Polymerization of ethylene over the supported Ziegler-Natta and metallocene catalysts on magnesium hydroxide and magnesium hydroxychloride

การสังเคราะห์พอลิเอธิลีนโดยใช้ตัวเร่งปฏิกิริยาซีเกลอร์-แนตตา และตัวเร่งเมทัลโลซีนบนสารประกอบแมกนีเซียมไฮดรอกไซค์ และแมกนีเซียมไฮดรอกซีคลอไรด์

*Phanthakan Kaewarsa (พันธกานต์ แก้วอาษา)**
*Dr. Choosak Poonsawat (ดร. ชูศักดิ์ พูนสวัสดิ์)***
*Dr. Somying Leelasubcharoen (ดร. สมหญิง ลีลาทรัพย์เจริญ)***

ABSTRACT

Polymerization of ethylene (high-density polyethylene, HDPE) catalyzed by a mixture of Ziegler-Natta and metallocene catalyst and cocatalyzed with alkyl aluminium compounds such as triethyl aluminium (TEA), trimethyl aluminium (TMA) and methylaluminoxane (MAO) were carried out in reactor. Hybrid catalysts supported on Mg $(OH)_2$ nanocrystalline when prepared by the hydrothermal method and Mg (OH) Cl was prepared by direct method. The ICP, DSC, FTIR, SEM and XRD were used to characterize supports, catalyst systems and polyethylene product. The Mg (OH) Cl/ BuMgCl/HCl/$TiCl_4$ gave highest activity 2735 X 10^5 g PE/mol metal.atm.h..

บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาการสังเคราะห์พอลิเอธิลีนชนิดความหนาแน่นสูง โดยใช้ระบบตัวเร่งปฏิกิริยาซึ่งประกอบด้วย ตัวเร่งปฏิกิริยาผสม ซึ่งเตรียมจากตัวเร่ง Ziegler-Natta และตัวเร่ง metallocene และใช้สารประกอบ alkylaluminium คือ TEA, TMA และ MAO เป็นตัวเร่งร่วม โดยมี Mg $(OH)_2$ และ Mg (OH) Cl เป็นตัว support จากนั้นทำการศึกษาลักษณะของ support, ระบบตัวเร่งปฏิกิริยา และพอลิเอธิลีนที่สังเคราะห์ได้ โดยใช้เทคนิค ICP, DSC, FTIR, SEM และ XRD และเมื่อเปรียบเทียบความสามารถของตัวเร่งปฏิกิริยา (activity) ที่ได้พบว่าพอลิเอธิลีนที่สังเคราะห์ได้จากการใช้ตัวเร่งปฏิกิริยา Mg (OH) Cl/BuMgCl/HCl/$TiCl_4$ ให้ค่า activity มากที่สุด คือ 2736 x 105 gPE/mol metal.atm.h.

Key Word : Ziegler-Natta catalysts, metallocene catalysts, polyethylene
คำสำคัญ : ตัวเร่งซีเกลอร์-แนตตา ตัวเร่งเมทัลโลซีน พอลิเอธิลีน

---

* *Graduate student, Master of science, Inorganic Chemistry, Department of Chemistry, Faculty of Science, Khon Kaen University.*

** *Asst.Prof. Department of Chemistry, Faculty of Science, Khon Kaen University Introduction*

Introduction

The Ziegler-Natta catalyst and metallocene catalysts are used for ethylene polymerization since 1950. Ziegler-Natta catalysts have the advantages of producing product with a controlled morphology, higher melting points. However produced polymer of ethylene was a highly branched polymer and removal of the catalyst from the final product. Metallocene catalysts have the advantages of high activity and special polymer properties such as narrow molecular weight distribution (MWD). Eventhough there are many advantages of the homogeneous metallocene catalyst, there are some problems for the commercial usage, such as difficulties in controlling the polymer morphology, instabilities for slurry or gas phase polymerization and requirement of a large amount of an expensive MAO.

Molecular weight and MWD are important in polymer processing because they determine both mechanical and rheological properties. Polyethylene with a narrow MWD leads to products with higher resistance to impact and environmental stress-cracking. On the other hand, poly-ethylene with a broad MWD shows greater flowability in the molten state at high shear rate, which is important for blowing and extrusion techniques. Therefore there is needed to prepare a broader MWD and higher MW polymer for multi-purposed application and processibility. Due to the relatively high molecular weight of polymers produced by the Ziegler-Natta catalyst, the narrow MWD via metallocene catalysts could be broadened by preparing Ziegler-Natta/metallocene hybrid catalysts. Hybrid catalysts can take advantage of the properties of both metallocene and Ziegler-Natta catalysts. In addition, hybrid catalyst would be expected to be utilized in prevailing process without significant process modification and to enhance processibility of the polymers.

The Ziegler-Natta catalysts are prepared by reacting certain transition metal halides with organometallic reagents such as alkyl aluminum, lithium and zinc reagents. The catalyst formed by reaction of triethylaluminum with titanium tetrachloride has been widely studied. The metallocene catalyst consists of a metal center, usually from the transition metals, surrounded by two cyclopentadienyl rings (Cp). The first metallocene developed was ferrocene which consisted of iron as the metal center and two Cp rings surrounding. Other metallocenes include: Cp_2ZrCl_2, Cp_2TiCl_2, Cp_2TiSiN and overcrowded metallocene. Cp_2ZrCl_2 catalyst has widely studied. It showed high activity due to a formation of methyl aluminoxane (MAO) as a result of the hydrolysis of trimethylaluminium (TMA) cocatalyst.

In this study it is desirable to prepare a heterogeneous catalyst systems. Ziegler-Natta and metallocene catalysts were prepared by impregnation onto solid support, respectively. Two types of inorganic supports, Mg (OH) Cl and $Mg(OH)_2$ were prepared by the direct and hydrothermal methods. These two types of catalysts Ziegler-Natta and metallocene were used for ethylene polymerization. Effects of catalyst system, cocatalyst, aluminium concentration, ethylene polymerization conditions (time, temperature, stir speed, solvent and ethylene pressure), and hydrogen concentration were investigated. The characterization of the support, catalyst system and polyethylene product were introduced. The kinetic profile and activity profile were also determined.

Experimental

Synthesis of support: $Mg(OH)_2$ support was prepared by addition of 0.1 mol of $Mg(NO_3)_2.6H_2O$ into reactor and filled with 0.1 M NaOH solution. The mixture was kept at 80°C for 2 hours. After cooling to room temperature, the white $Mg(OH)_2$ powders were collected, washed with distilled water and absolute ethanol and then dried under vacuum at 60°C for 4 hours. Mg (OH) Cl was prepared by addition of MgO to a solution of $MgCl_2.6H_2O$. Slurry was agitated for 4 hours and dried at 400°C for 24 h. Elemental analysis, ICP, SEM and XRD were used to characterize the support.

Catalyst preparation: In the glass reactor with flowing nitrogen, the support ($Mg(OH)_2$ or Mg (OH) Cl) was mixed with Bu_2MgCl in toluene, then refluxed at 90°C for 2 hours. After adding Cp_2ZrCl_2, the reaction was allowed at 50°C for 2 hours. The multiple treatment (3 times) $TiCl_4$ (ball mill) was added to the slurry and refluxed at 90°C for 2 hours. Finally, the catalyst system was washed with toluene and dried at 100°C for 4 hours under nitrogen and prepared as a slurry in toluene for polymerization.

Polymerization: In the reactor, 100 ml of toluene was introduced under nitrogen atmosphere; then, the reactor was vacuated and flowed with ethylene. The catalyst slurry and 1 M cocatalyst (TEA,TMA or MAO) were then added. Polymerization temperature was 60-70°C with a stirring speed of 700 rpm. After 2 hours, the reaction was washed with pentanol to remove organic impurity and dried under vacuum.

Results and Discussions

A. Element content by ICP analysis

Table1 Zr and Ti content in catalyst systems

Catalyst system	Zr		Ti	
	analysis (ppm)	Zr $(\%)x10^{-2}$	analysis (ppm)	Ti $(\%)x10^{-2}$
A	0	0	0.097	0.97
B	0	0	0.357	4.45
J	0.721	12	0.767	12.60
K	2.131	26.5	0.287	3.57
L	1.831	18.3	0	0
P	0	0	0.907	22.65
R	0.01	0.166	0.567	9.43
R*	0.008	0.081	0.367	3.66
S	0.141	1.41	0.157	1.57
T	0	0	0.597	5.96

B. Catalyst System Prepared Using Different Catalyst

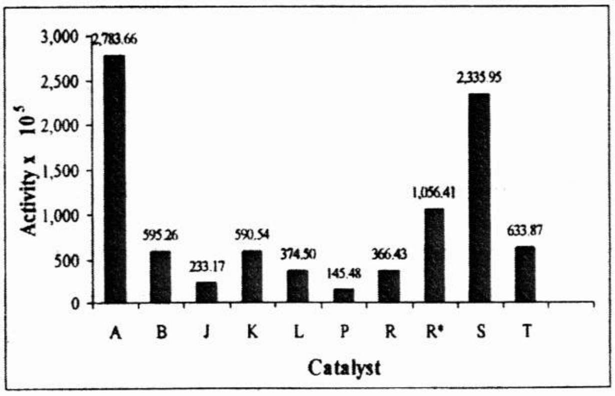

Figure 1 Activity profile of catalyst systems:

Mg (OH) Cl/BuMgCl/$TiCl_4$, catalyst **A**

Mg (OH)Cl/BuMgCl/$TiCl_4$ 2 เท่า , catalyst

Mg $(OH)_2$/Cp_2ZrCl_2/BuMgCl/$TiCl_4$, catalyst **J**

Mg $(OH)_2$/Cp_2ZrCl_2/BuMgCl/HCl/$TiCl_4$, catalyst **K**

Mg (OH) Cl/Cp_2ZrCl_2, catalyst **L**

Mg (OH) Cl/BuMgCl/$TiCl_4$, catalyst **P**

Mg (OH) Cl/Cp_2ZrCl_2/BuMgCl/$TiCl_4$, catalyst **R**

Mg (OH) Cl/Cp_2ZrCl_2/BuMgCl/$TiCl_4$/C5H10OH, catalyst **R***

Mg (OH) Cl/Cp_2ZrCl_2/BuMgCl/HCl/$TiCl_4$, catalyst **S**

Mg (OH) Cl/BuMgCl/HCl/$TiCl_4$, catalyst **T**

The different catalyst systems, shown in Figure 1, were studied. It can be seen that Mg (OH) Cl/BuMgCl/$TiCl_4$, catalyst A gave the highest activity. (Table 1).

C. Cocatalyst

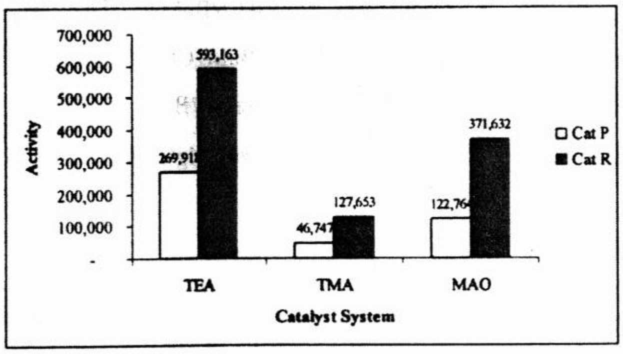

Figure 2 Activity profile of Mg (OH) Cl/BuMgCl/$TiCl_4$, **P** and Mg (OH) Cl/Cp_2ZrCl_2/BuMgCl/$TiCl_4$, **R**

The Catalyst system P and R with a cocatalyst TEA gave the highest activity. The decrease in activity (TMA and MAO as a cocatalyst) due probably to steric hindrances of active species on the support surface during polymerization and deactiveation of active metal sites during the supporting process.

D. Effect of polymerization condition

- Effect of Time

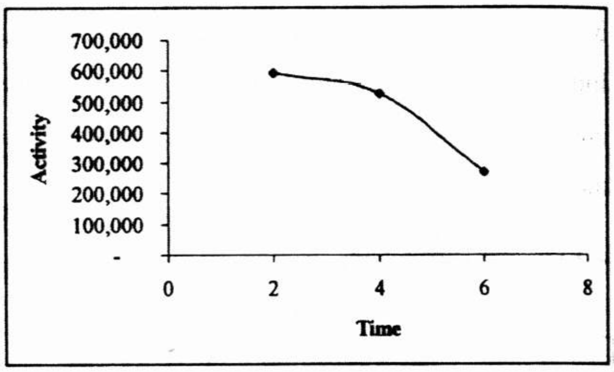

Figure 3 The effect of time to the polymerization of ethylene when using Mg (OH) Cl/Cp_2ZrCl_2/BuMgCl/$TiCl_4$, **R** as catalyst and TEA as cocatalyst.

The result of the effect of time on polymerization is presented in Figure 3. From the figure it can be seen that catalyst activity decreases with reaction time up to 6 hours after which a steady decline ensues, due probably to deactivation of the catalyst. The reaction time 2 hours gave a higher acitivity. The length of time over which the catalyst was stable is very impressive and is very important for an industrial application of the system.

- Effect of Temperature

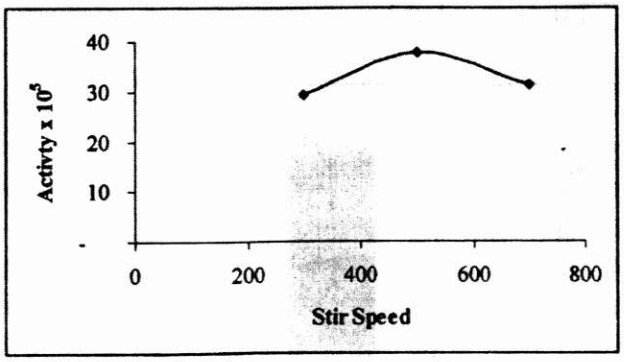

Figure 4 The effect of temperature to the polymerization of ethylene when using Mg (OH) Cl/Cp_2ZrCl_2/BuMgCl/$TiCl_4$/pentanol,**R*** as catalyst and TEA as cocatalyst

The result on variation of activity with temperature is presented in Figure 4. (From where it is obvious that 60°C is an optimum point below or above this point the activity is lower) Indicates that the catalytic system was notstable under high temperature, the activity decreased when the temperature was above 60°C.

- Effect of Stir speed

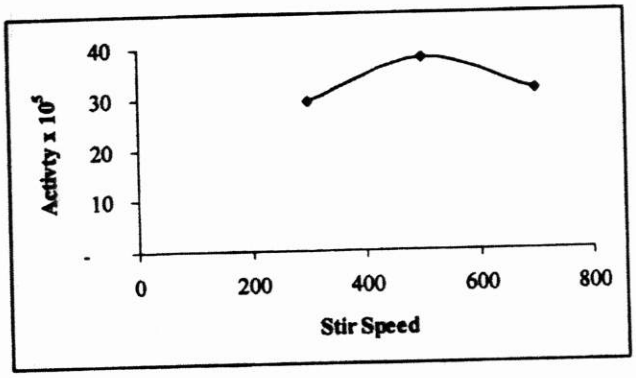

Figure 5 Activity profile of Mg (OH) Cl/ Cp_2ZrCl_2/BuMgCl/$TiCl_4$ /pentanol, **R***

Stir speed of 500 rps. was shown to be suitible for ethylene polymerization because it gave highest activity

- Effect of Solvent

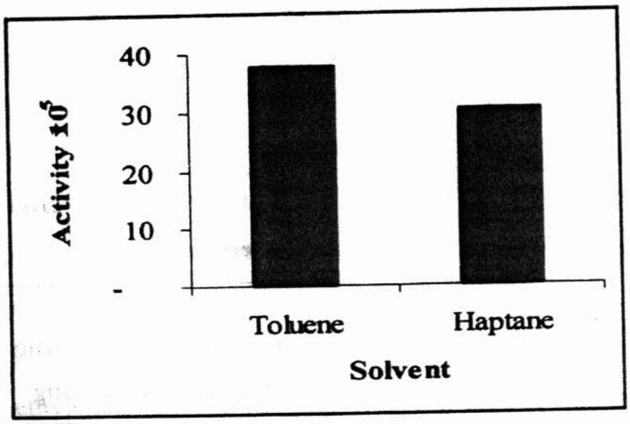

Figure 6 Activity profiles of Mg (OH) Cl/ Cp_2ZrCl_2/BuMgCl/$TiCl_4$ /pentanol, **R***

Figure 6 was obtained by using toluene as the solvent, the catalyst system R* gave higher activity than heptane because toluene is a nonpolar solvent so ethylene monomer can be better dispersed and reacted with the other monomer to form polymer chains.

E. Effect of HCl loading on hybrid catalyst

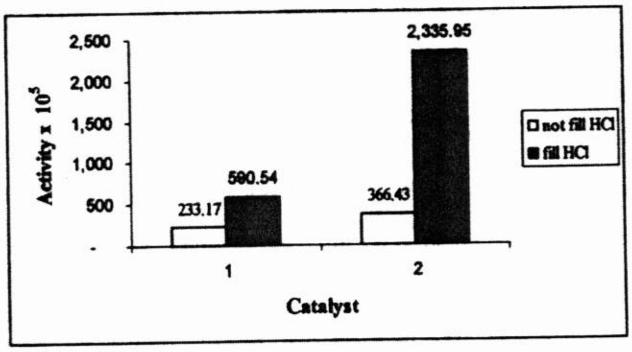

Figure 7 Activity profile of
(1) Mg $(OH)_2$/Cp_2ZrCl_2/BuMgCl/$TiCl_4$, **J**
Mg $(OH)_2$/Cp_2ZrCl_2/BuMgCl/HCl/$TiCl_4$, **K**
(2) Mg (OH) Cl/Cp_2ZrCl_2/BuMgCl/$TiCl_4$, **R**
Mg (OH) Cl/Cp_2ZrCl_2/BuMgCl/HCl/$TiCl_4$, **S**

F. Characterization

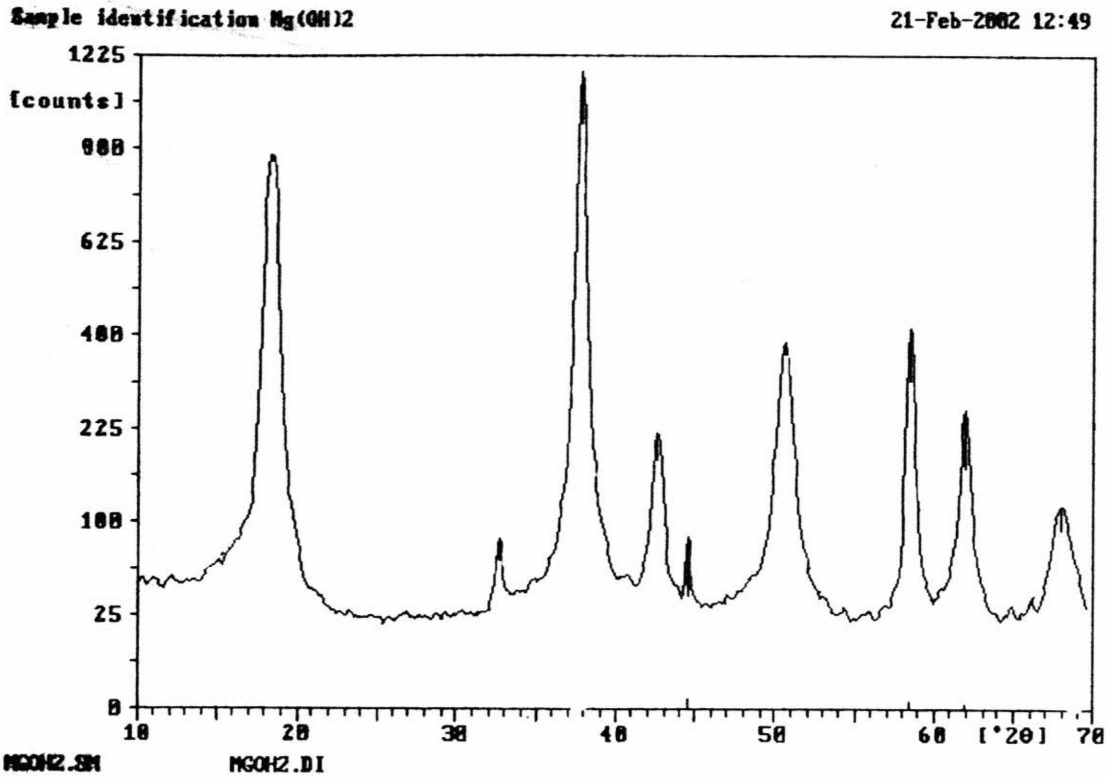

Figure 8 XRD pattern of Mg $(OH)_2$

The XRD pattern of Mg $(OH)_2$ was shown in Figure 8 All major peaks confirmed characteristics of Mg $(OH)_2$. The $Mg(OH)_2$ nanocrystalline have large surface area. This makes it a suitable support for entrapping organometallic complexes in the pores.

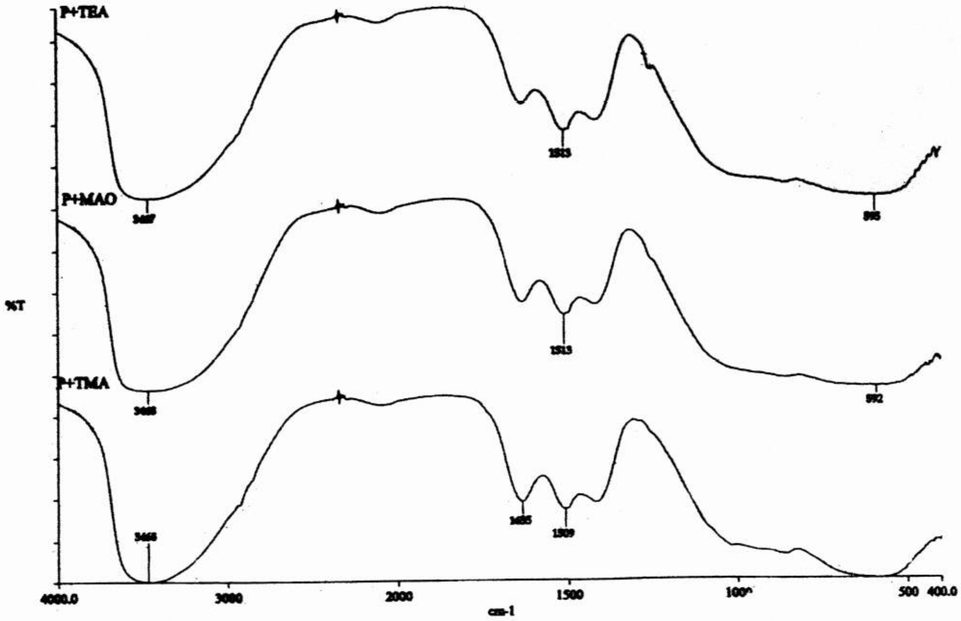

Figure 9 FTIR spectra of polyethylene products. The broad band peak at 3000-1900 cm^{-1} is attributed to C-H stretching of ethylene.

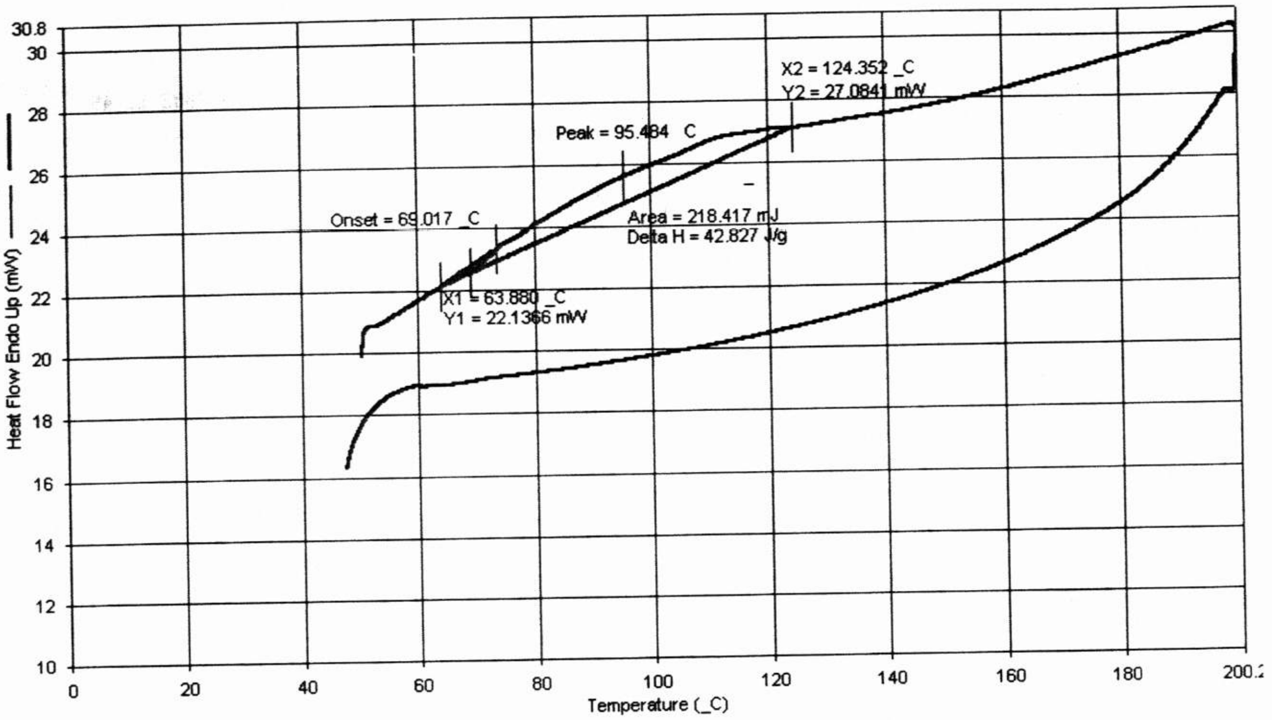

Figure 10 DSC thermogram of polyethylene products The polymer products by the catalyst system had a melting point at 110.4°C.

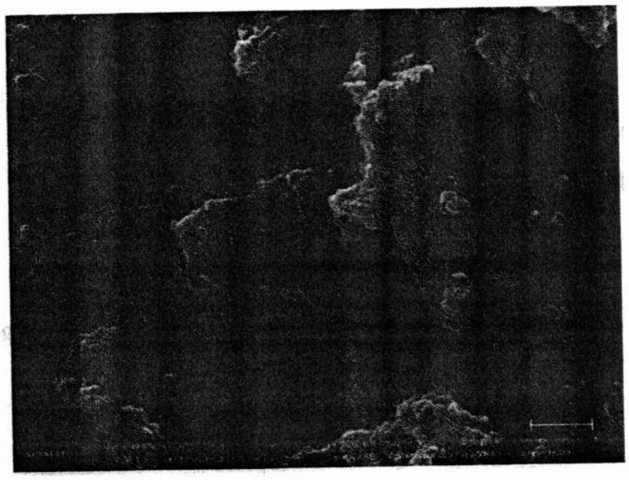

Figure 11 The morphorlogy of polyethylene product taken by SEM.

Conclusions

The various mixture of catalyst and support (catalyst systems) prepared can be an alternative catalyst system for the polymerization of ethylene because it gave high activity. Moreover from the result it can be concluded that the addition of HCl and grindgnard reagent (BuMgCl) and the multiple treatment with $TiCl_4$, $Mg(OH)_2$ nanocrystalline and Mg (OH) Cl ball mill in the catalyst systems play an important role in increasing the polymerization activity.

From the result it can be concluded that it is possible to creating a catalyst that can polymerize ethylene without an addition of the expensive MAO.

Acknowledgemen : This work was supported by the Postgraduate Education and Research Program in Chemistry (PERCH) and Graduate School, Khon Kaen University.

References

Cho, H. S., Chung, J. S., Han, J. H., Ko, Y. G and Lee, W. Y. 1998. Polymerization of ethylene and ethylene/1-hexene over Ziergler-Natta/ Metallocene hybrid catalysts supported on $MgCl_2$ prepared by a recrystallization method. **J. Applied Polymer Sci.** 70: 1707-1715.

Cho, H. S., Cho,i Y. H., Lee, W. Y. 2000. Characteristic of ethylene polymerization over Ziegler/Natta/metallocene catalysts comparison between hybrid and mixed catalysts. ***Catalysis Today.*** 63: 523-530.

Chung, J. S., Cho, H. S., Ko, Y.G., Lee, W. Y. Preparation of the Ziegler-Natta/ metallocene hybrid catalyst on $SiO_2/MgCl_2$ bisupport and ethylenepolymerization. ***J.Molecular Catalysis A: Chemical.*** 1999;144: 61-69.

Ding, Y. , Zhang, G. , Wu, H., Hai, B., Wang L. and Qian, Y. 2001.Nanoscale magnesium hydroxide and magnesium oxide powder: control over size, shape and structure via hydrothermal synthesis.***J.Chem.Mater.*** 13:435-440.Hsieh J.T.T, 1989.US Patent 4863886.