ผลของเคลย์ที่ถูกปรับปรุงด้วยไซเลนต่อพอลิเอทิลีนเคลย์นาโนคอมโพสิทที่เตรียมโดยอินซิทูพอลิเมอร์ไรเซชันด้วยตัวเร่งปฏิกิริยาเซอร์โคโนซีน/เอ็มเอโอ

นางสาวสุวิมล ภู่ระหงษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2555

EFFECT OF SILANE-MODIFIED CLAY ON POLYETHYLENE/CLAY NANOCOMPOSITES PREPARED BY *IN SITU* POLYMERIZATION WITH ZIRCONOCENE/MAO CATALYST

Miss Suwimon Poorahong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2012

Thesis Title EFFECT OF SILANE-MODIFIED CLAY ON POLYETHYLENE/CLAY NANOCOMPOSITES PREPARED BY IN SITU POLYMERIZATION WITH ZIRCONOCENE/MAO CATALYST
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สุวิมล ภู่ระหงษ์ : ผลของเคลย์ที่ถูกปรับปรุงด้วยไซเลนต่อพอลิเอทิลีนเคลย์นาโน
คอมโพสิทที่เตรียมโดยอินซิทูพอลิเมอร์ไรเซชันด้วยตัวเร่งปฏิกิริยาเซอร์โคโนซีน
/เอ็มเอโอ. (EFFECT OF SILANE-MODIFIED CLAY ON
POLYETHYLENE/CLAY NANOCOMPOSITES PREPARED BY *IN
SITU* POLYMERIZATION WITH ZIRCONOCENE/MAO CATALYST)
อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.บรรเจิด จงสมจิตร, 81 หน้า.

พอลิเอทิลีนเป็นพอลิเมอร์ที่นิยมนำมาใช้ประโยชน์อย่างมากเนื่องจากมีต้นทุนในการผลิตต่ำ ส่งผลกระทบต่อสิ่งแวดล้อมน้อย และนำไปใช้งานได้หลากหลาย แต่อย่างไรก็ตามพอลิเอทิลีนยังมีคุณสมบัติบางประการที่เป็นข้อจากัดต่อการใช้งาน พอลิเอทิลีนมีความแข็งแรงไม่เพียงพอ ทนความร้อนได้ต่ำ ต้านการซึมผ่านของแก๊สได้ไม่ดี และจุดติดไฟได้ง่าย พอลิเมอร์ที่เติมสารปรุงแต่งสามารถปรับปรุงคุณสมบัติของพอลิเมอร์ได้ โดยทั่วไปการเติมสารปรุงแต่งในพอลิเอทิลีนใช้สารปรุงแต่งขนาดไมโคร แต่ในช่วงที่ผ่านมาได้มีการนำสารปรุงแต่งที่มีขนาดนาโนมาใช้ ซึ่งพบว่า สารปรุงแต่งขนาดนาโนสามารถปรับปรุงคุณสมบัติของพอลิเอทีลีนได้ดีกว่า การเติมสารปรุงแต่งลงในพอลิเมอร์ เรียกว่า พอลิเมอร์ นาโนคอมโพสิท ในงานวิจัยนี้ศึกษาผลของการเติมสารปรุงแต่งนาโนเคลย์ต่อความว่องไวของตัวเร่งปฏิกิริยาเซอร์โคโนซีนในปฏิกิริยาพอลิเมอร์ไรเซชันของเอทิลีนรวมถึงศึกษาสมบัติของพอลิเอทิลีนเคลย์นาโนคอมโพสิทที่ได้จากการสังเคราะห์ด้วยวิธีอินซิทูพอลิเมอร์ไรเซชัน ซึ่งในงานวิจัยนี้เปรียบเทียบวิธีการเตรียมตัวรองรับของนาโนเคลย์ 2 ชนิด (อินซิทู และ เอกซิทู อิมเพรกเนชัน) และเปรียบเทียบคุณสมบัติต่างๆ ระหว่างนาโนเคลย์ที่ไม่ได้ปรับปรุงกับนาโนเคลย์ที่ถูกปรับปรุงด้วยไซเลน พบว่าวิธีเตรียมตัวรองรับแบบอินซิทู อิมเพรกเนชันให้ความว่องไวของตัวเร่งปฏิกิริยาสูงกว่าวิธีเอกซิทู อิมเพรกเนชัน นอกจากนั้นยังสามารถปรับปรุงสมบัติทางความร้อนได้ และนาโนเคลย์ที่ถูกปรับปรุงด้วยไซเลนให้ความว่องไวของตัวเร่งปฏิกิริยาสูงกว่า นาโนเคลย์ที่ไม่ได้ถูกปรับปรุง

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา 2555

5470436221 : MAJOR CHEMICAL ENGINEERING
KEYWORDS : POLYETHYLENE / METALLOCENE / NANOCOMPOSITES/ NANO CLAY / IN SITU

SUWIMON POORAHONG : EFFECT OF SILANE-MODIFIED CLAY ON POLYETHYLENE/CLAY NANOCOMPOSITES PREPARED BY *IN SITU* POLYMERIZATION WITH ZIRCONOCENE/MAO CATALYST. ADVISOR : ASSOC. PROF.BUNJERD JONGSOMJIT, Ph.D., 81 pp.

Polyethylene is the most widely used commodity plastics because of low production cost, reduced environmental impact and the wide range of application. However, the usage of polyethylene has some restrictions. Polyethylene has low mechanical strength, low thermal resistance, low gas permeability and easy to catch fire. The polymer was added by additive or filler, which that can improve polyethylene properties. Generally, the addition of additive into polymer use micro-size additive but in the recent year, nano-size additive was added to polymer. It was found that the nano-sized additive show better properties than micro-size additive. The addition of nano-sized additive or nanofiller is called polymer nanocomposties. In this research, for the first part of this study, the two different impregnation methods (*in situ* and *ex situ* impregnation method) were investigated. For the second part, unmodified and modified by silane compounds were conducted. The properties of polyethylene/clay nanocomposites were also investigated. It found that *in situ* impregnation method gives higher catalytic activity than *ex situ* impregnation method. The *ex situ* impregnation method resulted in maximal thermal properties and crystallization. The nanoclay was modified by tetracholosilane ($SiCl_4$), which it shows the higher activity than unmodified nanoclay.

Department : Chemical Engineering
Field of Study : Chemical Engineering
Academic Year : 2012

Student's Signature ....
Advisor's Signature ....

ACKNOWLEDGEMENTS

The author would like to express my greatest gratitude and appreciation to Associate Professor Bunjerd Jongsomjit, my thesis advisor, for his invaluable suggestions, guidance, useful discussions, and devotion to revise this thesis throughout encouragement during my study. His advice is always worthwhile and without him this work could not be possible. In addition, the author would also be grateful to Associate Professor Supakanok Thongyai, as a chairman, and Associate Assistant Professor Suphot Phatanasri, Dr. Ekrachan Chaichana, as the member of the thesis committee.

I would like to thank Ms.Mingkwan Wannaborworn, Ms.Sasiradee Jantasee,and Mr.Yuttapong Tanawannapong for their helpful suggestions and patience to correct my thesis and paper manuscript writings.

I wish to thank the member of the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University for their assistance and encouragement.

Finally, I would like to express my highest gratitude to my parents who alwayspay attention for all times and have provided their support and encouragement. The most success of graduation is devoted to my parents.

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CHAPTER I

INTRODUCTION

Polyolefins are the most important modern utility polymers. Especially, polyethylene and polypropylene are major usage of plastic materials worldwide. The industrial capacity for the production of polyethylene (such as HDPE, LDPE and LLDPE) and polypropylene cover 60% and 40% of the total polyolefin production, respectively [1]. Polyethylene is the most widely used commodity plastics because of low production cost, reduced environmental impact and the wide range of application. Polyethylene products are including clothing, tooth brushes, storage bottles, pipelines, bullet proof jackets, aerospace application and biomedical implants [2].

Generally, the production of polyolefin uses Ziegler-Natta catalysts. The $TiCl_4$ based Ziegler-Natta catalysts was discovered by Ziegler and Natta for the polymerization of ethylene in 1950s [3]. The Ziegler-Natta catalyst has the multiple sites of active centers due to broader molecular weight distribution compared to metallocene catalyst, which has single site nature. Thus, the molecular structure of the polymer cannot be well controlled because these catalysts have the different nature types of catalytic sites and non-uniform comonomer distribution (polymer molecules show higher molecular weight, the comonomer incorporation show lower) [4]. Metallocene catalysts have the one type of active site, whereas Ziegler-Natta catalysts have the multiple sites of active centers. Metallocene catalysts produces polymers with narrow molecular weight distribution (M_w/M_n=2) and the structure of metallocene can be easily changed. It is well know that metallocene catalyst shows higher mechanical, optical characteristic and worse process performance than Ziegler-Natta catalysts. In addition, catalytic activity of metallocene catalyst is 10-100 times higher than Ziegler-Natta catalysts [5]. The commercial of ethylene polymerization uses metallocene catalyst and methylaluminoxane (MAO) as co-catalysts, which it has an extensive effort for using the metallocene catalyst more effectively. However, it was well known that the disadvantages of homogeneous metallocene system have two parts. The first part is the lack of morphology control of the polymer particle leading to reactor fouling. The second part is restriction of using the solution process and the production of polymer mainly based on slurry processes and gas phase. Another important disadvantage is the requirements of methylaluminoxane (MAO) for achieve maximum metallocene catalytic activity [6]. Therefore, the metallocene catalyst is attached to inorganic support, which can solve the problems as mentioned above. Heterogeneous metallocene catalyst has several advantages that are important to industry such as improve product morphologies and the ability to be used in gas-phase and slurry-phase reactors.

However, the usage of polyethylene has some restrictions. Polyethylene has low mechanical strength, low thermal resistance, low gas permeability and easy to catch fire [7]. Thus, polyethylene properties were improved by four methods. The first method is changing the method of synthesis. The second method is adjusting the conditions of polymerization reactions. The third method is irradiation process and the last method is addition of additives into the polymer. The polymer was added by additive or filler, which that can improve polyethylene properties. Generally, the addition of additive into polymer use micro-size additive but in the recent year, nano-size additive was added to polymer. It was found that the nano-sized additive show better properties than micro-size additive. The addition of nano-sized additive or nanofiller is called polymer nanocomposties.

In the recent year, polymer nanocomposites (PNC) are the major development in the nanotechnologies. Nano-inorganic materials such as SiO_2, Al_2O_3 and clay have brought much attention to this research field. There are probably three methods to prepare polymer nanocomposite: (i) solution method, (ii) melt mixing and (iii) *in situ* polymerization. For the solution method, nano-size additive is added to a polymer solution using solvents such as toluene and chloroform, but the uses of solvents is not environmentally-friendly [8]. The melt mixing process, uses high temperature for the mixing of nanofiller and polymer that can cause the thermal degradation of the filler in polymer matrix [9]. For *in situ* polymerization, the nanofiller are added to monomer during the polymerization. *In situ* polymerization method has three advantages: a one-step synthesis of the polymer nanocomposite, develop compatibility between the clay and the polymer and increase clay dispersion in the polymer matrix [10].

Polymer/clay nanocomposites (PCN) include two-phase materials, which the polymers are reinforced by nanofillers and propose superior mechanical, thermal and barrier properties [11]. The structure of clay minerals used as nanofiller are montmorillonite, vermiculite or saponite and the widely used nanoclay is montmorillonite (MMT). However, the proper preparation of these materials is very difficult because polyolefin are hydrophobic and montmorillonite is hydrophilic [12]. Thus, the preparation of polymer/clay nanocomposite requires modification of clay mineral by adding compatibilizer to the system.

In this present study, effect of silane-modified clay on polyethylene/clay nanocomposites prepared by *in situ* polymerization with zirconocene/MAO catalyst are investigated for the first time. In this research, the catalytic activity of metallocene catalyst using commercial nanoclay as support is studied. For the first part of this study, the two different impregnation methods (*in situ* and *ex situ* impregnation method) are compared. For the second part, the unmodified and modified clay by silane compounds are investigated. The properties of polyethylene/clay nanocomposites are characterized using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGA) and Transmission Electron Microscopy (TEM).

1.1 Objective of the Thesis

To study effect of silane-modified clay on polyethylene/clay nanocomposites prepared by *in situ* polymerization with zirconocene/MAO catalyst. In this research, the activity of metallocene catalyst using commercial nanoclay as support was studied. For the first part of this study, the two different impregnation methods (*in situ* and *ex situ* impregnation method) were investigated. For the second part, unmodified and modified by silane compounds were conducted. The properties of polyethylene/clay nanocomposites were also investigated.

1.2 Scope of the Thesis

1. Synthesize the polyethylene/clay nanocomposite by *in situ* polymerization with metallocene catalyst upon the specified condition.
2. Determine the effect of *in situ* and *ex situ* impregnation method on the catalytic activity and polymer properties for the ethylene polymerization.
3. Determine the effect of modified with silane compound and unmodified nanoclay on the catalytic activity and polymer properties for the ethylene polymerization.
4. Characterize the nanoclay with X-ray Diffraction (XRD), Thermal Gravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR).
5. Characterize the polyethylene/clay nanocomposites with Scanning Electron Microscopy (SEM), Thermo Gravimetric Analysis (TGA), X-ray Diffraction (XRD), Differential Dcanning Calorimetry (DSC) and Transmission Electron Microscopy (TEM).

1.3 Benefits

1. Polyethylene/clay nanocomposites were synthesized by *in situ* and *ex situ* impregnation method with metallocene catalyst and addition of nanoclay as support was change the catalytic activity.
2. The properties of polyethylene/clay nanocomposite were improved because the dispersion of nanoclay in the polymer matrix.
3. This information was used as a reference for polymer industries.

1.4 Research methodology

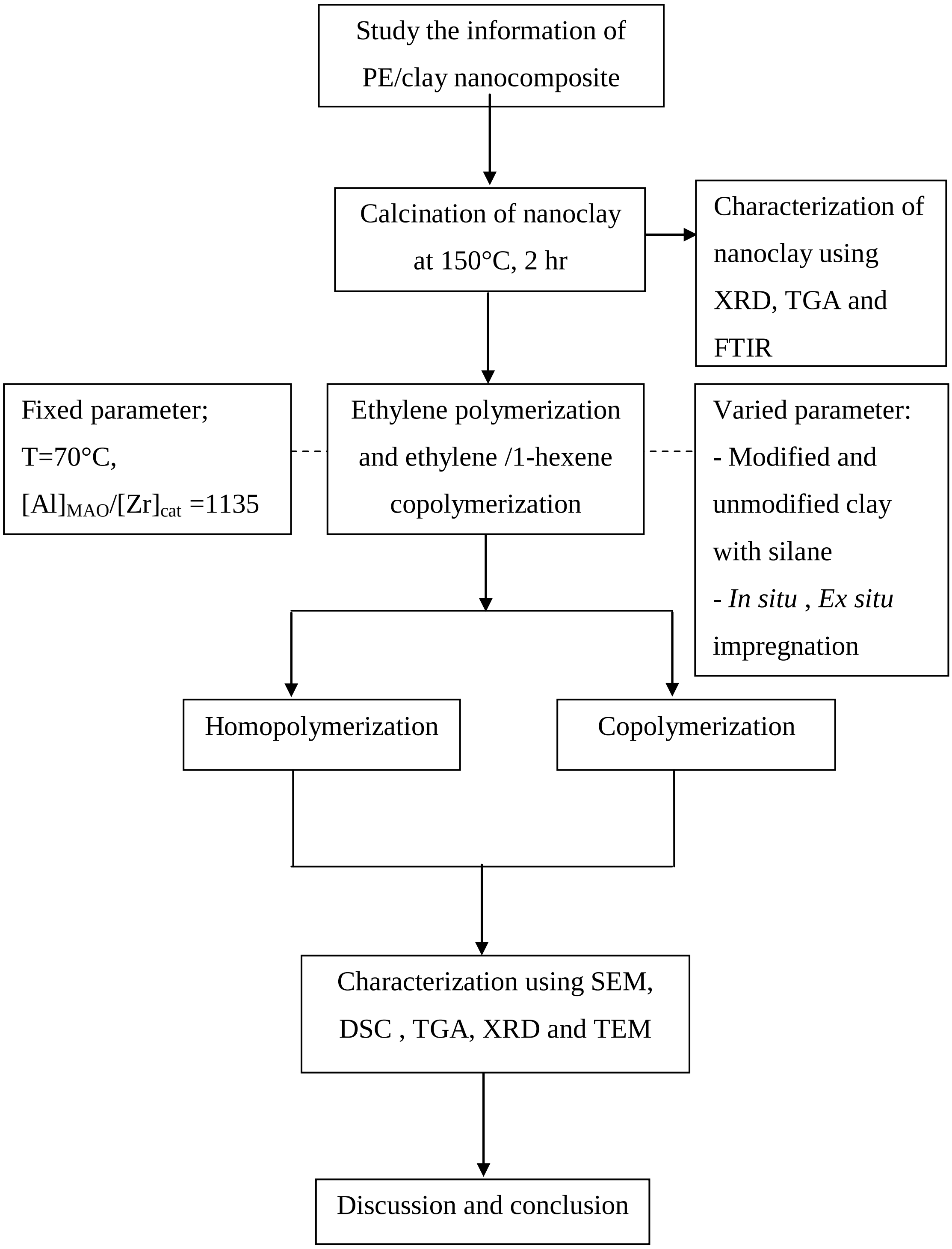


Figure 1.1 Flow diagram of research methodology

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Polyethylene

2.1.1 Polyethylene structure

Polyethylene was the first synthesized in 1898 by Hans von Pechmann. After that, polyethylene was the first industrial synthesized of PE in 1933. Polyethylene (PE) is the most widely used produce plastics and the global demand of PE is 50 million metric tons. Polyethylene has the simple chemical structure of commercial polymers as shown in Figure 2.1. Polyethylene was widely used article plastics because of low production cost, reduced environmental impact, high chemical resistance and wide range of application [1].

(a) Ethylene (b) Polyethylene

Figure 2.1 The structure of (a) ethylene and (b) polyethylene

2.1.2 Classification of polyethylene

The 60% of total production of polyolefin is polyethylene (i.e., HDPE, LDPE, and LLDPE). There are classified to three types of polyethylene according to density and structures, high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) as shown in Figure 2.2. The different structure of polymer depends on pressure, temperature and catalyst during polymerization reactions, which that affect on the physical properties of polymer.

HDPE (high-density polyethylene) has very less or does not have any branch in the polyethylene backbone and a density of greater or equal to 0.941 g/cm^3. The structures of HDPE offer higher crystalline polyethylene than other type of polyethylene. HDPE was synthesized by catalytic reaction with using multi-site (Ziegler-Natta catalysts) catalyst or using single-site catalysts (metallocenes catalysts). The production of HDPE was synthesized by homopolymerization or copolymerization of ethylene. These structures are prevalently used in products and packaging such as bottles, tubes, containers, water pipes, gas pipes and toys. HDPE can be produced by different processes which can be commercially divided into three types: (1) solution process; (2) slurry process and (3) gas-phase process.

LDPE (low-density polyethylene) have many long chain and short chain branching in the polyethylene backbone and a density range of 0.910 - 0.940 g/cm^3. The crystalline and physical properties ensure from the amount of long chain branching (LCB) and short chain branching (SCB). The ethylene polymerizations of LDPE are synthesized under high reaction pressure and high reaction temperature. LDPE is principally amorphous because the quantity and length of branches are very high.

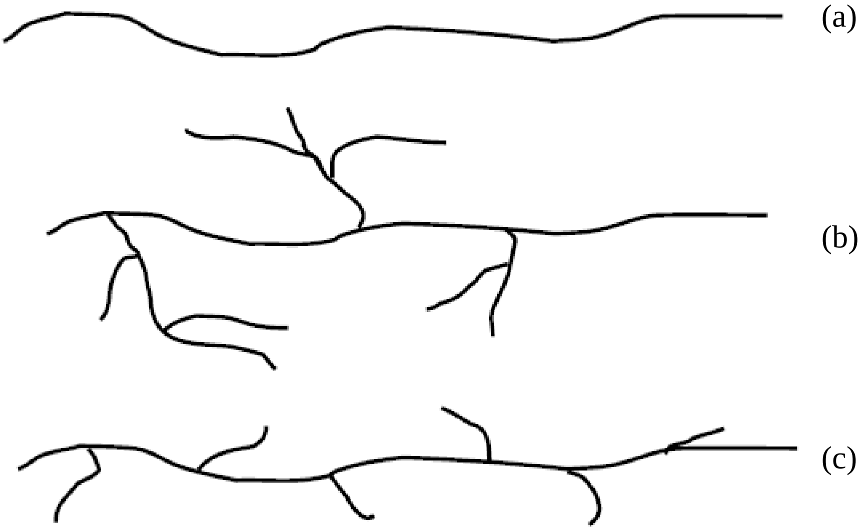


Figure 2.2 Chemical structures of various kinds of polyethylene (a) HDPE (b) LDPE (c) LLDPE [1]

LLDPE (linear-low density polyethylene) is described by a density range of 0.915 - 0.925 g/cm^3. LLDPE is produced by copolymerization of ethylene and α-olefins as comonomer such as 1-butene, 1-hexene, and 1-octene.The difference of LLDPE and LDPE is not containing long-chain branching, which LLDPE contains only short chain branching. The short chain branching of LLDPE is non uniform dispensed through the molecular weight. The distribution of short chain in the polymer affects on the properties of LLDPE, such as thermal properties, physical properties and mechanical properties. The LLDPE produce plastic wrap and stretch wrap.

2.2 Background on metallocene catalyst

2.2.1 Metallocene catalyst

In 1951 Wilkinson and Woodward discovered metallocene catalyst in the form of ferrocene as shown in Figure 2.3 [13].

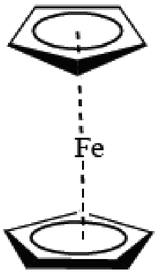


Figure 2.3 The structure of ferrocene [13]

After that, the others metallocene catalysts were synthesized for production of polymer. Metallocene is a special member, a class of organometallic compounds with a single site of active center leading to a narrow molecular distribution ($M_w/M_n=2$) [2]. The “sandwich compound” was the structure of metallocene catalyst because a л-bonded metal atom is positional between two aromatic ring systems. The simple structure of metallocene catalyst is shown in Figure 2.4.

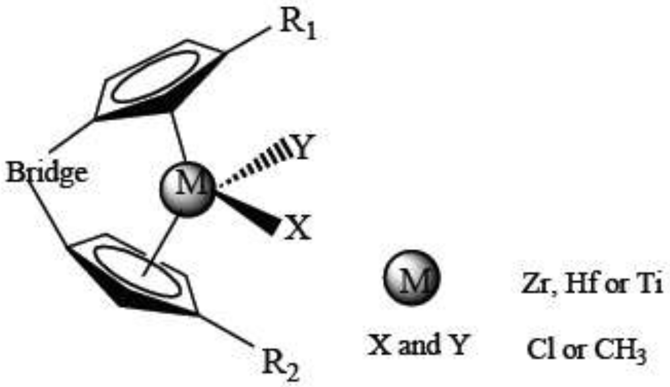


Figure 2.4 The simple structure of metallocene [13]

The simple structure of metallocene catalyst as described below

M is the center metal, normally Ti, Zr and Hf.

X and Y are halogen, normally Cl or methyl group (Me).

R_1 and R_1 are substituent, normally H or Me.

The properties of catalyst depend on different structures of metallocene such as type of ligand, type of substitution on ligand, type of substitution on ligand, the bridging between ligand, the metal and the cocatalyst. The structures of metallocenes that are used in the polymerization of olefins are shown in Figure 2.5 [5].

Metallocene catalysts must to be activated before using in ethylene polymerization. The metallocene catalyst can be activated by cocatalyst such as methylaluminoxane (MAO), triethylaluminum (TMA), triethylaluminum (TEA), triisobutylaluminum (TIBA) and cat ion forming agents. The methylaluminoxane (MAO) is the most widely used activator for metallocene catalyst. In addition, MAO performs as a scavenger by reacting with impurities such oxygen and water in the system. The structures of MAO as shown in Figure 2.6 [5].

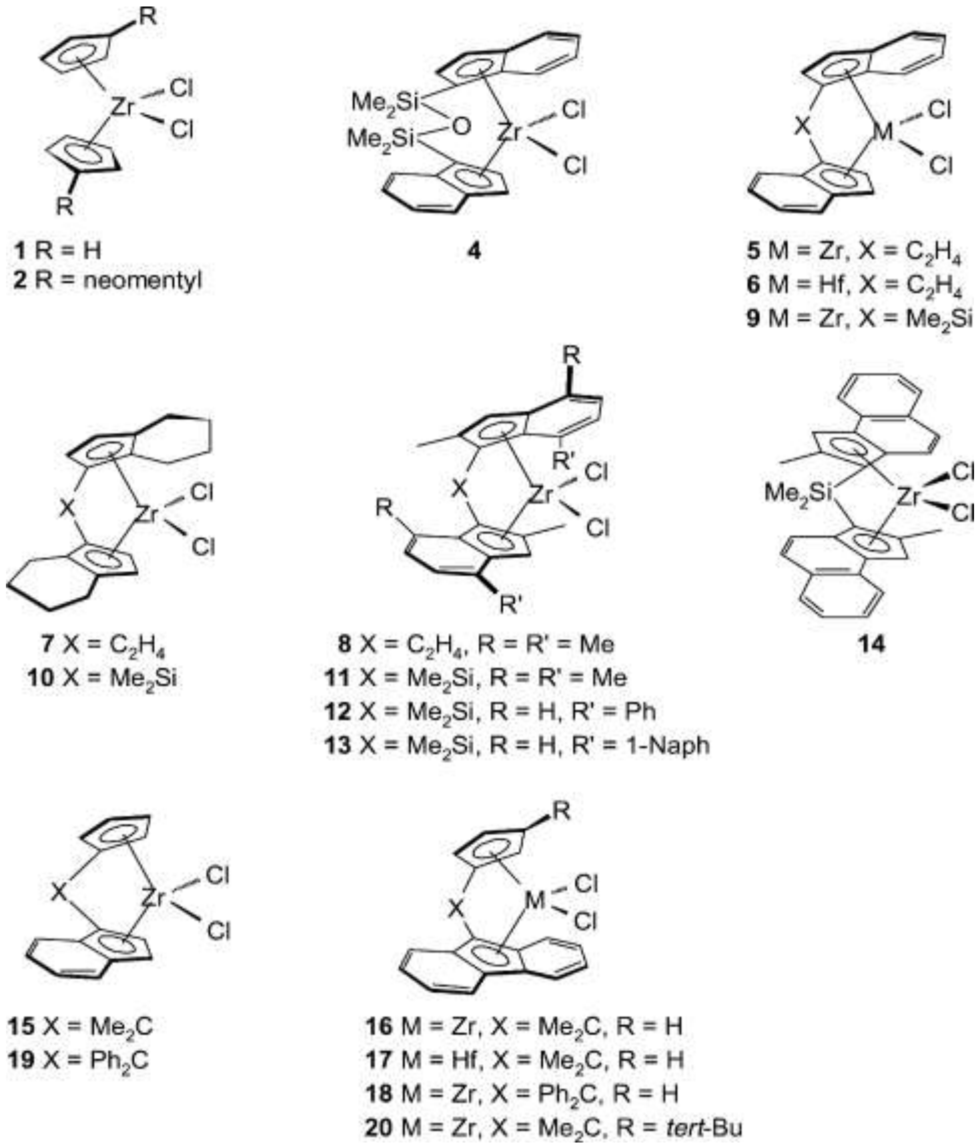
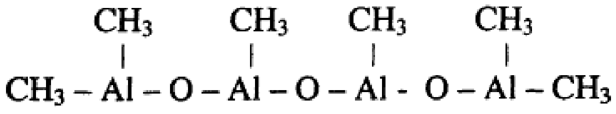


Figure 2.5 The structures of metallocenes that are used in the polymerization of olefins [5]



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{Al}}-O-\overset{\displaystyle CH_3}{\overset{|}{Al}}-O-\overset{\displaystyle CH_3}{\overset{|}{Al}}-O-\overset{\displaystyle CH_3}{\overset{|}{Al}}-CH_3}$$

Methylaluminoxane

Figure 2.6 The linear structures of MAO [5]

Rac-ethylenebis(indenyl)zirconium dichloride [Et(Ind)$_2$ZrCl$_2$] catalyst propose the *rac* form and these structure so called ansa-metallocenes. The ansa-metallocenes catalyst is chiral metallocene catalyst possesses C$_2$-symmetry. It can be activated by methylaluminoxane (MAO) to produce isotactic polyethylene. The stereochemical is controlled by the chiral ansa-indenyl ligands. *The ansa*-C$_2$ symmetric metallocene catalyst is widely used in industrial applications because it is highly iso-selective in ethylene polymerization and gives high activity. The activated form of rac-ethylenebis(indenyl)zirconium dichloride [Et(Ind)$_2$ZrCl$_2$] is shown in Figure 2.7 [14].

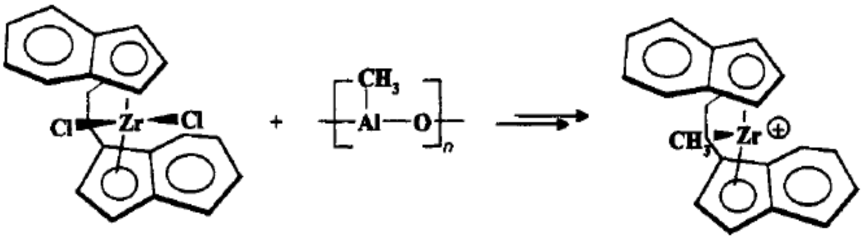


Figure 2.7 The activation of Et(Ind)$_2$ZrCl$_2$ [14]

2.3 Heterogeneous catalytic system

The commercial for the ethylene polymerization attract metallocene catalysts and methylaluminoxane (MAO) as a cocatalyst. However, homogeneous metallocene catalytic system has disadvantages such as the lack of morphology control of the polymer and reactor fouling. Another important disadvantage is the requirement of large amount of MAO must to achieve highest catalytic activity [15]. Therefore, the solving problem of metallocene catalyst is binding metallocene catalysts onto inorganic support. The heterogeneous metallocene catalytic system has several advantages such as improve product morphologies and able to be used in gas-phase and slurry-phase reactors.

There are three methods to prepare supported metallocene as follows [15]:

Method 1: This method is the binding of metallocene on the support (modified by previous treatment or not). At first, the metallocene catalyst is reacted with the support or filler in a solvent such as toluene or hexane. After that, the mixing solution is filtrated to obtain solid section and washed with a hydrocarbon. This method operates at room temperature or high temperatures and adequate contact time. The important parameters are mixing temperature and the contact time.

Method 2: The basic fundamental of this method is reaction of MAO as cocatalyst with the support, followed by reaction of the metallocene catalyst. At first, the support is attached with MAO in a solvent such as toluene or hexane under room temperature. After that, it is filtration and washing with toluene. Then, it is reacted with metallocene compound.

Method 3: The third method is synthesis of metallocene catalysts which ligands are chemically bonded with the support. First step, the cyclopentadienyl of ligands attach to support, followed by add the metal compound such as zirconium chloride onto the carrier. After that, the support is filtered and washed with toluene or hexane, and then it is dried under vacuum. The MAO or trialkylaluminum of cocatalyst can be used with the support of metallocene catalyst.

2.4 Polymer nanocomposite

2.4.1. Nanoclay

The polymer nanocomposite was the important development in the nanotechnology which started during the 1990 [16]. It is well know that the polymer nanocomposite is two-phase substance offer from polymer matrix and nanofiller. The nanofiller improve mechanical properties, barrier properties and flame resistance. The nanoclay such as Montmorillonite, hectorite or saponite are used as nanofiller. The crystal structures include stacked layers of two silica tetrahedral link with an edge-shared octahedral sheet of alumina as show in Figure 2.8 [17].

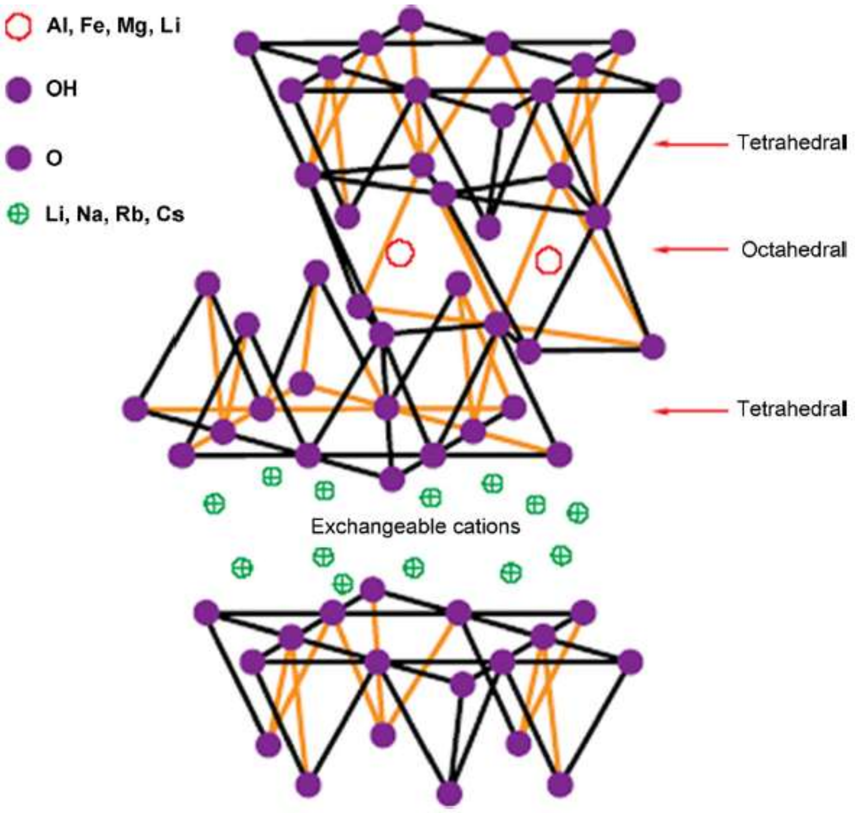


Figure 2.8 The structure of 2:1 layered silicates [17]

The most widely use of the layered silicates is montmorillonite (MMT) because of its natural abundance and high aspect ratio. The crystal structure of MMT has layer charges because of isomorphic substitution. The octahedral sheet occur substitutable with Mg^{2+} and Fe^{2+} for Al^{3+} as shown in Figure 2.9.

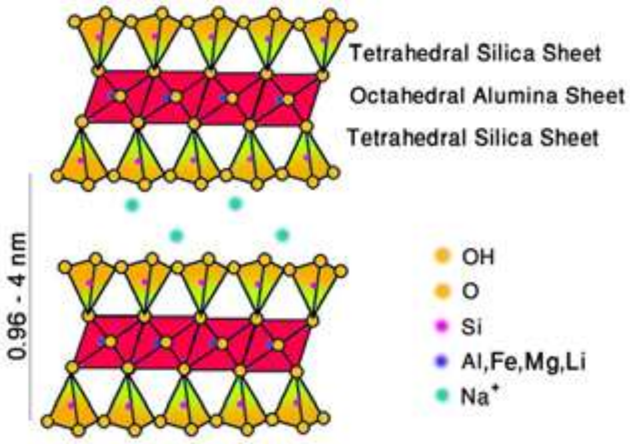


Figure 2.9 Structure of sodium montmorillonite [18]

2.4.2 Degree of dispersion

The nanoclay is hydrophilic material but polyethylene is hydrophobic. Therefore, the nanoclay does not well disperse in hydrophobic polyolefin. The one way to solving the problem is addition compatibilizer to system. The compatibilizer blended between nanoclay and polymer. The modification of support influenced the degree of dispersion. The degree of dispersion divided into three levels, which are shown in Figure 2.10 [16]. The first level is phase separated. The polymer and clay separated two phases, which are observed in a one material and polymer does not enter between clay plates. The second level is intercalated. Polymer insert between clay plates, which it increased interlayer spacing. The third level is exfoliated. The polymer matrix and the plates of clay have compatible blender. This structure is called the nanostructure.

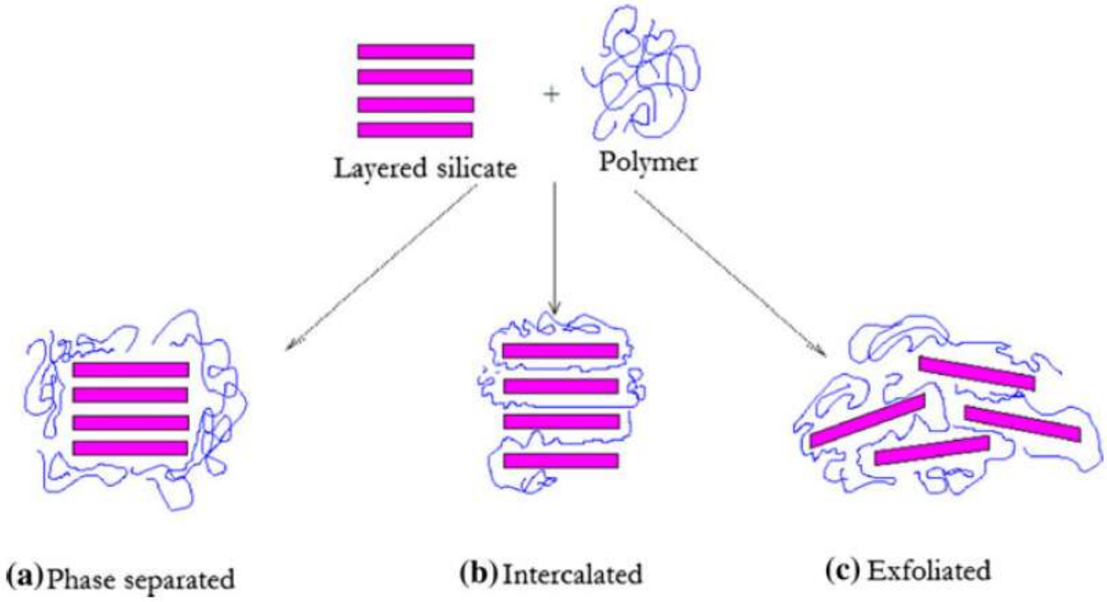


Figure 2.10 The three degree of dispersion for nanofiller in polymeric matrix [16]

The wide angle X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) was used for the degree of dispersion in polymer matrix. The interlayer spacing between individual platelets was determined by the peak of XRD curve with Bragg’s equation [19]. The Bragg’s equation is $2d\sin\theta = n\lambda$, where n is the order of reflection which may be any integer (1, 2, 3, . . .), λ is the wavelength of incident wave, θ is the complement of the angle of incidence, and d is interlayer spacing between individual platelets. In addition, Transmission Electron Microscopy (TEM) gives qualitative data on the dispersion of nanoclay. Moreover, the relationship between amount of sample and structural, morphological data is very small but the sample must be related to mechanical and rheological properties.

2.4.3 Preparation of polymer nanocomposite

The polymer nanocomposites were synthesized by divided three method: (i) solvent solution, (ii) melt compounding and (iii) *in situ* polymerization.

The first method is solvent solution, which it can be used as the reaction medium. The advantages of solvent solution are decreasing the viscosity of the bulk medium and dispersed the heat more uniformly. For solvent solution process, the nanofiller are added to polymer solution with solvent. The solvent can be soluble polymer and monomer but cannot soluble the nanoclay, which it integrate the polymer and filler molecules. After polymerization, the polymer solution was evaporative by solvent vaporization. The polymer can be non-volatile remain and cooling of the solution due to precipitation of the polymer. The precipitate can be concentrated and dried under vacuum. However, solvent vaporization process is natural difficulty in removing the last region of solvent from the polymer. The difficulty in removing of solvent because the solution more concentrated and viscosity increases. In addition, the solvent is not environmentally-friendly and the cost of solvent increase.

The second method is melt compounding process, which it operates at high temperature. The polyolefin such as polypropylene, polyethylene, and polystyrene has high molecular weight polymers leading to melted at high temperature. The nanofiller is pressed and mixed thoroughly with the polymer matrix melt due to a uniform dispersion and distribution of the nanofiller. The melt compounding process operated at high temperature. At high temperature, this method affect to concern with regards to surface modifications. The surfaces of nanoclay have an onset of degradation about

200°C. The 200°C is most temperature using for used for melts compounding of the polyethylene.

The third method is *in situ* polymerization. The preparation of exfoliated and intercalated polymer/clay nanocomposites commonly used this method. It has long been known that *in situ* polymerization divided two basic stages. The first method, the nanoclay was added to the liquid monomer. After that, *in situ* polymerization is occurred in the appearance of clay. The direct interaction between catalyst and surface of nanofiller cause distribution in polymer. The degree of dispersion is exfoliation and intercalation of clay in the polymer matrix. The *in situ* polymerization produce polymer nanocomposite due to the dispersion of viscosity. The important factor such as mixing temperature, time, shearing speed, molecular weight of polymer and incorporation of nanofillers are controllably the flow nature of the mixture. Low viscosities propose better flow ability and more homogeneous mixing. Moreover, low viscosity is more homogeneous mixing and better flow ability, which it assisted removing bubbles before chemical reactions.

2.4.4 Clay supported metallocene

The nanoclay is the one type of the supports for metallocene catalysts. Polymer nanocomposites (PNC) are dispersed in the polymer matrix due to improve the properties of the polymer even when a small amount of filler is used. In addition, the degree of dispersion of nanofiller relates to improvement in barrier and mechanical properties of polymer/clay nanocomposite.

Zhao et al. [7] studied polyethylene/clay composites that were prepared by melt compounding polyethylene and montmorillonite clay organically modified with different intercalating agents. The mechanical properties of PE and PE/clay composites, with increasing clay loading affects on the strength and modulus of PE/clay composites increase, but the impact strength decreases. The thermal stability of the PE/clay nanocomposites was determined by thermogravimetric analysis (TGA). PE/clay nanocomposites are more stable than pure PE.

Panupakorn et al. [20] synthesized PE/clay nanocomposites via in situ polymerization. The nanoclay as support of metallocene catalyst was studied. This research proposes to evaluate the types of nanoclay, amount of nanoclay and aging time between clay and MAO on activity. The result show clay particles are satisfactory dispersed in the polyethylene matrix. Clay TOB_2 show higher activity of polyethylene/clay nanocomposite than TOB_3 because different amine group content in the clay mineral. For effect of clay loading on catalytic activity, it was found that amounts of nanoclay increased with decreasing catalytic activities. The amount of clay with addition 5% by weight show maximal thermal properties and percentage of the crystallinity (X_c). Finally, the effect of aging time on catalytic activity revealed that increasing the aging time resulted in a slight decrease of catalytic activity. The maximum catalytic activity is addition of 5% by weight of clay.

Kuo et al. [21] investigated preparation of *in situ* polymerization with metallocence catalyst and montmorillonite (nanoclay) as support. The catalytic activity of polyethylene decreases with increasing the amount of the clay feed. The different polymerization Routes 1–3 affect on activity and clay content. For Route 1, the nanoclay was mixed directly with catalyst. Then, MAO as cocatalyst and the ethylene monomer added to system at room temperature. Route 2, the nanoclay was mixed with the MAO co-catalyst at 30°C for 1.5 hours. After that, it mixed with the metallocence catalyst at 55°C for 0.5 hours. Route 3, the nanoclay was mixed and agitated with MAO co-catalyst at 30°C for 2.5 hours. Then, it then mixed with the metallocence catalyst at 55°C for 2 hours. The result shows that Routes 2 and 3 show higher catalytic activities than Route 1 under similar reaction conditions due to the free spaces between the clay layers can deactivate of the metallocence catalyst. A comparison of Routes 2 and 3 shows that the time with clay mixture is treated with MAO does not improve the activity.

Zapata et al. [10] studied the preparation of PE/clay nanocomposites by *in situ* polymerization method divided two routes: (1) ethylene polymerization with the homogeneous metallocene catalyst using the clay particles, and (2) ethylene polymerization with the clay-supported metallocene. The nanoclay was treated by

ODA before treated with MAO. The metallocene catalyst was directly bindingness on the nanoclay. The clay-organomodifier agent is octadecylamine (ODA), which it is widely used in preparation of polyethylene nanocomposites. The resulted show the effect of these different preparation procedures on the catalytic activity. Routes 1, homogeneous polymerization system with clay particles shows the catalytic activity of clay particles higher than the pure system. The catalytic activity of addition O-Clo show lower than Na-Clo because deactivation of the ODA amino group on the metallocene catalyst. Routes 2, polymerization used clay-supported metallocene catalyst. The catalytic activity of Na-Clo as support show resulted lower than homogeneous system. The ODA-modified clay was used as metallocene support, the catalytic activity increase with the zirconium content. The metallocene supported on MAO-treated clays shows the MAO treatment of ODA-intercalated clay (Cat/MAO/O-Clo) yields higher activity than the clay in sodium form (Cat/MAO/Na-Clo). Transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD) show the layer clay exfoliated into polymer matrix

2.4.5 Modification of supports by silane

However, the prepration of materials is very difficult because polyolefins are hydrophobic and montmorillonite is hydrophilic. Thus, the preparation of polymer/clay nanocomposite requires a modification of clay mineral by adding compatibilizer to the system such as amino acid, alkylammonium and silane.

Silane is one of the compositions of silicon which is the element of nanoclay. Thus, the composition like clay, low cost and the silane modification is varying favor to many researchers.

Rao et al. [22] reported the experimental result in the stability of aerogels and demonstrating the structure improving the hydrophobic and physical properties of silica aerogels. The chlorine containing organosilane reacts with the surface OH groups and water to yield HCl as per the following chemical reaction.

$$\equiv \mathrm{Si-OH} + \mathrm{Cl_xSi(R)_{4-x}} \rightarrow \equiv \mathrm{Si-O-Si(R)_{3-x}Cl_{x-1}} + \mathrm{HCl} \qquad \text{(I)}$$

$$\mathrm{(R)_{4-x}SiCl_x} + \mathrm{H_2O} \rightarrow \mathrm{(R)_{4-x}SiCl_{x-1}OH} + \mathrm{HCl} \qquad \text{(II)}$$

Where x=1, 2 or 3 and R is an alkyl group.

Jongsomjit et al. [23] developed of silane modification on the copolymerization of ethylene with higher α-olefins. It was found that the activity of copolymerization between ethylene and 1-hexene increased about four times with the silane modification on the support. The silane modification could result in less steric effect on the support surface. Moreover, the MW of polymer show decreased about a half with silane modification because the occurrences of chain transfer reaction.

CHAPTER III

EXPERIMENTAL

In the present study, effect of silane-modified clay on polyethylene/clay nanocomposites prepared by *in-situ* polymerization with zirconocene/MAO catalyst upon various conditions was investigated. The experiments were divide into four parts as follows:

(i) Preparation of catalyst precursor
(ii) Supporting preparation
(iii) Ethylene polymerization
(iv) Characterization of nanoclay and PE/clay nanocomposite

All chemicals and procedure of experiments were listed below.

3.1 Chemicals

All chemicals in this study are listed in Table 3.1 as follows:

Table 3.1 Chemicals used in experiments.

NO.	Chemicals	Supplier	Details
1	Ethylene gas	Linde (ThailandCo., Ltd.	99.9%
2	Methylaluminoxane	Aldrich Chemical company	10% in toluene
3	Rac-ethylenebis(indenyl) zirconium dichloride	Aldrich Chemical company	-
4	Montmorillonite (Aluminum Pillared Clay)	Aldrich Chemical company	-
5	Toluene	EXXON Chemical Ltd., Thailand.	-
6	Argon	Thai Industrial Gas Co., Ltd.	99.999%
7	Hydrochloric acid	Sigma.	Fuming 36.7%
8	Methanol	SR Lab	commercial grade
9	1-Hexene	Alrich Chemical Company, Inc.	99+%

3.2 Equipment

All the equipments were used in experiment as listed below.

3.2.1 Glove Box

Glove Box (30905C system) was used in experiment from Vacuum Atmospheres Company of United States of America. The function of Glove Box was used for the preparation of catalyst and prevents catalyst deactivation without oxygen and moisture.

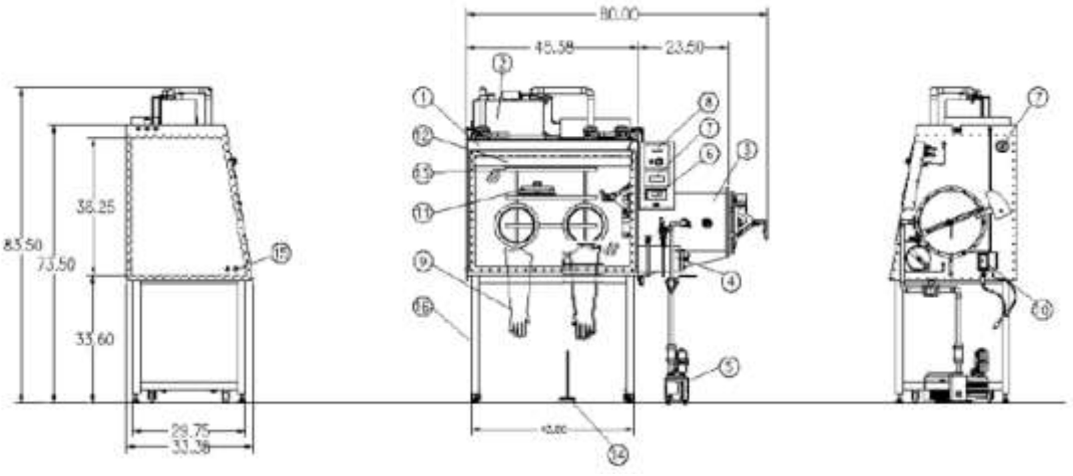


Figure 3.1 Glove box schematic diagram

1. Omni vac chamber
2. Purification unit
3. 15”dia x 24”lg. antechamber
4. 6”diz x 12”lg. mini antechamber
5. Vacuum pump, 4.1cfm
6. Control panel
7. Moisture analysis (Optional)
8. Oxygen analysis (Optional)
9. Butyl rubber glove
10. Electrical J-Box
11. Glove port cover
12. Fluorescent light
13. Shelves
14. Foot switch
15. Feedthru, ¼” NPT, 2 PL
16. Support frame

3.2.2 Schlenk Line

Schlenk Line consists of vacuum system and argon gas. The first part is vacuum system. The vacuum system is equipped with the solvent trap and pump, respectively. The vacuum system is connected directly to the solvent trap. The second part is purified inert gas. The inert gas was used in the experiment is argon gas. The argon gas is passed through glass tubing containing quartz wool and sodium hydroxide (NaOH) for increasing pressure drop.

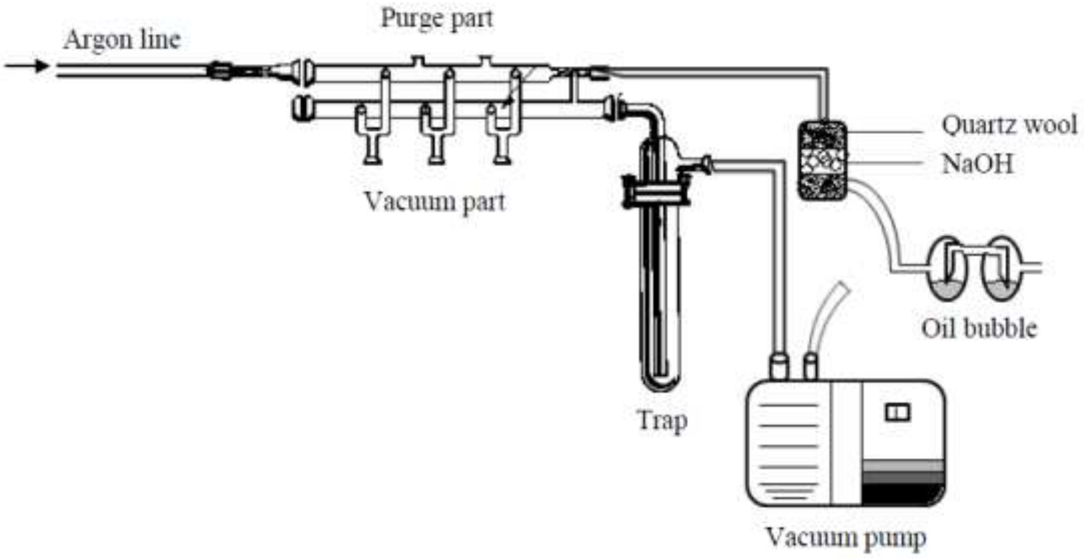


Figure 3.2 Schlenk line

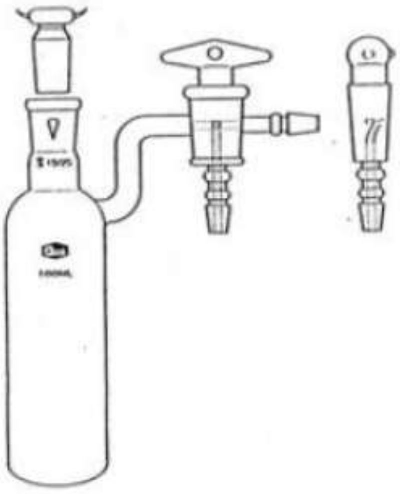


Figure 3.3 Schlenk tube

3.2.3 Schlenk tube

A tube consists of a ground glass and a side arm. The side arm is three-way glass valve. The sizes of schlenk tubes are 50, 100 and 200 ml used for calcination of nanoclay and keeping chemicals because sample was sensitive to oxygen and moisture.

3.2.4 Vacuum pump

Vacuum pump (model 195) was used in the experiment from Labconco Coporation. The effective of vacuum pump was 10^{-4} – 10^{-3} mmHg pressure. The range of pressure supplied for the vacuum line in the Schlenk line. The chamber or piping was connected to vacuum pump.

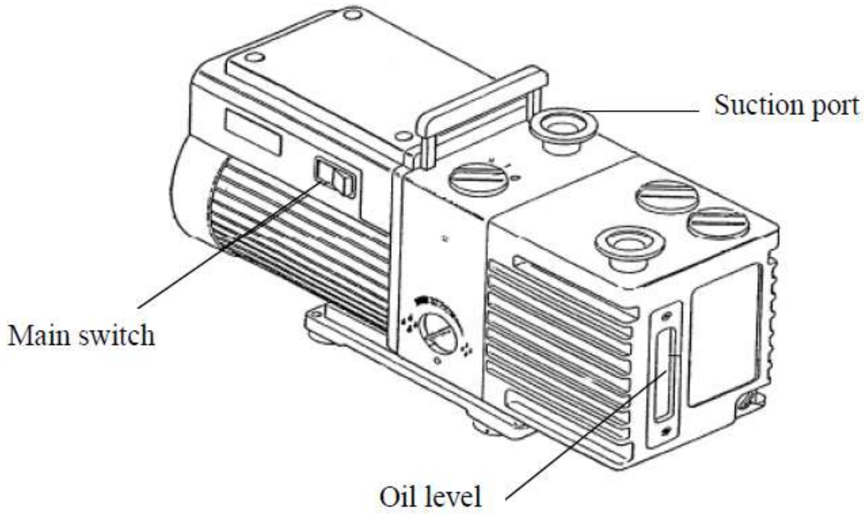


Figure 3.4 Vacuum pump

3.2.5 Magnetic Stirrer and Hot Plate

The magnetic stirrer and hot plate model RCT basic and C-MAG HS7 from IKA Labortechnik were used.

3.2.6 Reactor

A 100 ml semi-batch stainless steel autoclave reactor with a magnetic stirrer was used as the polymerization reactor.

3.2.7 Inert gas purification system

Argon gas (Ar) was used for preparation of catalyst and ethylene polymerization. The argon purification system consists of molecular sieve, columns of BASF catalyst R3-11G, and dehumidify unit. The role of molecular sieve required removal moisture. The BASF catalyst R3-11G acts as a scavenger leading to increased catalytic activity. The activity increases because argon gas removes oxygen contamination before preparation of catalyst and polymerization.

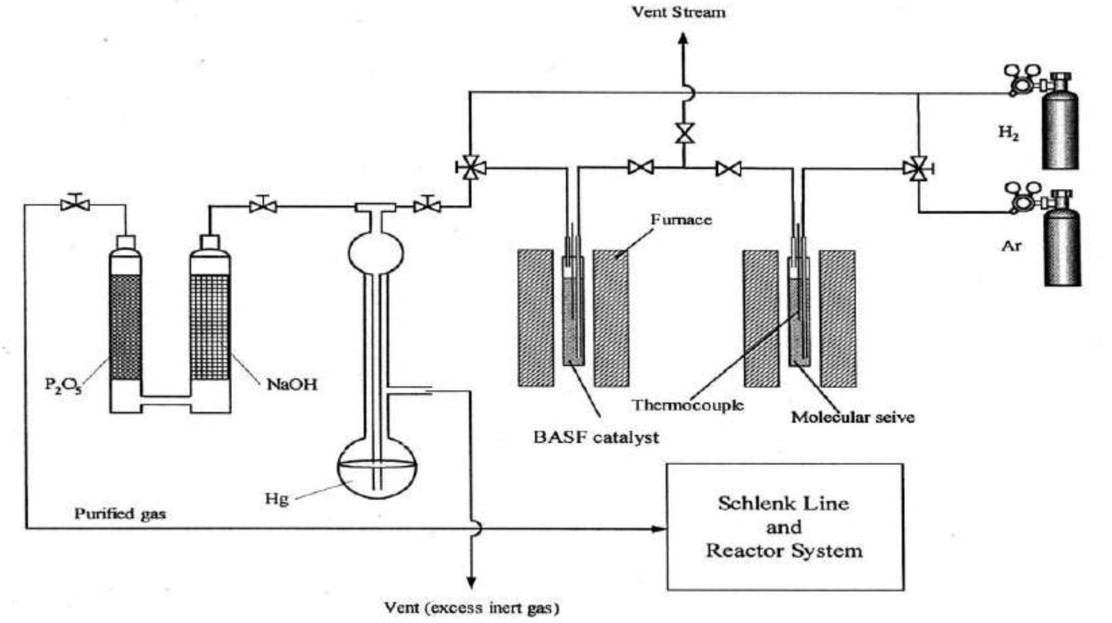


Figure 3.5 Inert gas purification system

3.3 Preparation of catalyst precursor

In the glove box, $Et(Ind)_2ZrCl_2$ amount 0.0083 g (1.98x10^{-5} moles) was added in 20 ml of toluene. After that the mixture was stirred at 700 rpm for 60 minutes or until giving yellow transparent solution.

3.4 Supporting preparation

3.4.1 Preparation of nanoclay

The nanoclay was heated at 150°C for 2 hours under argon atmosphere in order to remove impurities such as oxygen and moisture in nanoclay.

3.4.2 *In situ* clay-supported methylaluminoxane impregnation

In the glove box, the first step was the desired amount of the nanoclay and methylaluminoxane (MAO) ($[Al]_{MAO}/[Zr]=1135$) was added to reactor, respectively. Then, the mixture was stirrer for 30 minutes at room temperature.

3.4.3 *Ex situ* clay-supported methylaluminoxane impregnation

In the glove box, the first step was preparation of round bottom flask with magnetic stirrer. The second step, 1 g of clay was heated at 150°C for 2 hours under argon atmosphere and it was added into a round bottom flask. Then, 20 ml of toluene and the desired amount of methylaluminoxane were added into the round bottom flask, respectively. After that, the mixture was stirrer at 700 rpm for 30 minutes. In the third step, the mixture was removed by evacuation at room temperature. Then, the clay-supported methylaluminoxane was washed by toluene 5 times and it was dried under vacuum. Finally, the powder of clay-supported methylaluminoxane was obtained.

3.4.4 Modified clay

The nanoclay was treated by $SiCl_4$ because it can improve surface properties. In the first step, nanoclay was heated at 150°C for 2 hours under argon atmosphere. 1 g of nanoclay and 20 ml of toluene were added into a round bottom flask with magnetic stirrer, respectively. Then, the mixture was added by the desired amount of $SiCl_4$. In the second step, the mixture was stirred at 700 rpm for 1 hour. After that solvent was removed by evacuation at room temperature. The clay supported- $SiCl_4$ was washed by toluene 5 times and it was dried under vacuum.

3.5 Ethylene polymerization

All experiment was conducted under argon atmosphere using Schlenk techniques and glove box.

3.5.1 *In situ* ethylene polymerization

The ethylene polymerization reaction was implemented in a 100 ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 5 wt% of the nanoclay and 1.1 ml of methylaluminoxane (MAO) ($[Al]_{MAO}/[Zr]=1135$) were added to reactor. Then, the mixture was stirred at 700 rpm for 30 minutes aging at room temperature. After that the $Et(Ind)_2ZrCl_2$ 1.5 ml ($5x10^{-5}$ M) was added to the reactor and filled with toluene to make total volume of 30 ml. In the second step, the reactor was frozen in liquid nitrogen to stop reaction for 10 minutes and it was removed argon by evacuation. In the third step, the reactor was heated up to 70°C of polymerization temperature. The reaction was produced when 0.018 mol of ethylene was fed into the reactor. In the fourth step, after ethylene was consumed (6 psi from pressure gauge), the reaction was terminated by filling of acidic methanol (0.1% HCl in methanol) and stirred over night. After that the mixture was filtered, it was dried at room temperature. Finally, the white power of polymer was obtained.

3.5.2 Ethylene/1-hexene copolymerization

The ethylene polymerization reaction was implemented in a 100 ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 5 wt% of the nanoclay and 1.1 ml of methylaluminoxane (MAO) ($[Al]_{MAO}/[Zr]=1135$) were added into reactor. Then, the mixture was stirred at 700 rpm for 30 minutes aging at room temperature. After that the $Et(Ind)_2ZrCl_2$ 1.5 ml ($5x10^{-5}$ M) was added to the reactor and filled with toluene to make total volume of 30 ml. In the second step, the reactor was frozen in liquid nitrogen to stop reaction for 10 minutes and 1-

hexene (ethylene:1-hexene = 1:0.25) was put into the reactor. Then, the reactor was removed argon by evacuation. In the third step, the reactor was heated up to 70°C of polymerization temperature. The reaction was produced when 0.018 mol of ethylene was fed into the reactor. In the fourth step, after ethylene was consumed (6 psi from pressure gauge), the reaction was terminated by filling of acidic methanol (0.1% HCl in methanol) and stirred over night. After that the mixture was filtered, it was dried at room temperature. Finally, the white power of polymer was obtained.

3.6 Characterizations

3.6.1 Characterization of nanoclay

3.6.1.1 X-ray Diffraction analysis (XRD)

XRD was used to determine crystalline size, functions and interlayer spacing of nanoclay. The sample was put into plastic sample holder and excess sample was cut by glass side for smooth texture. An XRD pattern of nanoclay was observed using a BRUKER D-8 Advance X-ray Diffractometer at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The observation was proceeded by using CuK_α radiation with Ni filter and the operating conditions for measurement are listed below;

2θ range of detection	: 10-80°
Resolution	: 0.04°
Number of scan	: 10

3.6.1.2 Thermal Gravimetric Analysis (TGA)

TGA was used to determine thermal stability in terms of percent weight and temperature. The preparation of sample contained weighing a crucible and setting it on a tray. The crucible was loaded with the sample about 2-3 mg. Sample was analyzed by thermal gravimetric, SDT analyzer Model Q600 from TA Instrument at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The analysis was carried out under nitrogen atmosphere gas at gas flow rate of 100 ml/min. The sample was heated form 50°C to 800°C at a constant rate of 10°C/min, and then cooled simultaneously.

3.6.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to identify specific structural characteristics of the chemical group from the vibration properties such as functional group or molecular structure. The sample was weighted a small amount directly on the NaCl plates. The Nanoclay was analyzed by Nicolet 6700 FTIR spectrometer, which belongs to Mektec Manufacturing Corporation (Thailand) Ltd. at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University.

3.6.2 Characterization of PE/clay nanocomposites

3.6.2.1 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX)

SEM was used to observe the morphology of polymer nanocomposites and the dispersion of nanoclay in polymer matrix. The sample must be conductive to prevent charging by coating with gold particle by ion sputtering device. The sample was analyzed by JEOL model JSM-5800LV scanning electron microscopy and energy dispersive X-ray spectroscopy was analyzed by Link ISIS Series 300 program at Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

3.6.2.2 Differential Scanning Calorimetry (DSC)

DSC was used to determine the thermal properties especially melting temperature (T_m) in terms of heat flows as a function of time and temperature. The sample was prepared about 3-13 mg prior to use. The heating cycle was run 2 times. In the first scan, sample was heated from 50-150 °C for sample melt before first used and cooled to room temperature. Then, the sample was reheated in the second scan. The melting temperature was determined by a Perkin-Elmer diamond DSC from MEKTEC, at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The analyses were achieved at the heating rate of 20°C/min.

3.6.2.3 Thermo Gravimetric Analysis (TGA)

TGA was used to determine thermal stability in terms of percent weight and temperature. The preparation of sample contained weighing a crucible and setting it on a tray. The crucible was loaded with the sample about 2-3 mg. Sample was analyzed by thermal gravimetric, SDT analyzer Model Q600 from TA Instrument at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The analysis was carried out under nitrogen atmosphere gas at gas flow rate of 100 ml/min. The sample was heated form 50°C to 800°C at a constant rate of 10°C/min, and then cooled simultaneously.

3.6.2.4 X-ray Diffraction analysis (XRD)

XRD was used to determine crystalline size, functions and interlayer spacing of PE/clay nanocomposite. The sample was put into plastic sample holder and excess sample was cut by glass side for smooth texture. An XRD pattern of nanoclay was observed using a BRUKER D-8 Advance X-ray Diffractometer at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The observation was proceeded by using CuK_α radiation with Ni filter and the operating conditions for measurement are listed below;

2θ range of detection	: 10-80°
Resolution	: 0.04°
Number of scan	: 10

3.6.2.5 Transmission Electron Microscopy (TEM)

TEM was used to investigate the degree of dispersion of nanoclay in the polymer matrix. Sample was analyzed by JEM-2100 transmission electron microscopy at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of nanoclay

4.1.1 Size and composition

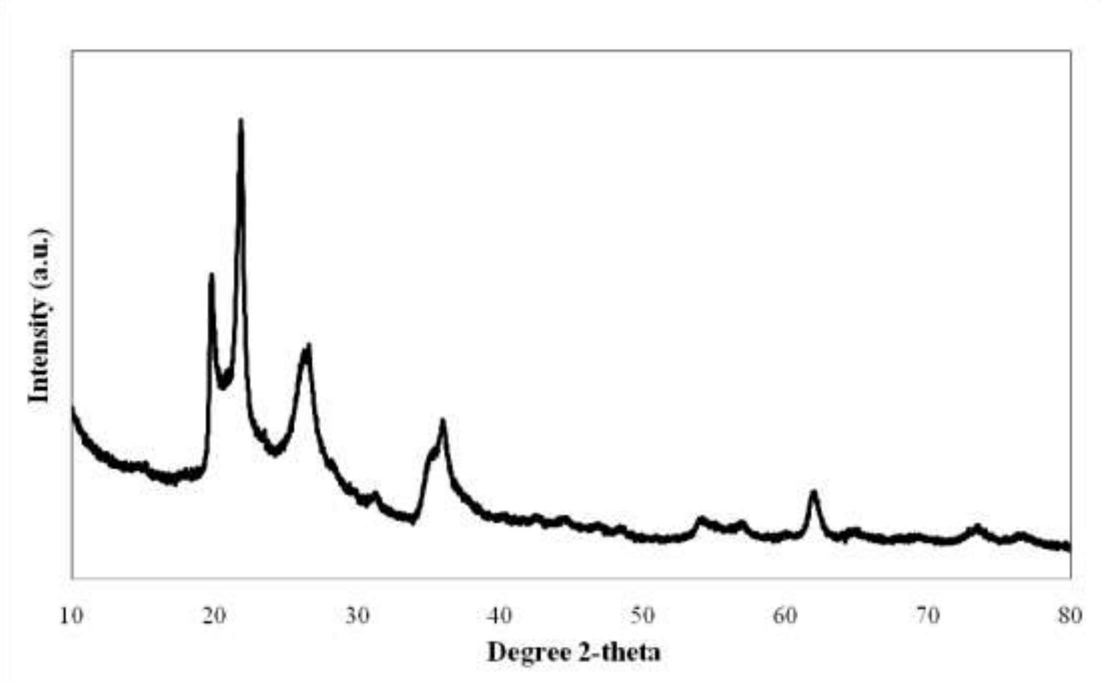


Figure 4.1 shown XRD patterns of nanoclay

The nanoclay was widely used to obtain polymer nanocomposite because the nanoclay are nano size and disperse in the polymer matrix due to improve the properties of the polymer. The most commonly use of structure is montmorillonite (MMT). Montmirillonite was commonly used because it is easy to insert the polymer between its layers. The XRD patterns of nanoclay are shown in Figure 4.1. The size of nanoclay was investigated by X-ray diffraction. From Debye-Scherrer formula [24], it was found that the average crystallite size of nanoclay is 11.2 nm and d-spacing (the interplanar spacing between the atoms) is 17.49 Å. The peaks of nanoclay structure are (2θ) 20, 26.5 and 36° corresponding to the montmorillonite crystalline structure. The peaks of montmorillonite crystalline structure in the position (2θ) 5° as well as, 20 and 26.5° are the quartz commonly found in nanoclay [25].

The surface area of nanoclay is 184 m^2/g having pore volume of 0.19 cm^3/g and the pore size of 4.28 nm.

4.1.2 Thermal stability

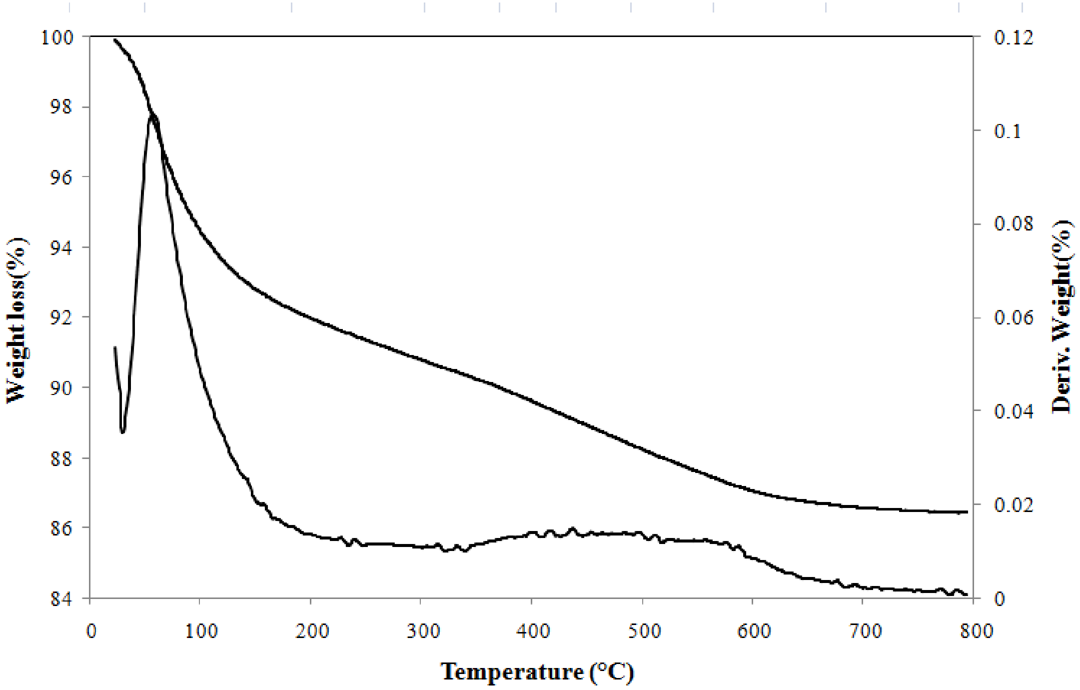


Figure 4.2 Thermal stability of nanoclay

Thermal stability of nanoclay was investigated by the TGA measurement. The TGA curve is shown in Figure 4.2 and the onset temperature of nanoclay is 70°C. The thermal stability of nanoclay at 5% and 10% weight loss temperature is 90°C and 371°C, respectively. Generally, the weight loss temperature of unmodified clay (Na^+-Montmorillonite) is about 100°C because the interlayers between clay plates contain moisture. From Figure 4.2, the weight loss temperature was observed about 200°C due to the decomposition of the alkyl aluminum salt.

4.1.3 Morphology

The morphology of nanoclay was determined by scanning electron microscopy (SEM) as shown in Figure 4.3. The particle is rough surface and clay particles agglomerate.

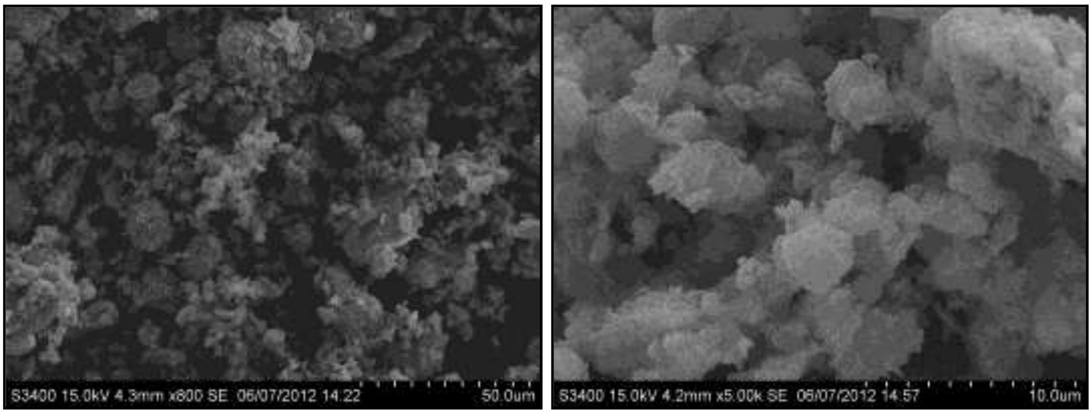


Figure 4.3 Morphologies of clay

PART 1: A comparative study on LLDPE/clay nanocomposites synthesized by different impregnation methods

4.2 Ethylene polymerization

There were 6 systems for PE and LLDPE in this comparison. All chemical such as catalyst, MAO and co-monomer were in liquid phase, but ethylene introduced in gas phase. The nanoclay was used as support and additive in the heterogeneous system.

Table 4.1 Polymerization data with nanoclay/Et(Ind)$_2$ZrCl$_2$/MAO.

run	Sample	Impregnation method	Polymer[a] yield (g)	Activity[b] (kg PE/mol Zr.h)
1	PE	-	0.8375	15,931
2	PE/clay	*in situ*	0.6582	9,184
3	PE/clay/MAO	*ex situ*	0.7211	6,637
4	LLDPE	-	0.1072	18,250
5	LLDPE/clay	*in situ*	0.8607	13,414
6	LLDPE/clay/MAO	*ex situ*	0.4599	7,828

[a] The yield of polymer was limited by ethylene fed (0.018 mol). The molar ratio of ethylene:comonomer was 4:1.

[b] The activities were measured by polymerization temperature of 70°C, [ethylene] = 0.018 mol, $[Al]_{MAO}/[Zr]_{cat}$ = 1135 in toluene with total volume = 30 ml, $[Zr]_{cat} = 5\times10^{-5}$ Molar and mixing time of MAO and nanoclay was 30 minutes.

The catalytic activities of metallocene catalyst were investigated during copolymerization of ethylene and 1-hexene as shown in Table 4.1. From this table, for the metallocene catalytic system, the heterogeneous systems (*in situ* impregnation and *ex situ* impregnation method) show lower activity than the homogeneous system because the nanoclay could result in more steric affect on the system. It is well know that the disadvantage of the heterogeneous system is support surface generating active sites with low propagation rate. The support is steric hindrance on the heterogeneous system due to the lower generation of active sites. Generally, the interaction of MAO on the support surface is strong interaction because lower generation of active sites. Another reason, the ethylene could result in more difficult insert to polymer chain leading to the lower catalytic activity. Therefore, the metallocene catalyst of the heterogeneous system usually show lower activity than the homogeneous system because one main reason that is the generation of active site with lower propagation rate due to interactions with the support surface [26].

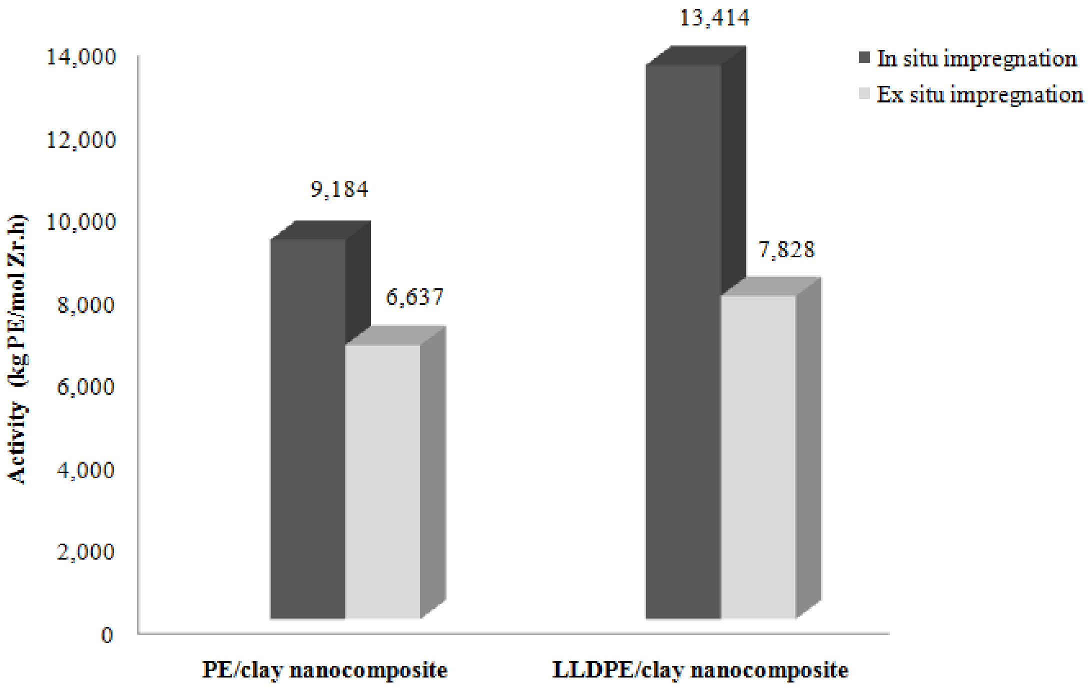


Figure 4.4 Catalytic activities of polyethylene nanocomposites synthesized by different impregnation methods

When focusing on the comparison between both of the heterogeneous systems with different impregnation methods. The *in situ* impregnation method was prepared by impregnating MAO onto the nanoclay for 30 minutes after that introducing it the system during homopolymerization and copolymerization without washing and drying. The *ex situ* impregnation method was prepared by impregnating MAO onto nanoclay after that washing and drying for 5 times. This method finds the amount of aluminum species in the nanoclay support; ICP-OES technique was used. The ratio of $[Al]_{MAO}/[Zr]_{cat}$ has already can been fixes at 1135 in toluene with total volume of 30 ml.

Catalytic activities of the heterogeneous system with zirconocene catalyst were investigated during copolymerization of ethylene and 1- hexane as shown in Table 4.1. From this table, the system with *in situ* impregnation method exhibits slightly higher activity than the *ex situ* impregnation method. The *in situ* impregnation method should have more active species on the surface because this method was done without washing and drying. The *ex situ* impregnation method was prepared by impregnating MAO onto nanoclay after that washing and drying. Therefore, it was disappear of MAO during preparation.

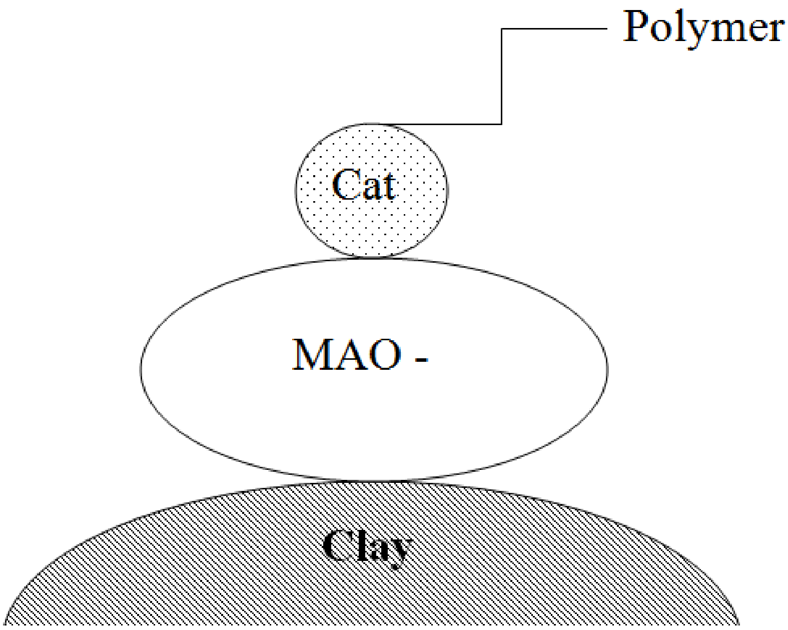


Figure 4.5 Conceptual models indicating the position of species in polymer composites [27]

Based on the results, the system with *in situ* impregnation method exhibits slightly higher activity than the *ex situ* impregnation method because *in situ* impregnation method has more active species on the surface. However, the *ex situ* impregnation method loses active sites during polymerization process. Another reason is strong interaction of MAO and support due to lower activity [27].

4.3 Characterization of LLDPE/clay nanocomposites

4.3.1 Dispersion of nanoclay

Degree of dispersion of nanoclay in polyethylene matrix was measured by small angle X-ray diffraction analysis (SAXRD). The SAXRD patterns of clay, pure polyethylene, PE/clay nanocomposite (*in situ* impregnation) and PE/clay nanocomposite (*ex situ* impregnation) are shown in Figure 4.6. The SAXRD pattern for nanoclay provides diffraction peak at $2\theta = 5.05°$, which is the peak of clay. In the preceding article, the broad peak of XRD curve show high dispersion of nanoclay in polyethylene matrix [25]. The mixing process cause exfoliated degree dispersion of nanoclay. The addition of methylaluminoxane (MAO) during the clay treatment step is reacted with hydroxyl group on clay surface. Then, the metallocene catalyst was reacted with MAO leading to creating covalent bond, which assisted to avoid catalyst leaching during the polymerization [28]. Therefore, the broad peak is well dispersion of nanoclay in the polyethylene matrix. From Figure 4.6, the degree of dispersion is exfoliated level because strong interaction between the polyethylene chains and the clay surface both of *in situ* impregnation and *ex situ* impregnation methods.

Transmission electron microscopy (TEM) images confirm the exfoliated degree dispersion of nanoclay. In Figure 4.7, it was found that the clay particles are randomly dispersed throughout polyethylene matrix. The most clay particle agglomeration is spited to fine particle size.

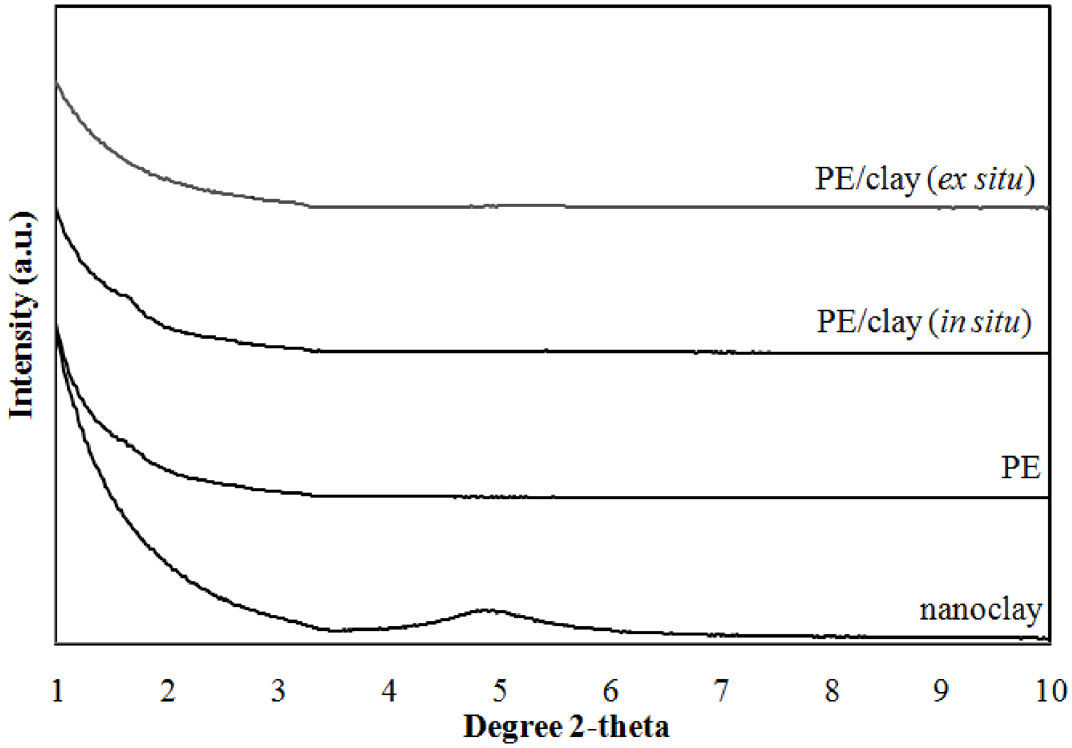


Figure 4.6 XRD patterns of nanoclay, PE, PE/clay nanocomposite (*in situ*) and PE/clay nanocomposite (*ex situ*)

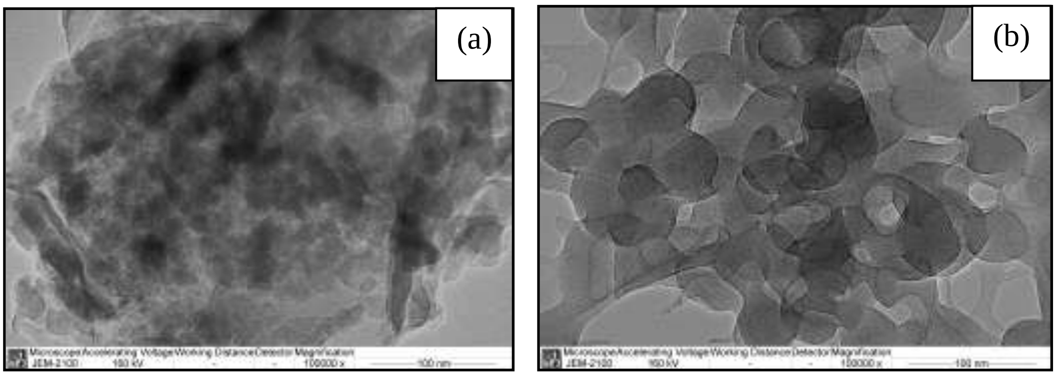


Figure 4.7 TEM image of PE/clay nanocomposite
(a) PE/clay (*in situ*), (b) PE/clay (*ex situ*)

4.3.2 Thermal stability

Thermal stability was determined by TGA measurement, indicating the degree of interaction of MAO and support in polymer. The temperatures at 5% and 10% weight loss are shown in Figure 4.8. PE/clay nanocomposite is degrades slower than pure PE. This suggests that the clay layer hindering heat transfer though the polyethylene nanocomposite [29]. The nanoclay has good barrier action, which can improve the thermal properties of polymer/clay nanocomposite [7]. PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *ex situ* impregnation method show the higher temperature at 5% and 10% weight loss than PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *in situ* impregnation method. The *ex situ* impregnation method was prepared by impregnating MAO onto nanoclay after that washing and drying. The *ex situ* impregnation method will occur more interaction because MAO bound to the support with strong interaction. Another reason, PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *ex situ* impregnation method showed the better thermal stability than that of PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *in situ* impregnation method because *ex* situ impregnation method has larger particle. The *ex situ* impregnation method was prepared by impregnating MAO onto nanoclay after that washing and drying for 5 times. The nanoclay was impregnated by MAO due to particle agglomerate.

Therefore, PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *ex situ* impregnation method showed the better thermal stability than PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *in situ* impregnation method because it has stronger interaction between nanoclay and MAO and larger particle.

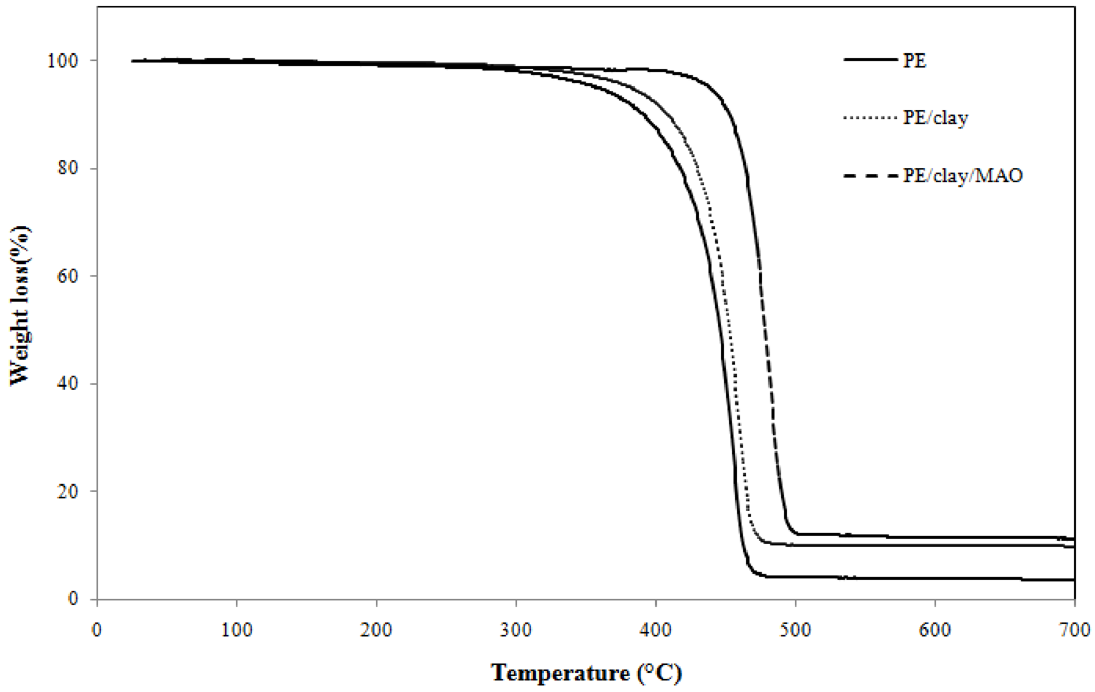


Figure 4.8 TGA curves of PE and PE/clay nanocomposite

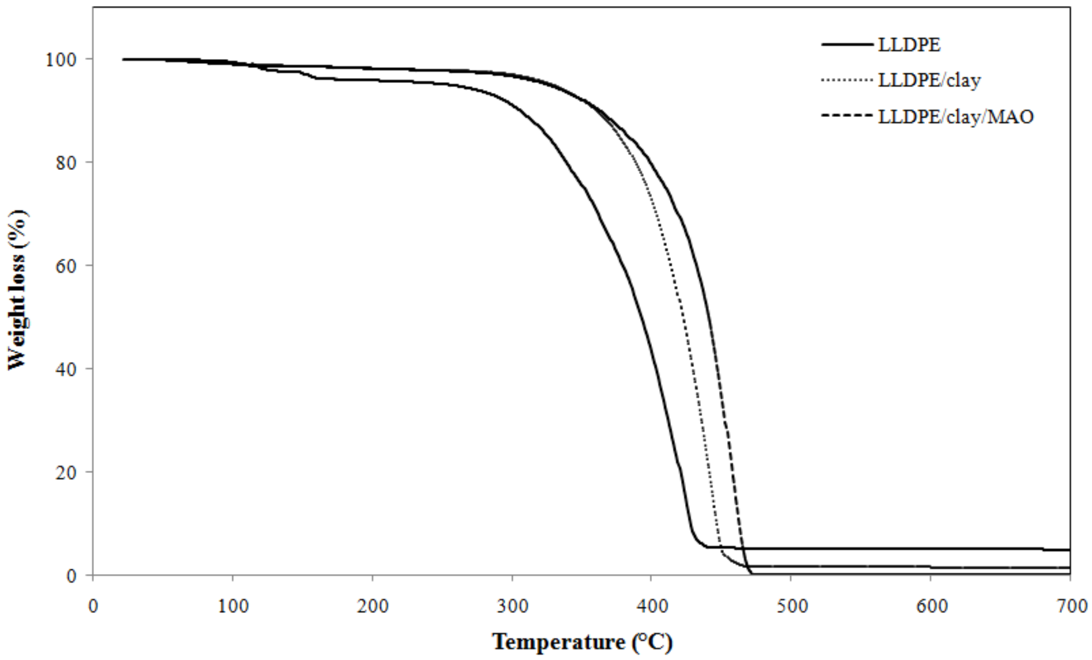


Figure 4.9 TGA curves of LLDPE and LLDPE/clay nanocomposite

4.3.3. Melting and crystallization behavior

The crystallinities (χ) of polymer nanocomposites were estimated by differential scanning calorimeter (DSC). The percent of crystalline is defined in equation 4.1 [19]:

$$\chi\,(\%) = (\Delta H_{exp/}\ \Delta H^{*}) \text{ x } (1/\ W_f) \qquad (4.1)$$

Where χ (%) = % crystallinity

ΔH_{exp} = heat of fusion which obtained from DSC.

ΔH^{*} = heat of fusion of complete crystalline of HDPE (293 J/g).

W_f = weight fraction of HDPE in the polymer nanocomposite.

Table 4.2 Melting and crystallization behavior.

Run	**Sample**	**System**	**T_m[a](°C)**	**ΔH_{exp}[b] (J/g)**	**X_c[c] (%)**
1	PE	-	131	141	48
2	PE/clay	*in situ*	132	142	51
3	PE/clay/MAO	*ex situ*	131	146	52
4	LLDPE	-	119	15	5
5	LLDPE/clay	*in situ*	122	19	7
6	LLDPE/clay/MAO	*ex situ*	113	50	18

[a] Melting temperature (T_m) was obtained from DSC measurement.

[b] Heat of fustion (ΔH_{exp}) was obtained from DSC measurement.

[c] Crystallinity (χ) was calculated from equation in Appendix B.1.

The melting temperatures of polymer nanocomposites with metallocene catalyst were determined by differential scanning calorimeter (DSC). The results of melting temperatures are demonstrated in Table 4.2. From the above table, the melting temperatures of PE with addition of nanoclay show no significant change. The melting temperatures of polymer nanocomposites are observed in the range of 131 to 132°C. It is suggested that the branchless structure of the polymer composite [30]. The crystalline of pure PE is 48%, whereas addition of nanoclay both *in situ* impregnation and *ex situ* impregnation in the composite present an increase in crystalline to 51% and 52%, respectively. It is suggest that the amount of nanoclay performing as heterophase crystal nucleation agent in the polymer matrix [31].

According to the data in Table 4.2, the polymer nanocomposites were produced by *in situ* impregnation and *ex situ* impregnation methods having the range of % crystallinity between 48 and 52.

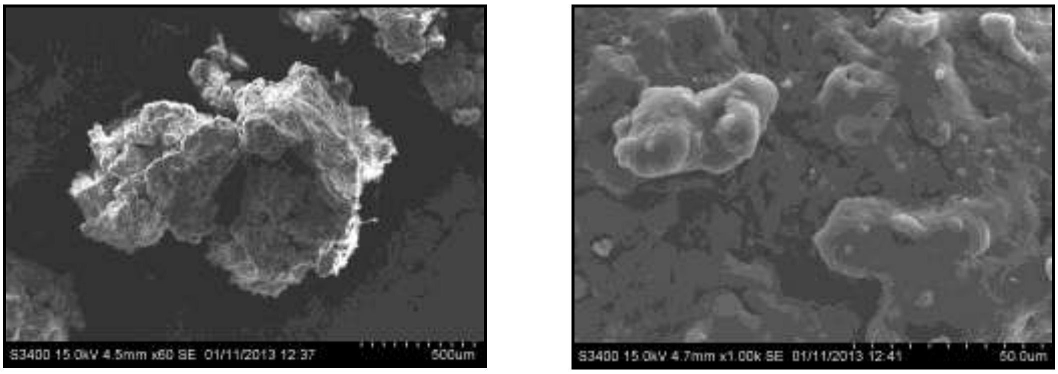
Considering the effect of clay on copolymerization system, DSC curve of LLDPE with addition of nanoclay observed the melting temperature in the range of 113 to 122°C. Especially, copolymerization system of metallocene catalyst by adding 1-hexene, the polymer is more amorphous. The crystalline of pure LLDPE is 5%, whereas addition of nanoclay both *in situ* impregnation and *ex situ* impregnation in the composite present an increase in crystalline to 7% and 18%, respectively. It is suggest that the amount of nanoclay performing as heterophase crystal nucleation agent in the polymer matrix [31].

4.3.4 Morphology

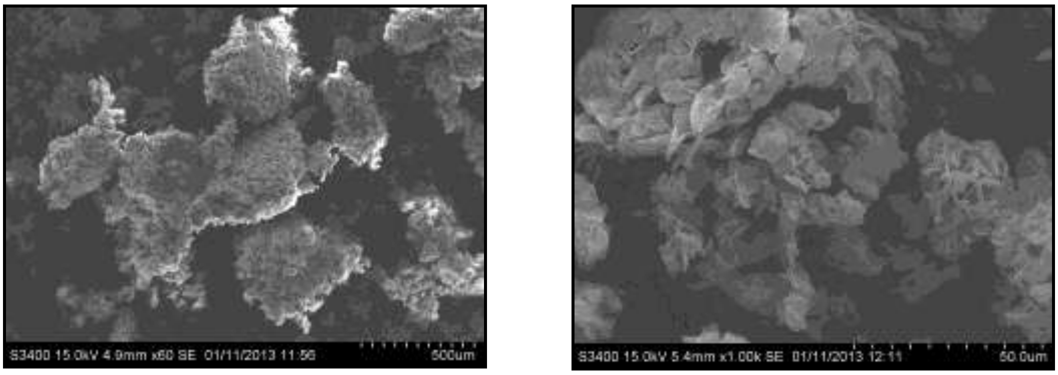
Morphologies of polymer from scanning electron microscopy (SEM) are shown in Figure 4.10.

The polymers obtained from the homogeneous system look different from the heterogeneous system. However, the polymers obtained from the heterogeneous system exhibited a small difference in morphology. The PE/clay nanocomposite was produced by in *situ* impregnation, which it is similar to that with *ex situ* impregnation method because of the different interaction of the nanoclay and polymer inside the polymer matrix. The LLDPE/clay nanocomposite was produced by *ex situ* impregnation method having the spherical shape. Therefore, it can be reported that the LLDPE/clay nanocomposite produced by *ex situ* impregnation method can improve the morphology of polyethylene.

PE



PE/clay



PE/clay/MAO

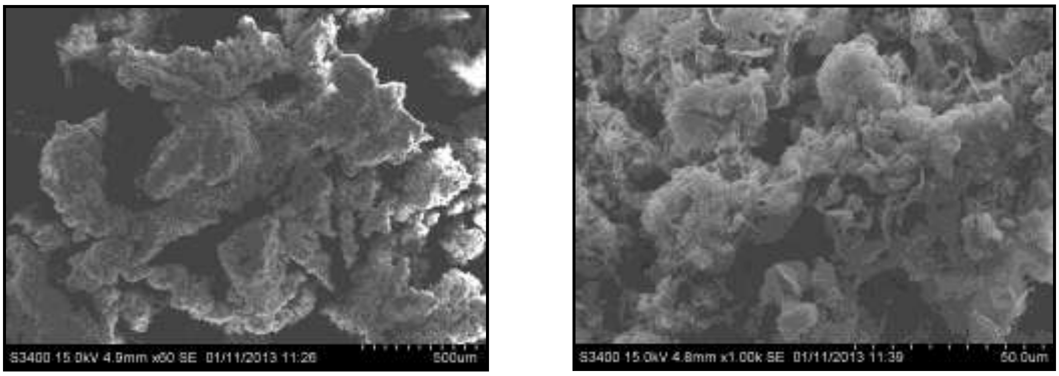
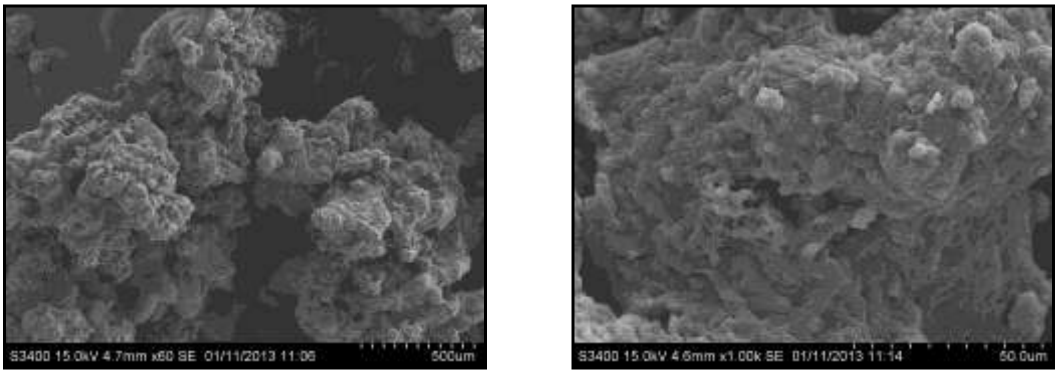
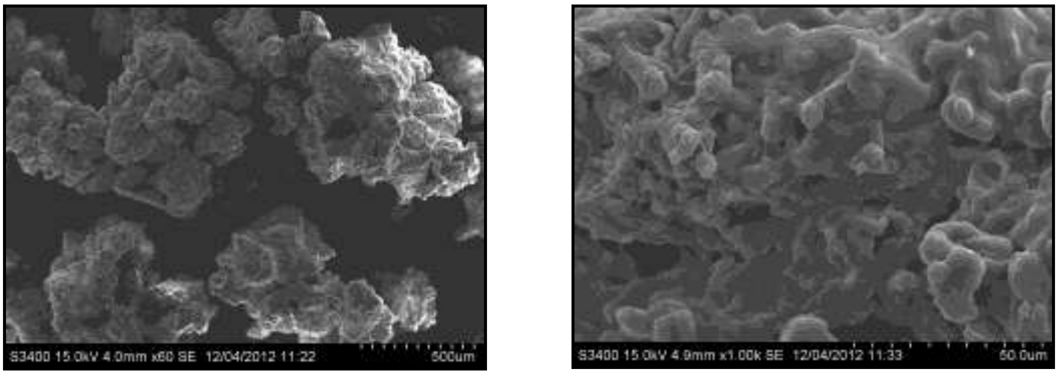


Figure 4.10 SEM images of PE/clay nonocomposite

LLDPE



LLDPE/clay



LLDPE/clay/MAO

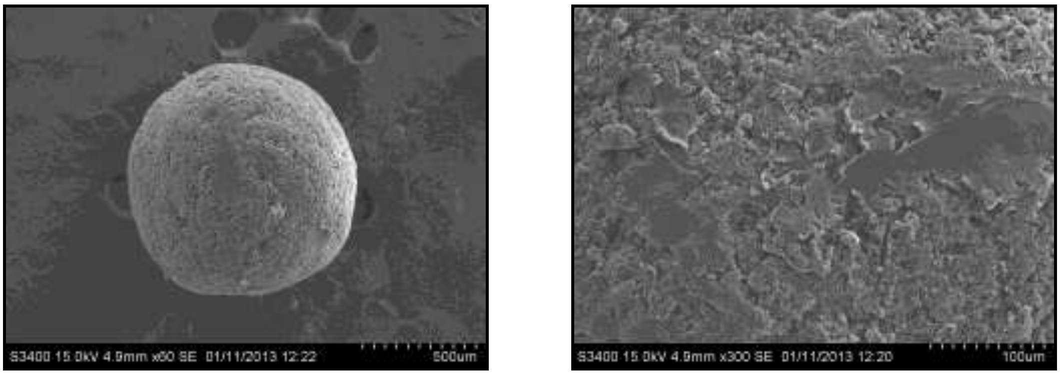


Figure 4.11 SEM images of LLDPE/clay nonocomposite

4.3.5 The amounts of nanoclay in polymer nanocomposite

Table 4.3 The wt% of nanoclay in polymer nanocomposites.

Run	Sample	System	Clay (g)	Polymer (g)	Wt% clay
1	PE	-	-	0.8375	-
2	PE/clay	*in situ*	0.0265	0.6582	3.87
3	PE/clay/MAO	*ex situ*	0.1845	0.7211	20.37
4	LLDPE	-	-	0.1072	-
5	LLDPE/clay	*in situ*	0.0265	0.8607	2.99
6	LLDPE/clay/MAO	*ex situ*	0.1845	0.4599	28.63

Table 4.3 shows the wt% of nanoclay in polymer nanocomposites. Considering the amount of nanoclay on heterogeneous system, it can be seen that PE/clay and LLDPE/clay with *ex situ* impregnation method exhibit higher wt% of nanoclay than PE/clay and LLDPE/clay with *in situ* impregnation method.

Degree of dispersion of nanoclay in polyethylene matrix was determined by the small angle X-ray diffraction analysis (SAXRD). The SAXRD patterns of PE/clay nanocomposite (*in situ* impregnation) and PE/clay nanocomposite (*ex situ* impregnation) are shown in Figure 4.6. It was suggested that high dispersion of nanoclay throughout polyethylene matrix was obtained [25]. This exfoliated degree dispersion of nanoclay may be due to direct mixing process. The wt% of nanoclay was no significant change in degree of dispersion.

Thermal stability was determined by TGA measurement. PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *ex situ* impregnation method showed the better thermal stability than that of PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *in situ* impregnation method because *ex* situ impregnation method has larger particle. The *ex situ* impregnation method was prepared by impregnating MAO onto nanoclay after that washing and drying for 5 times. The nanoclay was impregnated by MAO due to particle agglomerate. Another reasons, the wt% of nanoclay in polymer/clay nanocomposite with *ex situ* impregnation method shows higher than polymer/clay nanocomposite with *in situ* impregnation.

The crystallization of polymer nanocomposites with metallocene catalyst was determined by differential scanning calorimeter (DSC). The crystallinity of polymer/clay nanocomposite synthesized by *ex situ* impregnation method exhibits slightly higher than *in* situ impregnation method. It is suggested that the amount of nanoclay increasing due to the nanoclay can act as a heterophase crystal nucleation agent in the polymer matrix [31].

Morphologies of polymer were determined by scanning electron microscopy (SEM). The polymer/clay nanocomposite produced by *in situ* impregnation is similar to that with *ex situ* impregnation method because of the different interaction of the nanoclay and polymer inside the polymer matrix. The different wt% of nanoclay for both *in situ* impregnation and *ex situ* impregnation did not affect on morphologies of polymer nanocomposite.

PART 2: Modification of supports by silane

4.4 Characteristics of support

The nanoclay was modified by tetracholosilane ($SiCl_4$). The crystallization properties and surface properties of support were determined by X-ray diffraction spectroscopy (XRD). Figure 4.12 show the XRD patterns of nanoclay and nanoclay treated by tetracholosilane ($SiCl_4$). The first peak of nanoclay corresponds to the interlayer spacing of nanoclay. It is seen that the interlayer spacing increase from 17.50 Å ($2\theta = 5.05$) to 17.93 Å ($2\theta = 4.92$) after the tetracholosilane ($SiCl_4$) treatment due to the presence of $SiCl_4$ in the clay intergallery. The modification support is an important step for improving the properties of the clay as a catalyst support, because the metallocene catalyst can be fixed more easily into the clay interlayer space than nanoclay [10]. After modification, tetracholosilane ($SiCl_4$) give a more hydrophobic character to the clay surface, which is an important aspect to improve clay and polymer.

After modification with tetracholosilane ($SiCl_4$), the difference supports were determined by SEM. The observed morphologies are shown in Figure 4.13. The Morphology of nanoclay was modified by silicon tetrachloride ($SiCl_4$), which it is similar to that with unmodified nanoclay.

The amount of $[Al]_{MAO}$ present in different support is presented in Table 4.4. This method finds the amount of aluminum species in the nanoclay support; ICP-OES technique was used. It was found that the average of $[Al]_{MAO}$ on clay and clay/ $SiCl_4$ were 24.07 and 24.63 mg/L, respectively. Therefore, $SiCl_4$ modification on nanoclay surface can result in increased amounts of $[Al]_{MAO}$ present on the $SiCl_4$ modified support. This can be attributed to the increased adsorption ability of $[Al]_{MAO}$ and nanoclay by $SiCl_4$ modification.

The ratio of Si/Al present in different support is present in Table 4.5. This method finds the ratio of Si/Al in the nanoclay support; ICP-OES technique was used.

It was found that the Si/Al ratio on nanoclay and clay/ $SiCl_4$ were 1.95 and 2.00, respectively. Therefore, $SiCl_4$ modification on nanoclay surface can result in increased amounts of silicon atom present on the $SiCl_4$ modified support.

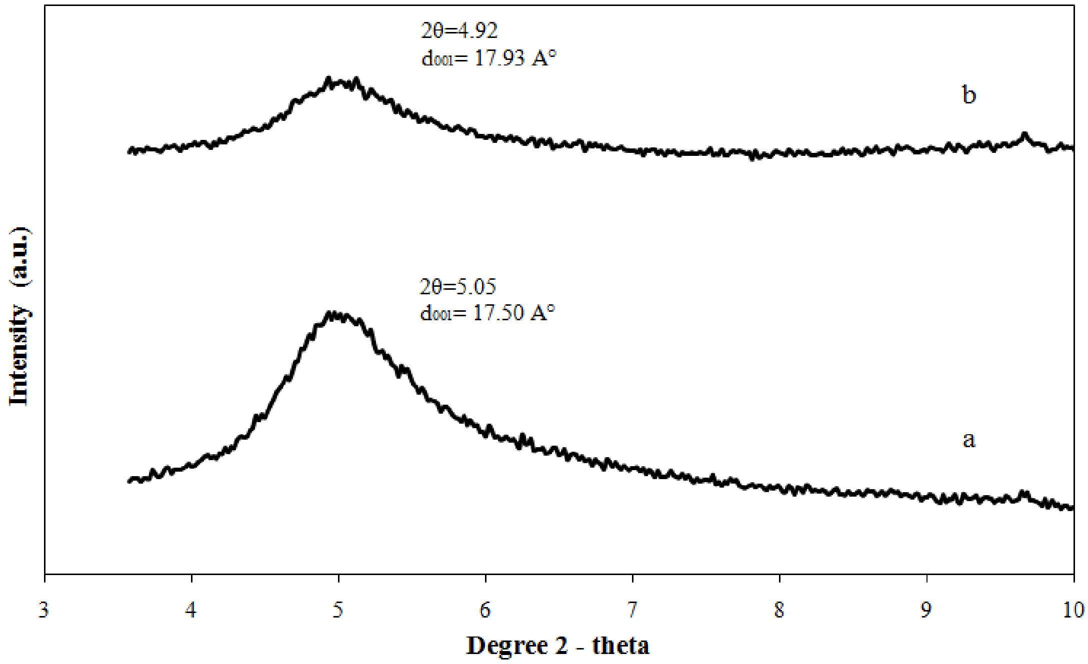


Figure 4.12 XRD patterns of (a) Clay and (b) Clay/$SiCl_4$

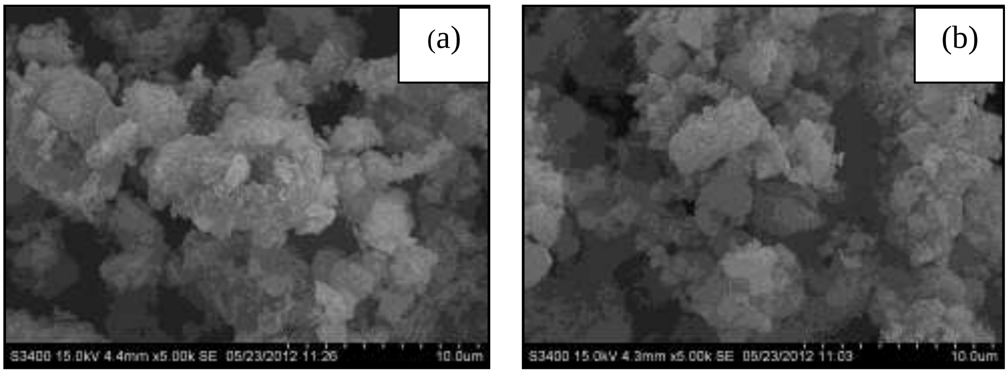


Figure 4.13 Morphologies of the nanoclay (a) clay, (b) clay/$SiCl_4$

Table 4.4 The amounts of $[Al]_{MAO}$ present in different support.

Catalyst precursor	$[Al]_{MAO}$ on the support (mg/L)
Clay/MAO	24.07
Clay/$SiCl_4$/MAO	24.63

Table 4.5 The ratio of Si/Al present in different support.

Sample	Si/Al ratio
Clay	1.95
Clay/$SiCl_4$	2.00

4.5 Ethylene polymerization

Table 4.6 Polymerization data with nanoclay / $Et(Ind)_2ZrCl_2$/MAO.

run	Sample	Impregnation method	Polymer[a] yield (g)	Activity[b] (kg PE/mol Zr.h)
2	PE/clay	*in situ*	0.6582	9,184
3	PE/clay/MAO	*ex situ*	0.7211	6,637
5	LLDPE/clay	*in situ*	0.8607	13,414
6	LLDPE/clay/MAO	*ex situ*	0.4599	7,828
7	PE/clay/$SiCl_4$	*in situ*	0.6065	9,704
8	PE/clay/$SiCl_4$/MAO	*ex situ*	0.7666	7,049
9	LLDPE/clay/$SiCl_4$	*in situ*	1.1579	15,353
10	LLDPE/clay/$SiCl_4$/MAO	*ex situ*	0.4514	8,398

[a] The polymer yield was limited by the amount of ethylene fed (0.018 mol). The molar ratio of ethylene:comonomer was 4:1.

[b] Activities were measured at polymerization temperature of 70°C, [ethylene]= 0.018 mol, $[Al]_{MAO}/[Zr]_{cat} = 1135$ in toluene with total volume = 30 ml, $[Zr]_{cat} = 5\times10^{-5}$ Molar and mixing time of MAO and nanoclay was 30 minutes.

Ethylene polymerization was introduced at polymerization temperature of 70°C, ethylene concentration of 0.018 mol, $[Al]_{MAO}/[bZr]_{cat}$ at 1135 in toluene with total volume of 30 ml, zirconium concentration of 5×10^{-5} Molar and mixing time of MAO and nanoclay was 30 minutes. The nanoclay was modified by tetracholosilane ($SiCl_4$). The results of ethylene polymerization are shown in Table 4.6.

From Table 4.6, it is shown that the nanoclay was modified by tetracholosilane ($SiCl_4$), exhibites the higher activity than unmodified nanoclay. The explanation is that the chlorine atoms of silane compound on the nanoclay surface can transform with the hydroxyl groups. Moreover, the nanoclay was modified by tetracholosilane ($SiCl_4$), it is suggested that silane modification show result in less steric effect on the support surface [33]. In addition, it is suggested that silane acts as spacer group on the surface of silica based on the work reported by Soga *et* al.

4.6 Characterization of LLDPE/clay nanocomposites

4.6.1 Dispersion of nanoclay

The nanoclay was modified by tetracholosilane ($SiCl_4$). Degree of dispersion in polyethylene matrix was determined by the small angle X-ray diffraction analysis (SAXRD). The SAXRD patterns of Clay/$SiCl_4$, PE/clay/$SiCl_4$ nanocomposite (*in situ* impregnation), PE/clay/$SiCl_4$ nanocomposite (*ex situ* impregnation), LLDPE/clay/$SiCl_4$ nanocomposite (*in situ* impregnation) and LLDPE/clay/$SiCl_4$ nanocomposite (*ex situ* impregnation) are shown in Figure 4.14. The SAXRD pattern for Clay/$SiCl_4$ provides diffraction peaks at $2\theta = 4.92°$, which is the peak of modified clay. The mixing process cause exfoliated degree dispersion of treaded-clay. The addition of methylaluminoxane (MAO) during the clay/$SiCl_4$ treatment step is reacted with hydroxyl group on clay surface. Therefore, the broad peak is well dispersion of clay/$SiCl_4$ in the polyethylene matrix.

Transmission electron microscopy (TEM) images confirm the exfoliated degree dispersion of nanoclay. In Figure 4.15, it can be seen that the clay/$SiCl_4$ particles are randomly dispersed throughout polyethylene matrix. The most clay particle agglomeration is spited to fine particle size.

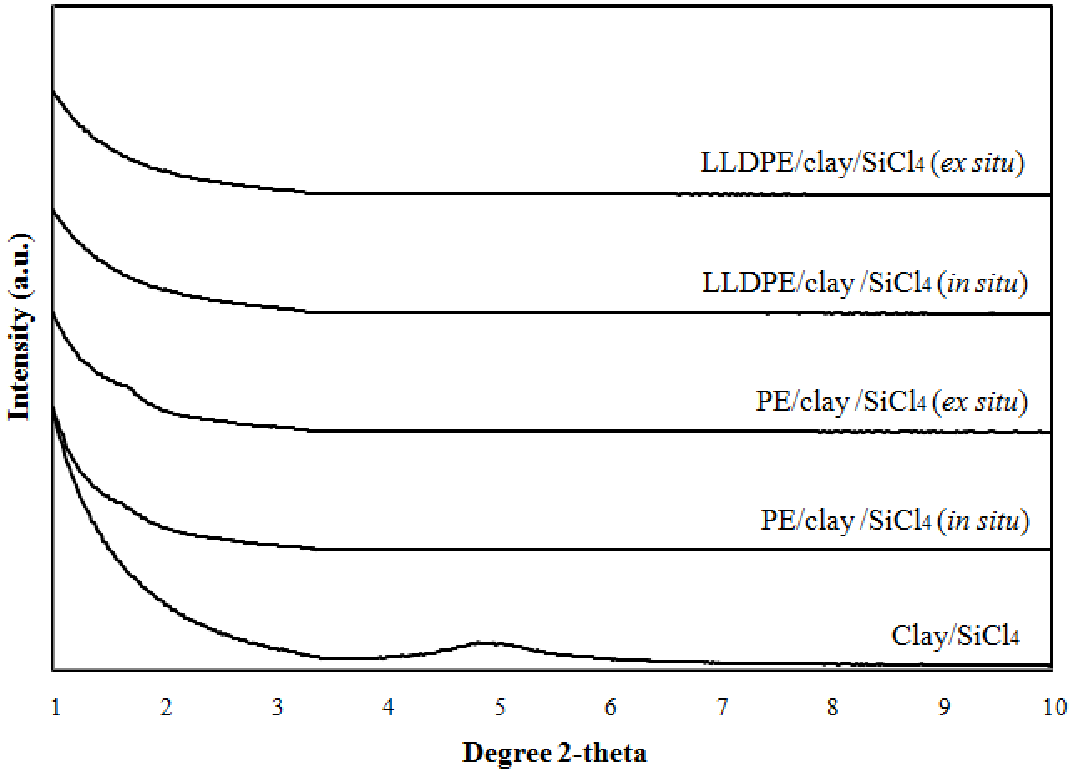


Figure 4.14 XRD patterns of PE/clay/$SiCl_4$ nanocomposite and LLDPE/clay/$SiCl_4$ nanocomposite

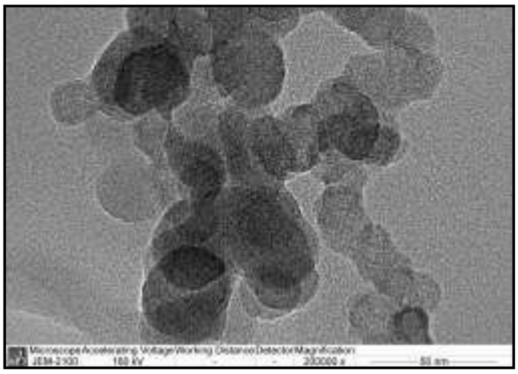


Figure 4.15 TEM image of PE/clay/$SiCl_4$ (*in situ*).

4.6.2 Thermal stability

The nanoclay was modified by silicon tetrachloride ($SiCl_4$). It shows the lower temperature at 5% and 10% weight loss than the unmodified clay because silane compound acts as a spacer group, which can decreasing stronger interaction between nanoclay and MAO and increasing adhesion between the nanoclay and polymer.

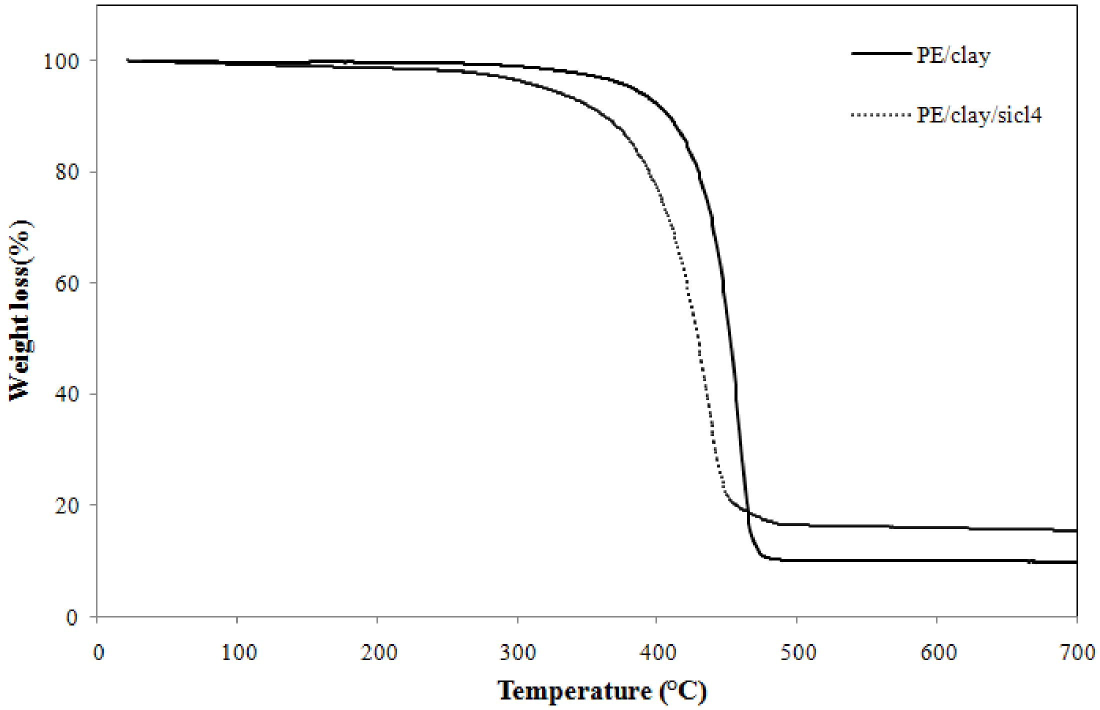


Figure 4.16 TGA curves of PE/clay and PE/clay/$SiCl_4$ nanocomposite

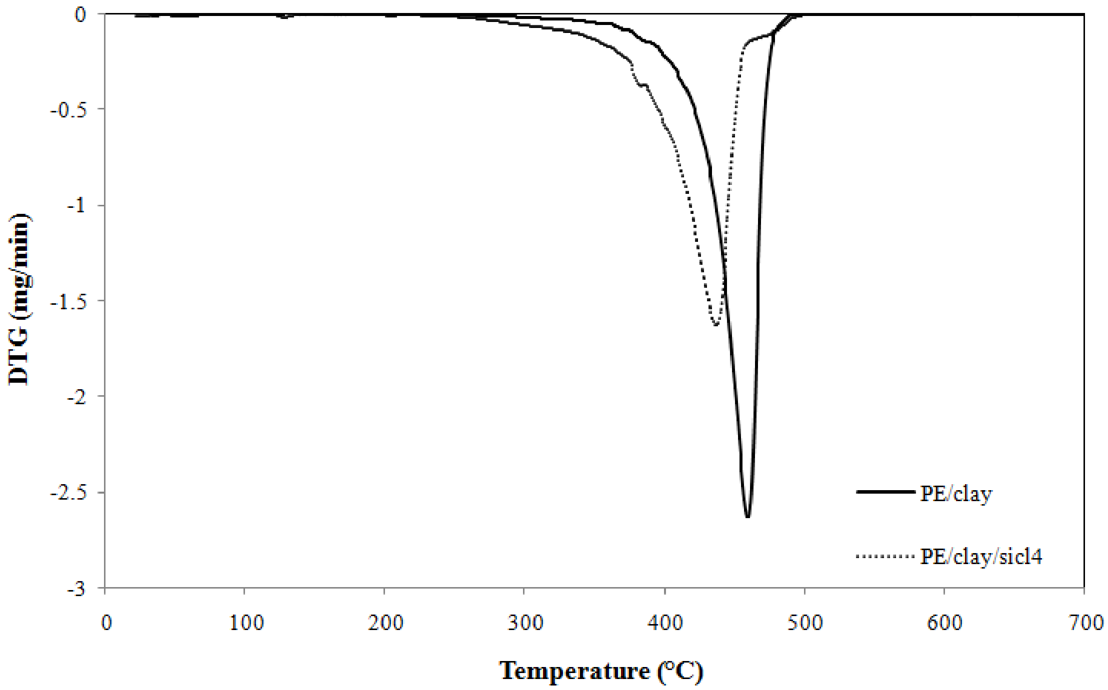


Figure 4.17 DTG curves of PE/clay and PE/clay/SiCl$_4$ nanocomposite

4.6.3. Melting and crystallization behavior

The crystallinities (χ) of polymer nanocomposites were estimated by differential scanning calorimeter (DSC). The percent of crystalline is defined in equation 4.1 [19]:

$$\chi\,(\%) = (\Delta H_{exp/}\ \Delta H^{*})\ \mathrm{x}\ (1/\ W_f) \qquad (4.1)$$

Where χ (%) = % crystallinity

ΔH_{exp} = heat of fusion which obtained from DSC.

ΔH^{*} = heat of fusion of complete crystalline of HDPE (293 J/g).

W_f = weight fraction of HDPE in the polymer nanocomposite.

Table 4.7 Melting and crystallization behavior

Run	**Sample**	**System**	**T_m[a](°C)**	**ΔH_{exp}[b] (J/g)**	**X_c[c] (%)**
2	PE/clay	*in situ*	132	142	51
3	PE/clay/MAO	*ex situ*	131	146	52
5	LLDPE/clay	*in situ*	122	19	7
6	LLDPE/clay/MAO	*ex situ*	113	50	18
7	PE/clay/$SiCl_4$	*in situ*	131	147	52
8	PE/clay/$SiCl_4$/MAO	*ex situ*	131	151	53
9	LLDPE/clay/$SiCl_4$	*in situ*	121	13	5
10	LLDPE/clay/$SiCl_4$/MAO	*ex situ*	110	42	15

[a] Melting temperature (T_m) was obtained from DSC measurement.

[b] Heat of fustion (ΔH_{exp}) was obtained from DSC measurement.

[c] Crystallinity (χ) was calculated from equation in Appendix B.1.

The melting temperatures of polymer nanocomposites with metallocene catalyst were determined by differential scanning calorimeter (DSC). The results of melting temperatures are demonstrated in Table 4.7. From the above table, the melting temperatures of polymer/claynanocomposite and polymer/claynanocomposite with adding silane compound show no significant change. The nanoclay was modified by silicon tetrachloride ($SiCl_4$), it has melting temperatures is about 131°C. The crystalline of polymer/claynanocomposite and polymer/claynanocomposite with adding silane compound show no significant change.

According to the data in Table 4.7, the polymer nanocomposite was modified by silane compound having the range of % crystallinity between 52 and 53.

Considering the effect of clay/$SiCl_4$ on copolymerization system, DSC curve of LLDPE/clay nanocomposite with addition of silane show no significant change compare the nanoclay. Especially, copolymerization system of metallocene catalyst by adding 1-hexene, the polymer is more amorphous. The crystalline of pure LLDPE is 5%, whereas addition of nanoclay both *in situ* impregnation and *ex situ* impregnation in the composite present an increase in crystalline to 5% and 15%, respectively.

The XRD pattern confirms the reduction of crystallinity in LLDPE/clay compared to PE/clay. In Figure 4.18, it can be seen that small amorphous peak was observed about 19.5-20 degree. The nanoclay and nanoclay with silane show no significant change.

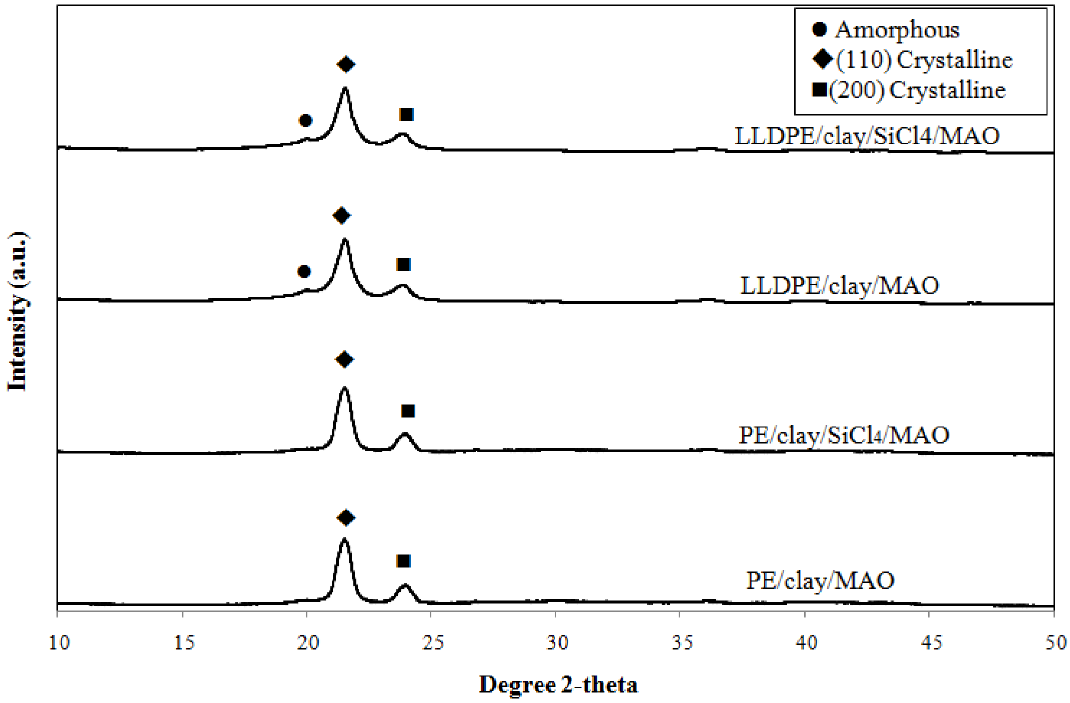


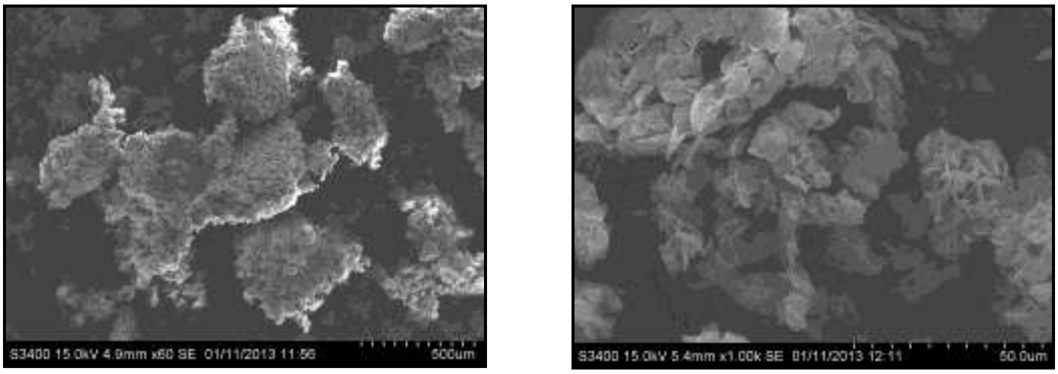
Figure 4.18 XRD patterns of PE/clay/MAO, PE/clay/SiCl4/MAO, LLDPE/clay/MAO and LLDPE/clay/SiCl4/MAO nanocomposite

4.6.4 Morphology

Morphologies of polymer from scanning electron microscopy (SEM) are shown in Figure 4.19-4.22.

The nanoclay was modified by silicon tetrachloride ($SiCl_4$), which it is similar to that with unmodified nanoclay. Therefore, it can be reported that the support modified by silicon tetrachloride did not improve the morphology of polyethylene.

PE/clay



PE/clay/$SiCl_4$

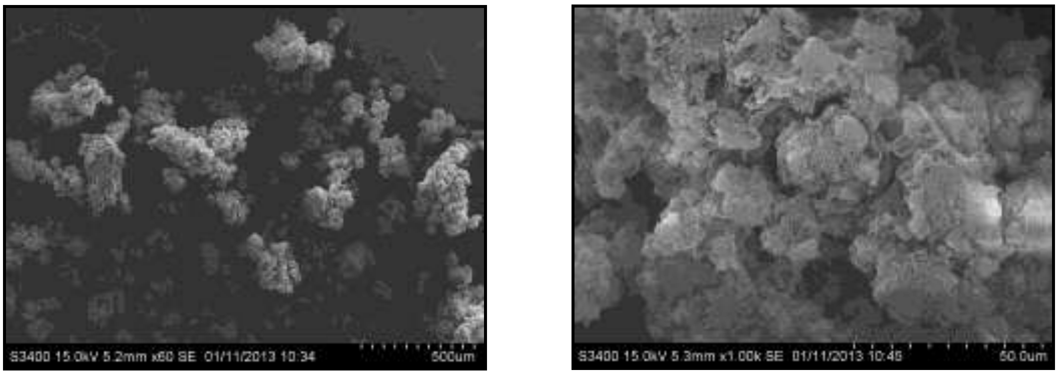
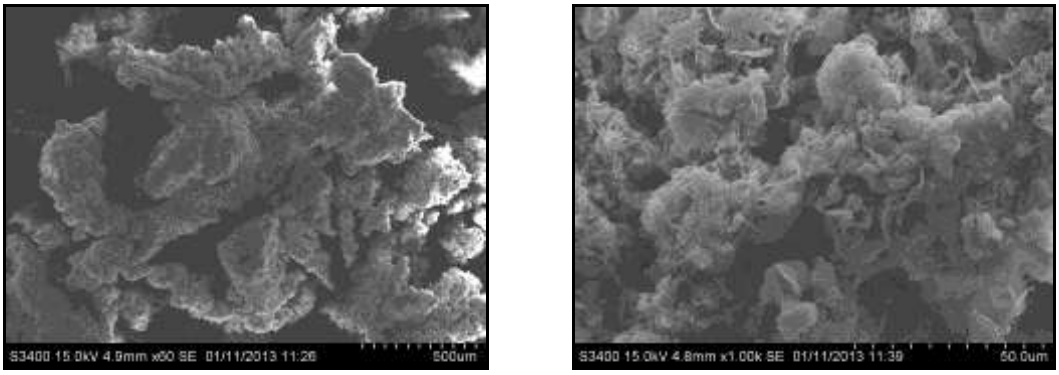


Figure 4.19 SEM images of PE/clay nonocomposite and PE/clay/$SiCl_4$ nonocomposite

PE/clay/MAO



PE/clay/$SiCl_4$/MAO

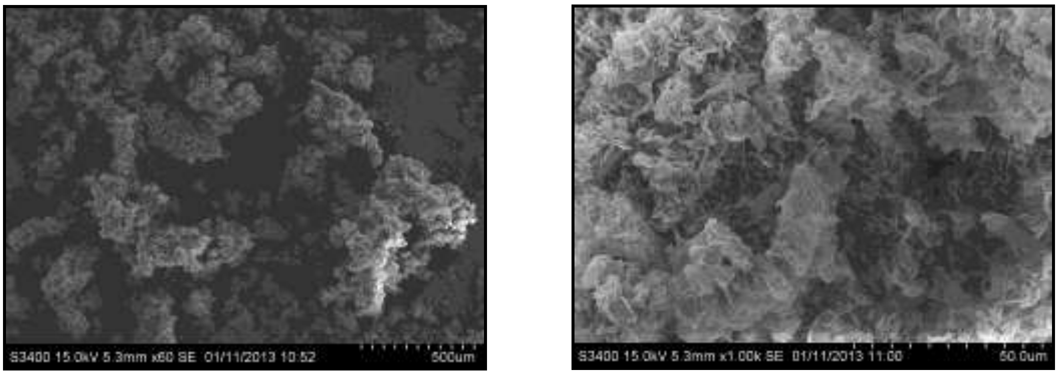
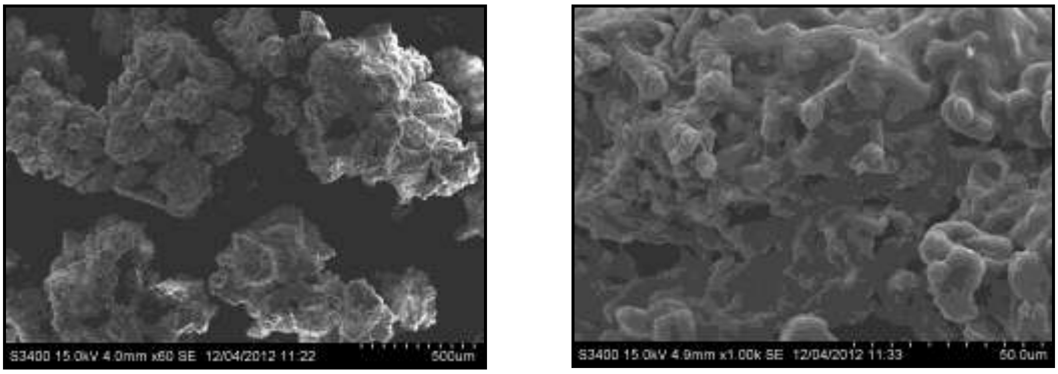


Figure 4.20 SEM images of PE/clay/MAO nonocomposite and PE/clay/$SiCl_4$/MAO nonocomposite

LLDPE/clay



LLDPE/clay/$SiCl_4$

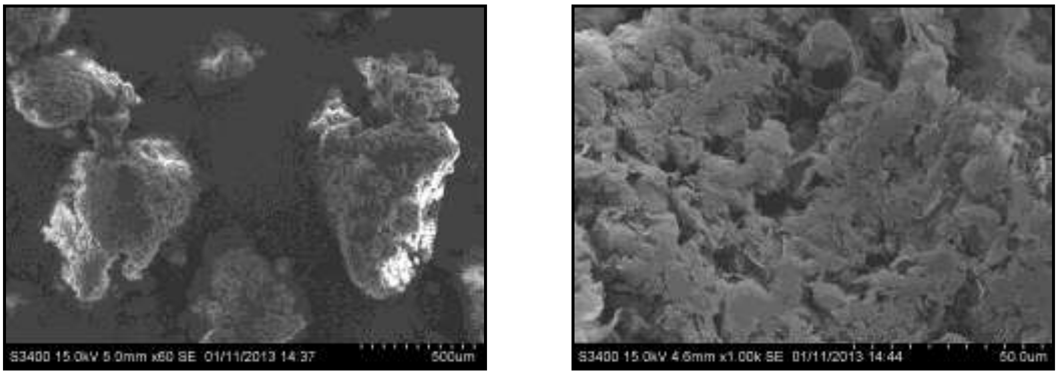
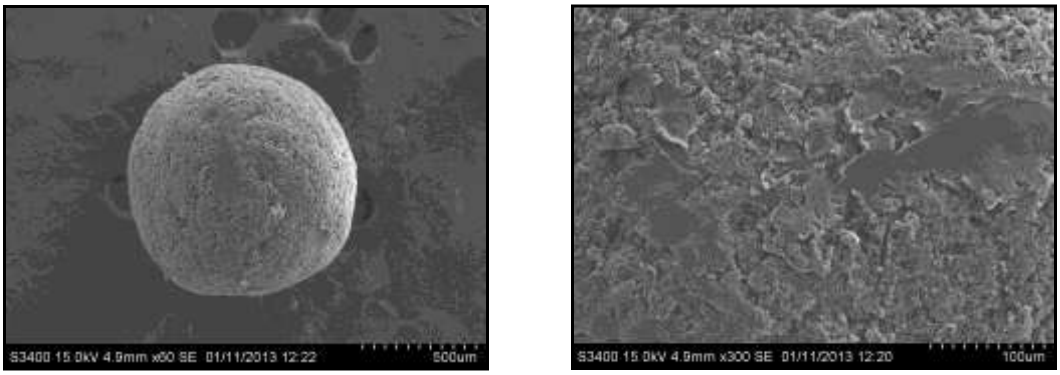


Figure 4.21 SEM images of LLDPE/clay nonocomposite and LLDPE/clay/$SiCl_4$ nonocomposite

LLDPE/clay/MAO



LLDPE/clay/$SiCl_4$/MAO

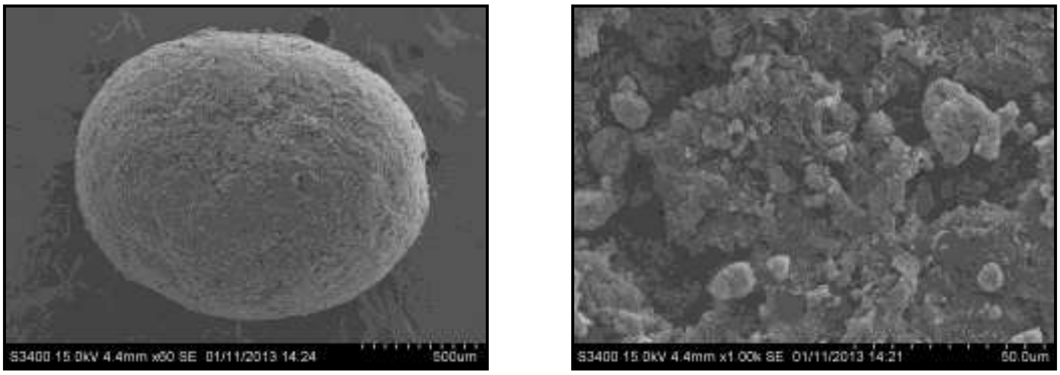


Figure 4.22 SEM images of LLDPE/clay/MAO nonocomposite and LLDPE/clay/$SiCl_4$/MAO nonocomposite

4.6.5 The amounts of nanoclay/$SiCl_4$ in polymer nanocomposite

Table 4.8 The wt% of nanoclay/$SiCl_4$ in polymer nanocomposite.

Run	Sample	System	Clay (g)	Polymer (g)	Wt% clay
2	PE/clay	*in situ*	0.0265	0.6582	3.87
3	PE/clay/MAO	*ex situ*	0.1845	0.7211	20.37
5	LLDPE/clay	*in situ*	0.0265	0.8607	2.99
6	LLDPE/clay/MAO	*ex situ*	0.1845	0.4599	28.63
7	PE/clay/$SiCl_4$	*in situ*	0.0265	0.6065	4.19
8	PE/clay/$SiCl_4$/MAO	*ex situ*	0.1866	0.7666	19.58
9	LLDPE/clay/$SiCl_4$	*in situ*	0.0265	1.1579	2.24
10	LLDPE/clay/$SiCl_4$/MAO	*ex situ*	0.1866	0.4514	28.25

The nanoclay was modified by tetracholosilane ($SiCl_4$). Degree of dispersion in polyethylene matrix was determined by the small angle X-ray diffraction analysis (SAXRD). The SAXRD patterns of polymer/clay nanocomposite modified with tetracholosilane (*in situ* impregnation and *ex situ* impregnation method) reveal the broad peak. It was suggested that high dispersion of nanoclay throughout polyethylene matrix was obtained. The wt% of nanoclay was no significant change in degree of dispersion.

Thermal stability of PE/clay nanocomposite and LLDPE/clay nanocomposite with tetracholosilane synthesized by *in situ* impregnation and *ex* situ impregnation method was investigated. The amount of nanoclay was slightly different in system. Therefore, the wt% of nanoclay has no effect on thermal stability.

The crystallinity of polymer nanocomposites with metallocene catalyst was determined by differential scanning calorimeter (DSC). The crystallinity of polymer/clay nanocomposite with tetracholosilane synthesized by *ex situ* impregnation method was slightly different. The wt% of nanoclay was slightly changed in the crystallization of polymer nanocomposites.

The nanoclay was modified by silicon tetrachloride ($SiCl_4$), which it is similar to that with unmodified nanoclay. Therefore, it can be reported that the support modified by silicon tetrachloride did not improve the morphology of polyethylene. The wt% of nanoclay addition silicon tetrachloride cannot improve morphologies of polymer nanocomposite.

CHAPTER V

CONCLUSIONS & RECOMMENDATION

5.1 Conclusions

5.1.1 A comparative study on LLDPE/clay nanocomposite synthesized by different impregnation method

At the beginning, PE/clay nanocomposite and LLDPE/clay nanocomposite synthesized by *in situ* impregnation method with zirconocene catalyst gives higher activity than PE/clay nanocomposite and LLDPE/clay nanocomposite synthesized by *ex situ* impregnation method.

From XRD pattern and TEM images confirm exfoliate degree dispersion of nanoclay both *in situ* impregnation and *ex situ* impregnation method. The clay particles are randomly dispersed throughout polyethylene matrix.

PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *ex situ* impregnation method showed the better thermal stability than PE/clay nanocomposite and LLDPE/clay nanocomsite synthesized by *in situ* impregnation method because it has stronger interaction between nanoclay and MAO and larger particle.

The polymer nanocomposites were produced by *in situ* impregnation and *ex situ* impregnation method present the range of % crystallinity between 48 and 52. The melting temperatures of polymer nanocomposites are observed in the range of 131 to 132 °C.

The morphology of PE/clay nanocomposite was produced by in *situ* impregnation, which it is similar to that with *ex situ* impregnation method because the different interaction of the nanoclay and polymer inside the polymer matrix. The LLDPE/clay nanocomposite was produced by *ex situ* impregnation method, which is the spherical shape. Therefore, it can be reported that the LLDPE/clay nanocomposite was produced by *ex situ* impregnation method improves the morphology of polyethylene.

5.1.2 Modification of supports by Silane

The nanoclay was modified by tetracholosilane ($SiCl_4$), which it shows the higher activity than unmodified nanoclay.

From XRD pattern and TEM images shown well disperse of nanoclay in the polyethylene matrix. Exfoliation became possible through a strong interaction between the polyethylene chains and the modified clay surface. The clay/$SiCl_4$ particles are randomly dispersed throughout polyethylene matrix.

The modified nanoclay shown the lower temperature at 5% and 10% weight loss than unmodified clay because silane compound acts as spacer group decreasing stronger interaction between nanoclay and MAO.

The polymer nanocomposite was modified by silane compound present the range of % crystalline between 52 and 53 and the melting temperatures is 131°C.

The Morphology of nanoclay was modified by silicon tetrachloride ($SiCl_4$), which it is similar to that with unmodified nanoclay. Therefore, it can be reported that the support was modified by silicon tetrachloride not improve the morphology of polyethylene.

5.2 Recommendation

PE/clay nanocomposites should be further determined other main properties for any applications. These are molecular weight, molecular weight distribution (MWD), flame retardant, and mechanical properties. In addition, PE/clay nanocomposites and LLDPE/clay nanocomposite should be further determined by ^{13}C NMR.

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APPENDICES

APPENDIX A

Differential scanning calorimetry (DSC)

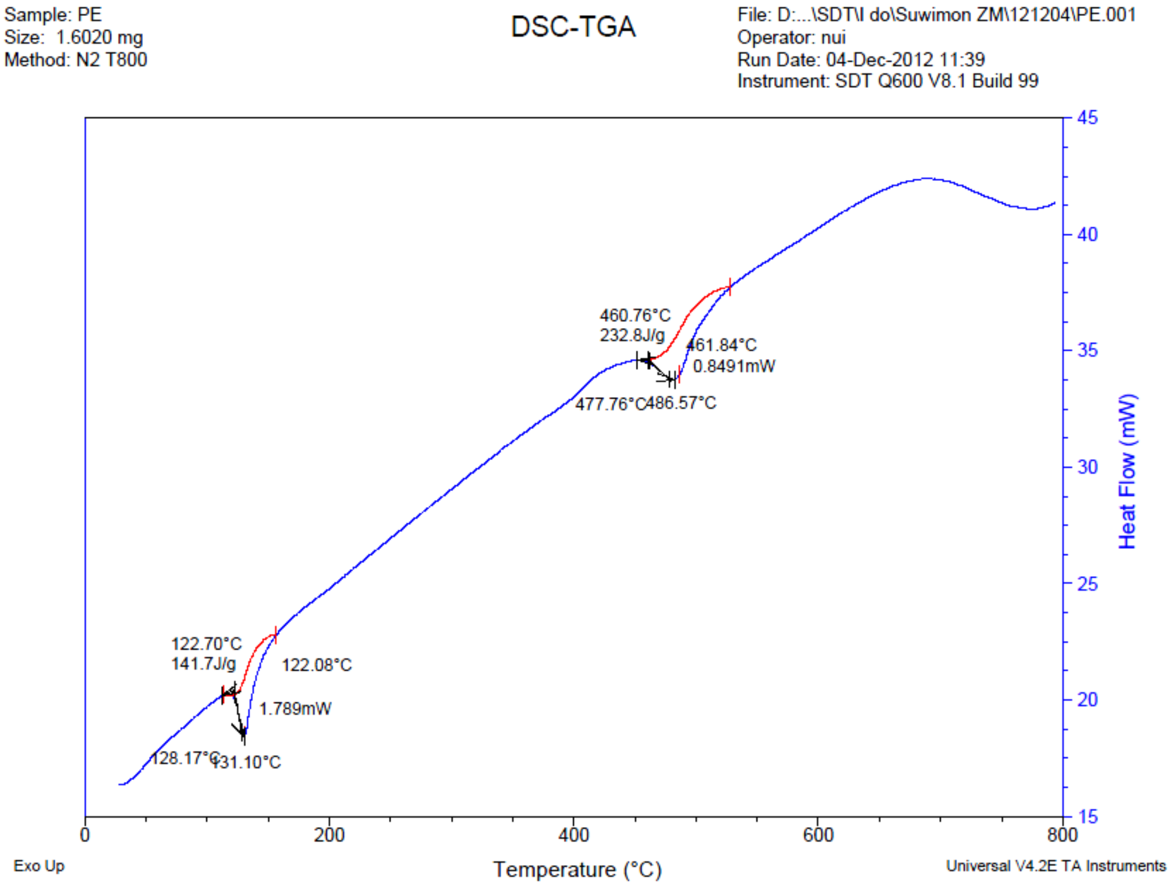


Figure A-1 DSC Curve of PE

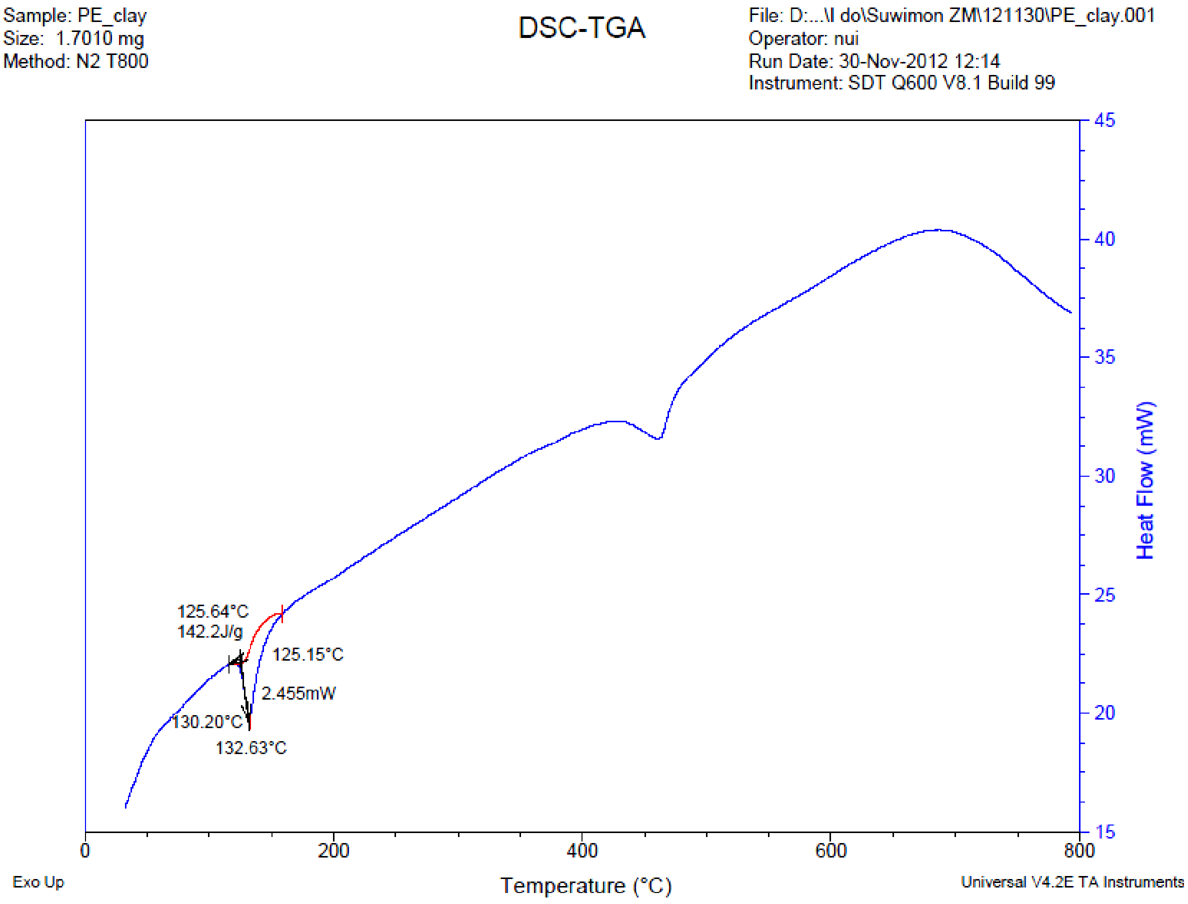


Figure A-1 DSC Curve of PE/clay nanocomposite

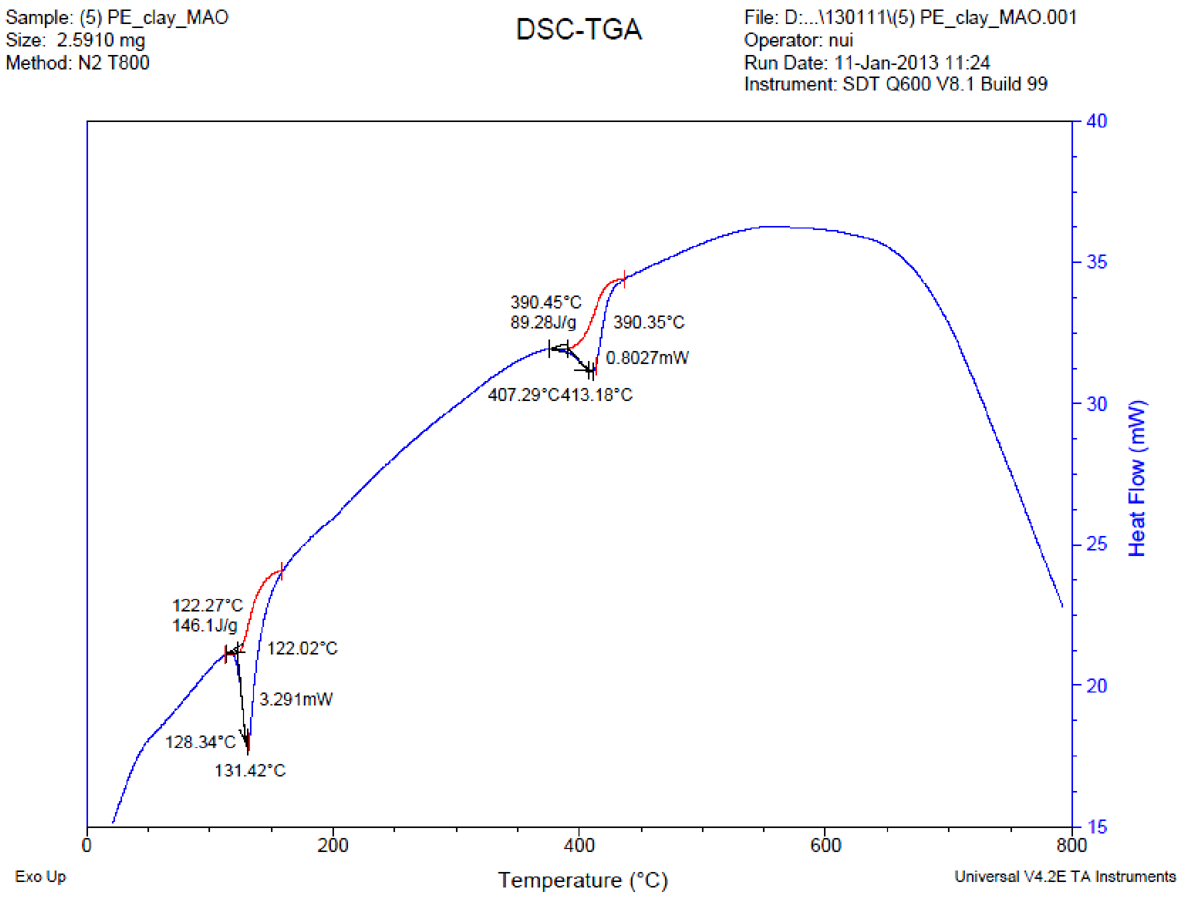
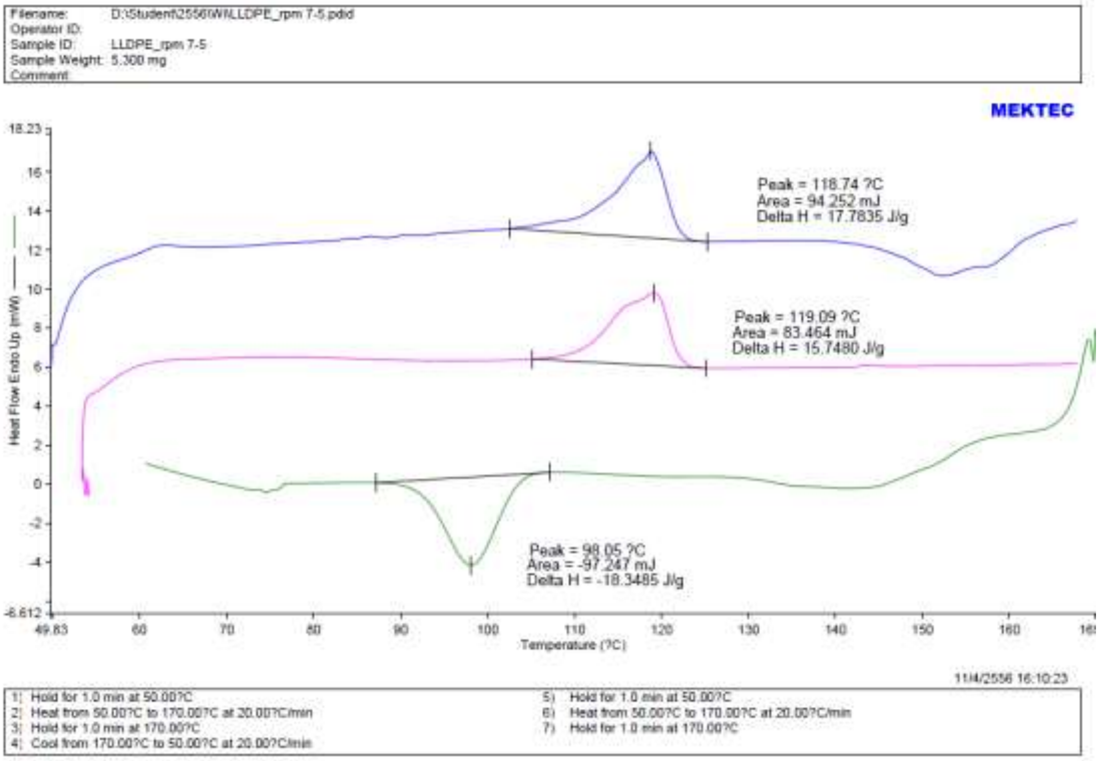


Figure A-1 DSC Curve of PE/clay/MAO nanocomposite



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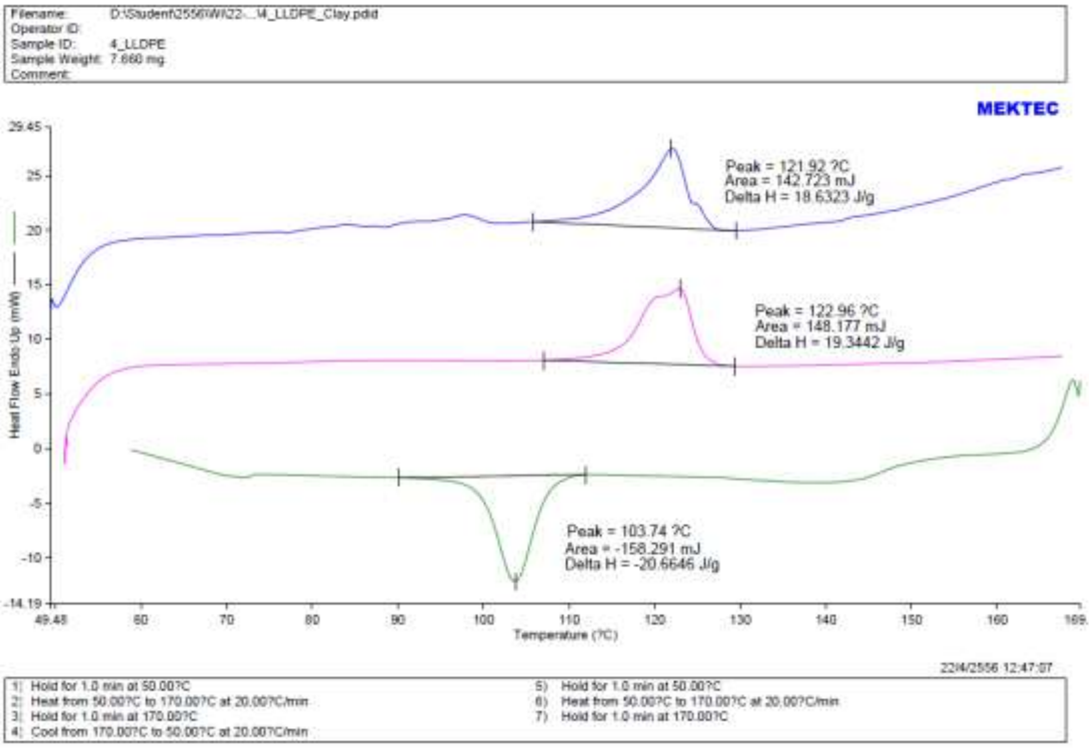
Sample Weight: 5.300 mg
Comment:

11/4/2556 16:10:23

1) Hold for 1.0 min at 50.00?C
2) Heat from 50.00?C to 170.00?C at 20.00?C/min
3) Hold for 1.0 min at 170.00?C
4) Cool from 170.00?C to 50.00?C at 20.00?C/min
5) Hold for 1.0 min at 50.00?C
6) Heat from 50.00?C to 170.00?C at 20.00?C/min
7) Hold for 1.0 min at 170.00?C

Figure A-1 DSC Curve of LLDPE



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Comment:

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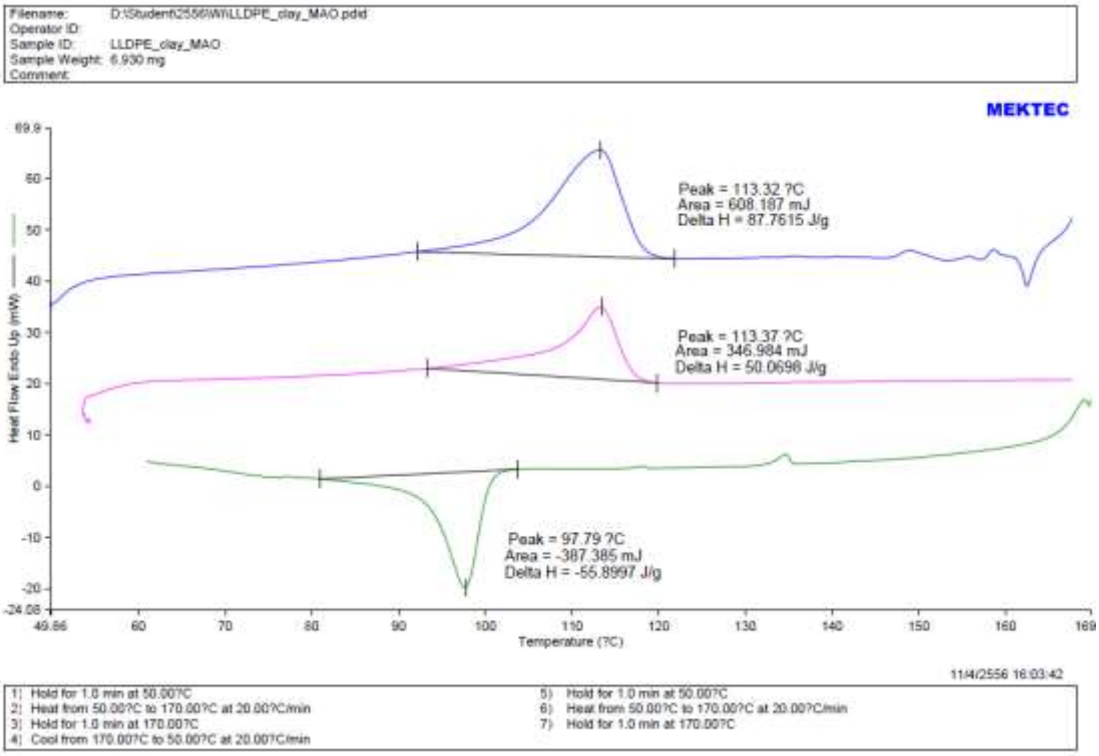
3) Hold for 1.0 min at 170.00?C
4) Cool from 170.00?C to 50.00?C at 20.00?C/min
5) Hold for 1.0 min at 50.00?C
6) Heat from 50.00?C to 170.00?C at 20.00?C/min
7) Hold for 1.0 min at 170.00?C

Figure A-1 DSC Curve of LLDPE/clay nanocomposite



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Comment:

11/4/2556 16:03:42

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2) Heat from 50.00?C to 170.00?C at 20.00?C/min
3) Hold for 1.0 min at 170.00?C
4) Cool from 170.00?C to 50.00?C at 20.00?C/min
5) Hold for 1.0 min at 50.00?C
6) Heat from 50.00?C to 170.00?C at 20.00?C/min
7) Hold for 1.0 min at 170.00?C

Figure A-1 DSC Curve of LLDPE/clay/MAO nanocomposite

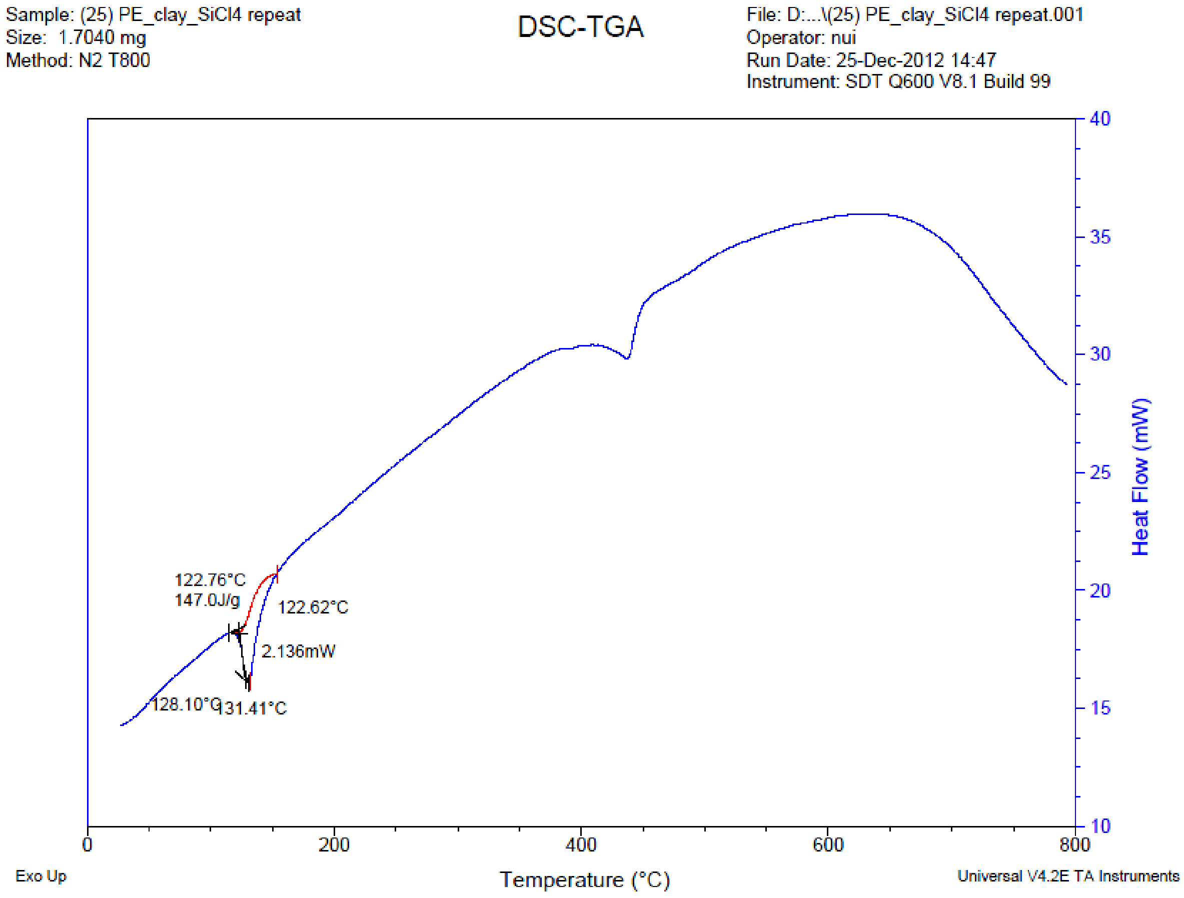

Figure A-1 DSC Curve of PE/clay/$SiCl_4$ nanocomposite

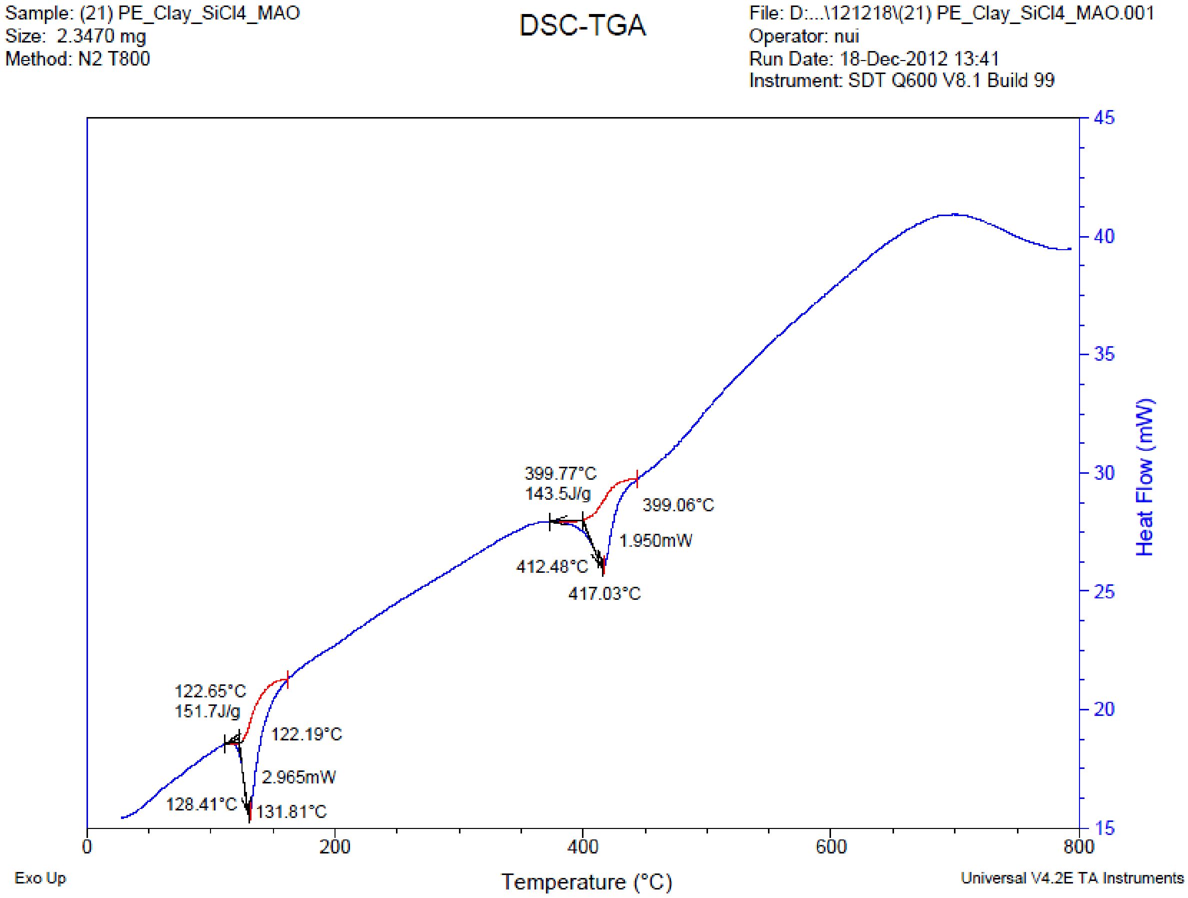

Figure A-1 DSC Curve of PE/clay/SiCl$_4$/MAO nanocomposite

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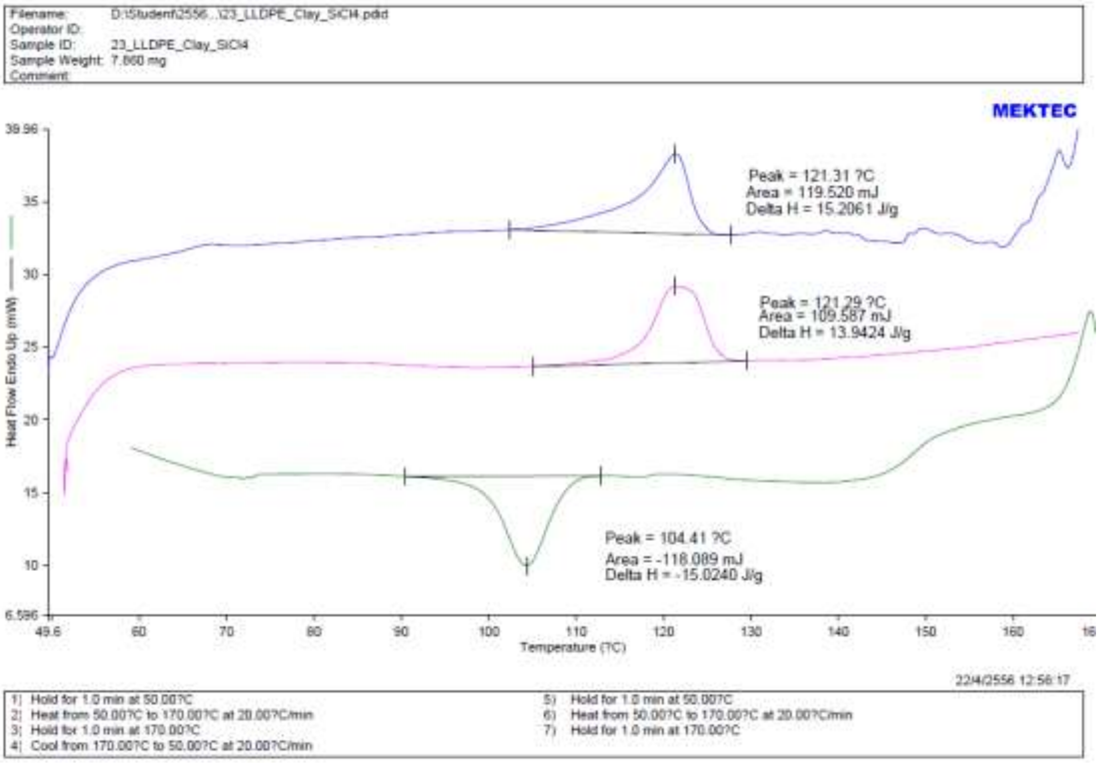

22/4/2556 12:56:17

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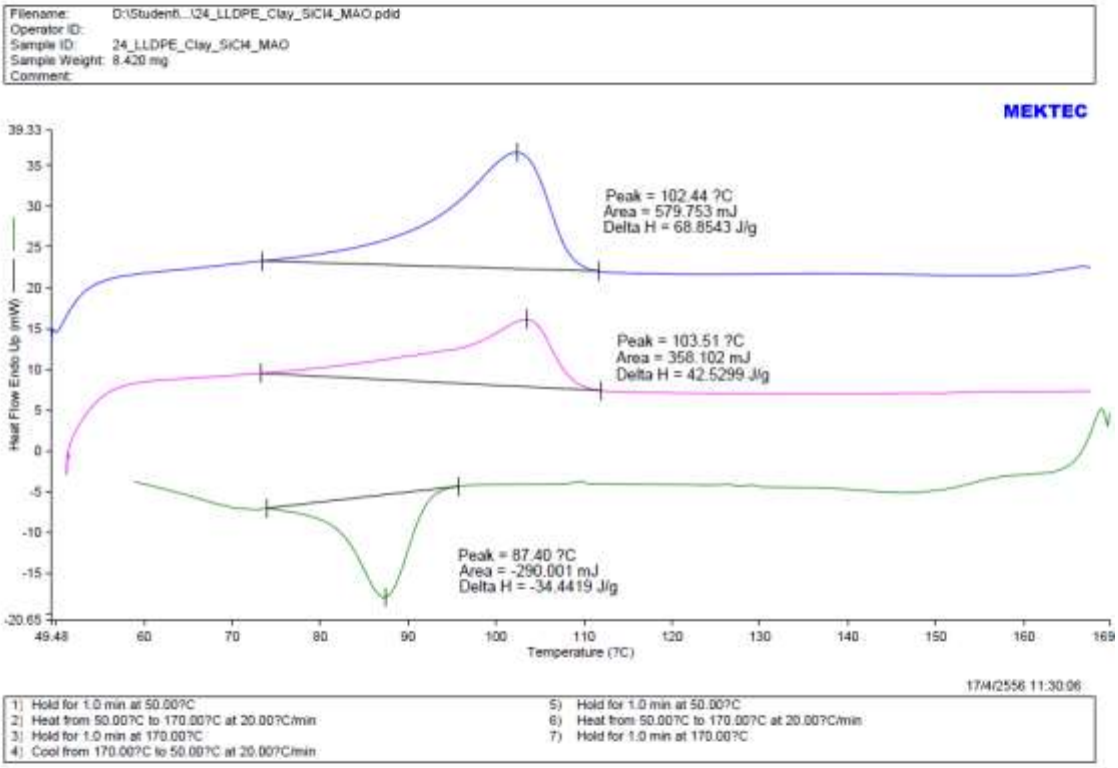
2) Heat from 50.00?C to 170.00?C at 20.00?C/min
3) Hold for 1.0 min at 170.00?C
4) Cool from 170.00?C to 50.00?C at 20.00?C/min
5) Hold for 1.0 min at 50.00?C
6) Heat from 50.00?C to 170.00?C at 20.00?C/min
7) Hold for 1.0 min at 170.00?C

Figure A-1 DSC Curve of LLDPE/clay/$SiCl_4$ nanocomposite



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Comment:

1) Hold for 1.0 min at 50.00?C
2) Heat from 50.00?C to 170.00?C at 20.00?C/min
3) Hold for 1.0 min at 170.00?C
4) Cool from 170.00?C to 50.00?C at 20.00?C/min
5) Hold for 1.0 min at 50.00?C
6) Heat from 50.00?C to 170.00?C at 20.00?C/min
7) Hold for 1.0 min at 170.00?C

Figure A-1 DSC Curve of LLDPE/clay/$SiCl_4$/MAO nanocomposite

APPENDIX B

Calculation of polymer properties

B.1 Calculation of crystallinity in polymer nanocomposites

The degree of crystallinity (Xc) of polymer nanocomposites were estimated in accordance with the following equation [25]:

$$X_c\ (\%) = (\Delta H_{exp/}\ \Delta H^*)\ x\ (1/\ W_f)$$

Where ΔH_{exp} is heat of fusion which obtained from DSC.

ΔH^* is heat of fusion of complete crystalline of HDPE (293 J/g).

W_f is weight fraction of HDPE in the polymer nanocomposite.

VITAE

Miss Suwimon Poorahong was born in January 9th, 1988 in Rayong, Thailand. She finished high school from Klaeng Withayasathawone School, Rayong and received Bachelor’s Degree in Chemical Engineering from the Faculty of Engineering, King Mongkut's University of Technology Thonburi in 2010. She subsequently completed the requirements for a Master’s Degree in Chemical Engineering at the Department of chemical Engineering, Faculty of Engineering, Chulalongkorn University in 2012.

List of publication

Poorahong S., and Jongsomjit B “LLDPE/CLAY NANOCOMPOSITE PRODUCED BY IN SITU POLYMERIZATION”. (The proceeding of the Pure and Applied Chemistry International Conference 2013 (PACCON 2013), Chonburi)