comparative with EB.

## Morphology of catalyst and polymer

SEM micrographs were obtained to observe morphology of the catalyst and polymer, shown in Figs 4.7 and 4.8. Both samples showed somewhat spherical shape.

The APS of resultant PE powder produced with EB-catalysts was slightly increased. The fine content of powder was reduced from 49% to 29 %. Bulk density of powder produced with EB-catalyst was slightly higher than powder produced with free-EB catalyst. The results of APS, % fine content, and bulk density (BD) of powder are shown in Table 4.8.

Table 4.8. APS, % fine content, and bulk density (BD) of powder

Source of powder	APS (μm)	% fine content	BD (g/cm^3)
free-EB catalyst	130	49	0.31
EB catalyst	135	29	0.35
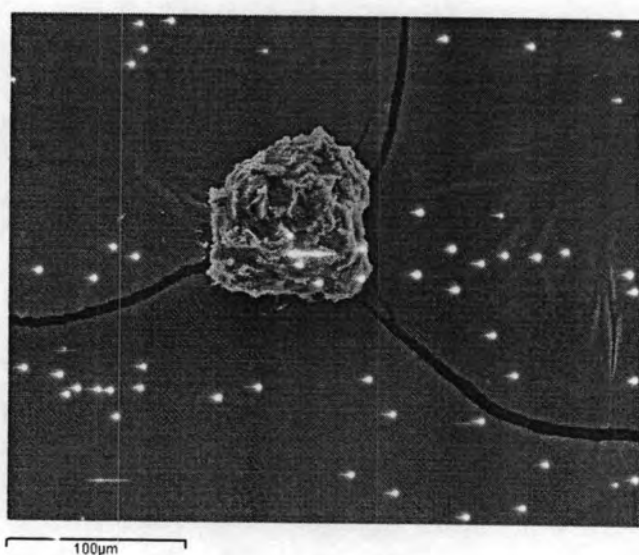
Fig. 4.7 SEM micrograph of EB-catalyst obtained at x 350 magnification.
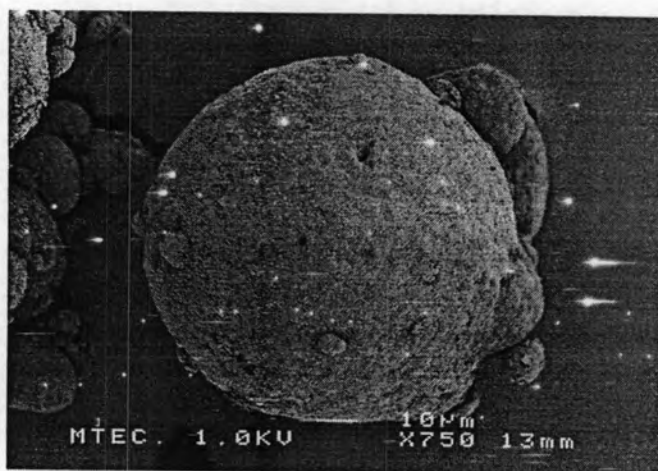
Fig. 4.8 SEM micrograph of polymer obtained from EB-catalyst at x750 magnification.

4.9 The catalyst with EB addition under aging

From the results, the effect of heat treatment time and molar ratio of Ti increased with an increasing of heat treatment time. This study focused on improvement of yield and hydrogen response of catalysts with an increasing of Ti content in catalyst.

In the study of the effect of aging time on AB value, the same reaction condition as in the study of the effect of addition of EB was used, $Al_2Et_3Cl_3$:Ti molar ratio = 0.50:1, Ti:Mg molar ratio = 3:1, EB:Mg molar ratio = 0.12:1, treatment temperature = 110 ^{o}C. The aging time was varied (2, 5, and 10 h). The results are shown in Table 4.9. It was found that Ti:Mg molar ratio in the catalyst with EB addition and holding the suspension at 110°C was increased from 0.05 to 0.12 with aging time for 10 h. This indicated that the aging time could increase the efficiency of Ti coordination on $MgCl_2$. The activity of catalyst increased when aging time was increased.

The AB value was slightly increased when the aging time was increased. The calculated activity balance (AB value) of the catalyst system as prepared using 10 h of aging time was the highest (7.2).This catalyst produced polyethylene with the highest also yield.

Other aging times did not affect the APS value of catalyst. The prepared catalyst had a narrow size distribution.

Table 4.9. Properties and activities of catalyst with ethyl benzoate (EB) addition by varying aging time ($Al_2Et_3Cl_3$:Mg molar ratio = 0.50:1, Ti:Mg molar ratio = 3:1, EB:Mg molar ratio = 0.12:1, treatment temperature =110°C but aging time was varied for 2, 5, and 10 h)

Aging time (h)	Properties of catalysts			Activity (kg PE/g cat.) 1bar H_2	$MFI_{2.16}$ (g/10 min) 1bar H_2	Activity (kg PE/g cat.) 3bar H_2	$MFI_{2.16}$ (g/10 min) 3bar H_2	*Activity Balance (AB)
	Ti:Mg molar ratio	APS (μm)	PSD					
2	0.05	13.1	1.8	9.5	1.86	8.3	12.3	6.1
5	0.07	12.5	2.0	15.0	1.30	13.2	10.5	7.1
10	0.12	14.0	2.3	17.3	0.98	15.0	10.3	7.2

AB = [average CA x log[(MFI_2/MFI_2)]/|ΔCA| : where, MFI_2* = melt flow index at 3 bar of H_2 pressure, MFI_2 = melt flow index at 1 bar of H_2 pressure, CA = catalyst activity

4.10 Effect of dicyclopentyldimethoxysilane (DCPDMS) a morphology controlling agent

Dicyclopentyldimethoxysilane ($C_{11}H_{24}O_2Si$) was added to the solution of magnesium ethyl carbonate (DCPDMS:Mg molar ratio = 0.25:1). The same reaction condition as in the study of the effect of addition of EB was used, $Al_2Et_3Cl_3$:Ti molar ratio = 0.50:1, Ti:Mg molar ratio = 3:1, EB:Mg molar ratio = 0.12:1, and treatment temperature = 110°C for 10 h. The APS of catalyst was 33.5 μm. The APS of catalyst which was two times increased. Results showed that when DCPDMS was added, the Ti:Mg molar ratio (0.07), activity and AB value (5.8) were decreased but hydrogen response was increased. The possible structures of the $MgCl_2$ supports with DCPDMS is shown in Figure 4.9. DCPDMS plays a role as a binding agent.
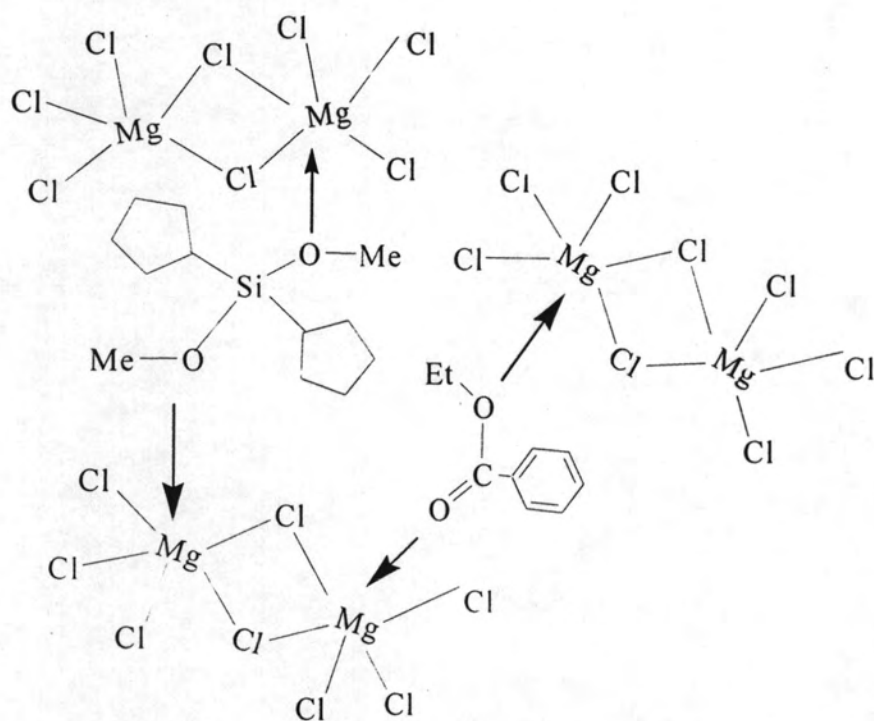
Fig. 4.9 The possible binding of DCPDMS and EB with MgCl₂.

Morphology of catalyst and polymer

The APS of PE powder prepared from the added DCPDMS catalyst was increased from 135 μm to 260 μm and fine polymer content was less than PE powder prepared from the EB catalyst. The results of APS, % fine polymer content, and bulk density (BD) of powder are shown in Table 4.10.

SEM micrographs of the catalyst and polymer are shown in Figs 4.10 and 4.11. The catalyst (Fig. 4.10a) obtained from added DCPDMS was quite spherical. In Fig. 4.11, polymer had more fibril linkage between the primary particle of polymer. DCPDMS was assumed to prevent mechanical fragment during polymerization and enhance the APS value of powder.
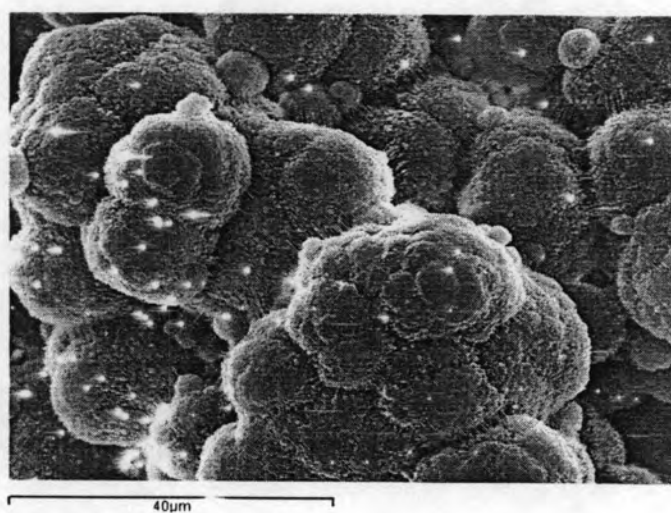
Table 4.10. APS of PE powder from different catalysts

Source of powder	APS (μm)	% fine content	BD (g/cm^3)
free-EB catalyst	130	49	0.31
EB catalyst	135	29	0.35
DCPDMS/ EB catalyst	260	7	0.36

(a)   (b)
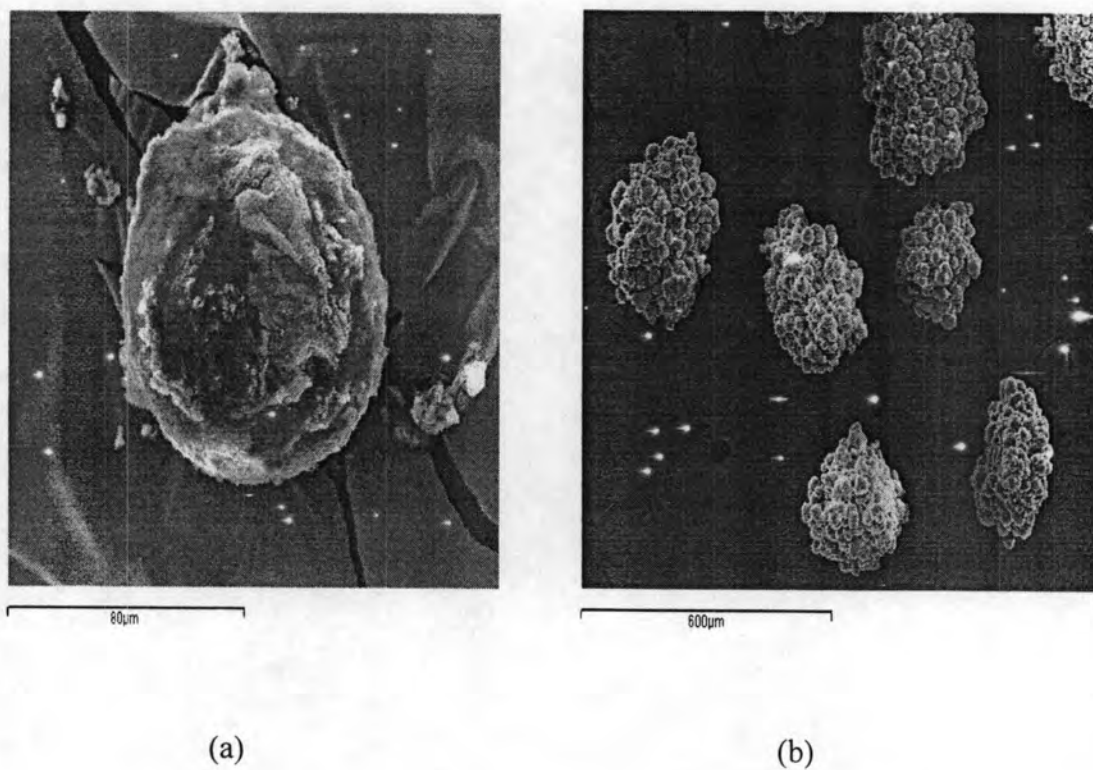
Fig. 4.10 SEM micrographs of (a) catalyst containing DCPDMS at x 350 magnification and (b) polymer at x 350 magnification.

Fig. 4.11 SEM micrograph of polymer obtained from DCPDMS catalysts at x 1500 magnification.

4.11 Catalysts and polymers evaluation

The properties of supported catalysts prepared from magnesium ethyl carbonate were compared with those of supported catalyst prepared from magnesium ethoxide such as yield and hydrogen response, morphology (shape, size), MW, and MWD.

4.11.1. Yield and hydrogen response

It was obviously seen that polyethylene yield, hydrogen response, and AB value of the prepared catalyst were higher than those of the comparative catalyst. The results are shown in Table 4.11. The experimental results showed that the catalysts demonstrated high hydrogen response and activity balanced (AB) suitable for bimodal HDPE.

Table 4.11. Comparison of polyethylene yield and hydrogen response of different catalysts

Items	Yield (kg PE/ g catalyst)		Melt flow ratio ($MFI_{2.16}$)		AB
	1 bar of hydrogen	3 bar of hydrogen	1 bar of hydrogen	3 bar of hydrogen	
Prepared catalyst	12.0	9.4	2.05	51.2	5.8
Comparative catalyst	6.5	4.9	1.5	10.5	3.0

4.12.2. Morphology

SEM micrographs of the catalyst and polymer morphology are shown in Figs. 4.12 and 4.13. The morphology of the prepared catalyst (Fig. 4.12a) and produced polymer from this catalyst (Fig. 4.13a) were bigger than those of the comparative catalyst (Fig. 4.12b) and produced polymer from this catalyst (Fig. 4.13b).

(a)   (b)
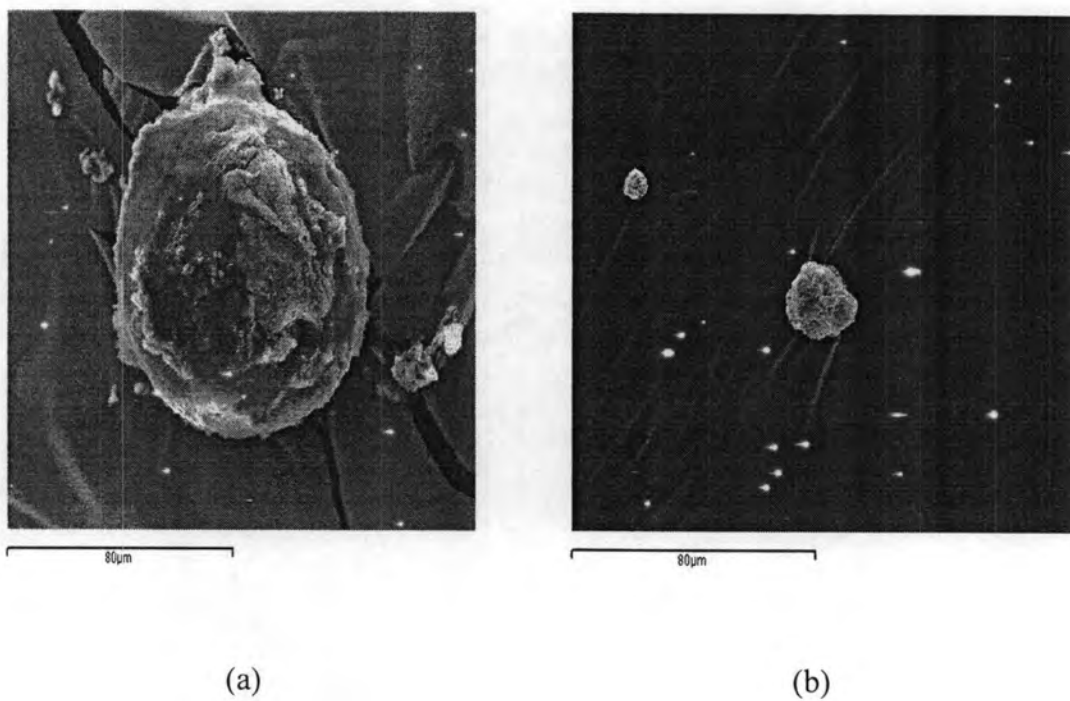
Fig. 4.12 SEM micrographs of catalysts (a) prepared catalyst and (b) comparative catalyst at x 350magnification.

(a)   (b)
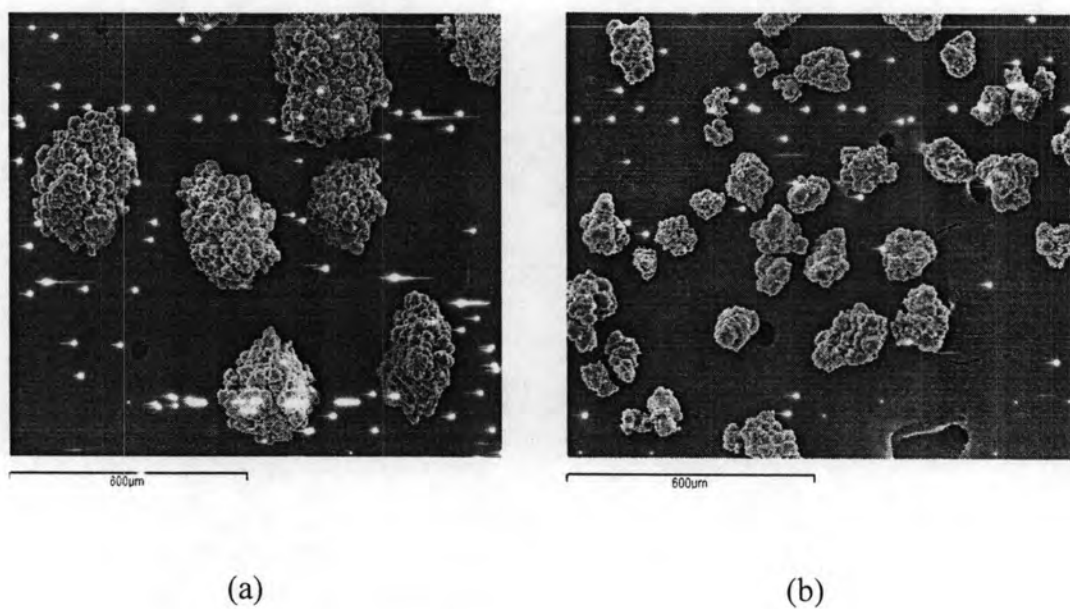
Fig. 4.13 SEM micrographs of polyethylene produced from: (a) prepared catalyst and (b) comparative catalyst at x 100 magnification.

4.12.3. Particle size and bulk density of polyethylene powder

The particle size of polyethylene powder is an imperative factor for drying capacity of slurry high density polyethylene process. Very fine polyethylene powder gives high efficiency to hexane absorption.

The determination of bulk density of powder particles according to the ASTM D1895 provides a possibility to check the consistency of powder or granule batches in respect of their structure (corn of powder) and uniformity (granule cut). Powder possessing high bulk density increased storage capacity of powder in silos.

Table 4.12. APS of PE powder from different source of catalyst

Source of powder	APS (µm)	% fine content	BD (g/cm^3)
Prepared catalyst	260	7	0.36
Comparative catalyst	155	10	0.40

The average particle size (APS) of polyethylene powder from prepared catalyst was 260 µm, containing a lot of fine particles. Bulk densities of powder were in the range of 0.29 to 0.34 g/cm^3. However, catalyst gave APS of powder higher than comparative catalyst and % fine content less than 7%.

4.12.4. Molecular weight and molecular weight distribution (MWD)

The molecular weight and molecular weight distribution of obtained polyethylene were measured at 160°C by Gel Permeation Chromatography (PL-GPC high temperature) using o-dichlorobenzene as a solvent. Molecular weight and molecular weight distribution (MWD) of polymers polymerized by using prepared catalysts and comparative catalysts are shown in Table 4.13. Molecular weight distribution of polymer produced from this work was broader than of the comparative one.

Table 4.13. Molecular weight and molecular weight distribution (MWD) of polymer.

sample	Mn	Mw	Mz	MWD
This work	2.05×10^4	2.43×10^5	2.98×10^6	11.9
Comparative	3.03×10^4	1.99×10^5	0.81×10^6	6.6

It is well known that molecular weight (MW) and molecular weight distribution (MWD) are very significant parts in determining the physical and mechanical properties of polymers. The high molecular weight polymer has good mechanical properties, but it is difficult to be processed. An increase in MWD tends to improve environmental stress cracking resistant (ESCR) and melt flow rate at high shear rate because at high shear rate polymer having broader molecular weight distribution (MWD) will get lower viscosity, which is important for blow molding and extrusion processes.

The performance of prepared catalyst was compared with comparative catalyst shown in Table 4.14. The advantages of the prepared catalyst are higher PE yield, AB value and APS. The polymer was produced with low fine content and bulk density. However, it is noted that the catalyst produced polymer with broader MWD compared to the commercial catalyst.

Table 4.14. Comparison of performance of the prepared catalyst with the commercial catalyst

Item	Prepared catalyst	Commercial catalyst
Yield (kg PE/g cat)	12.0	6.1
MFI$_5$ at 1 bar of H$_2$	1.2	1.6
AB	5.8	3.0
MWD	11.9	6.6
APS of powder (μm)	260	155
Fine content (%)	7	10
Bulk density (g/cm^3)	0.36	0.40

4.12.5. Physical properties of polymer

Moaulus and complex viscosity of polymer were determined by a cone and plate rheometer. Moduli of polyethylene which produced by using prepared catalysts and comparative catalysts are shown in Fig. 4.14. The storage modulus (G') represents elastic deformation of material (energy storage: solid like) but loss modulus (G") represents viscous deformation of material (energy dissipation: liquid like). At cross over point (COP) of G' and G", elastic and viscous deformations are equal. The COP results of both catalysts exhibited at high frequency indicating the low molecular weight of polymer (liquid like). The modulus of comparative PE was higher than that of PE polymer from the prepared catalyst. Therefore, polyethylene from the comparative catalyst was tougher than polyethylene from the prepared catalyst.
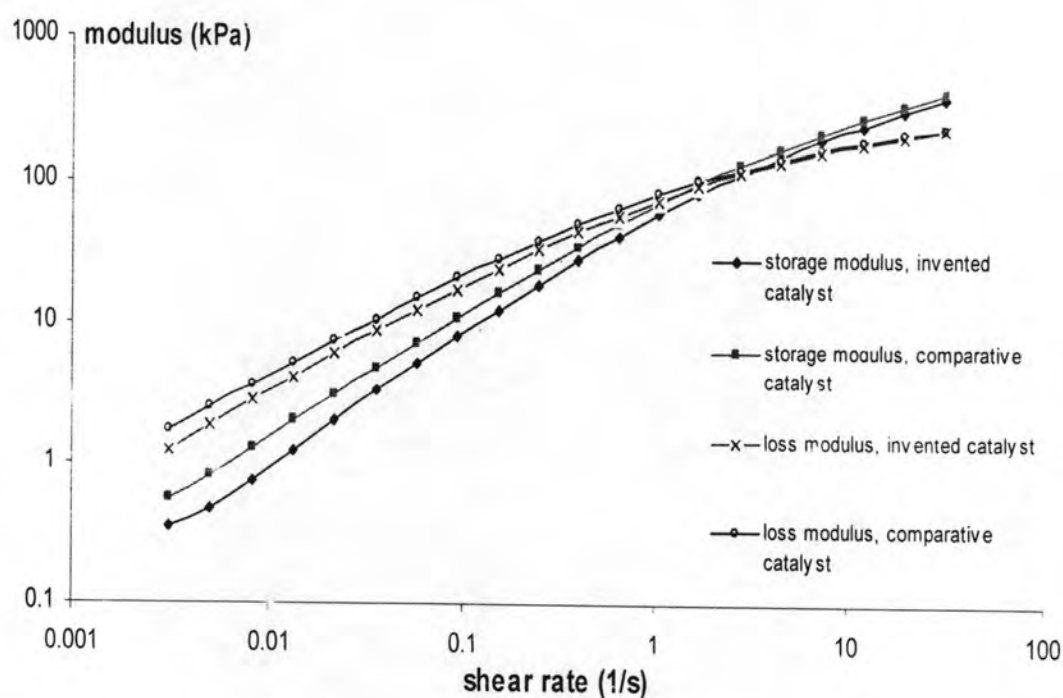

Fig. 4.14 Modulus of polyethylene.

The complex viscosities of polyethylene are shown in Fig. 4.15. The complex viscosity at polymer of low to medium frequency (10^{-1} to 10^2 rad/s) correlates to processability, energy consumption, and output but not to molecular

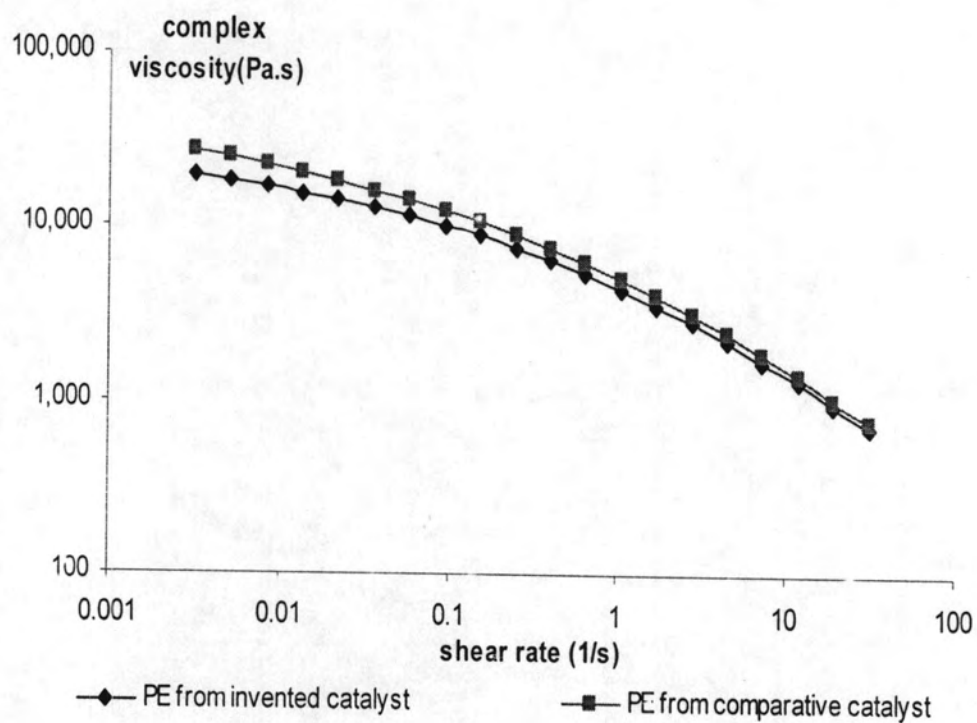weight. Polyethylene prepared from the catalyst in this work provided good processability than the comparative products.

Fig. 4.15 Complex viscosity of polyethylene.