Effects of immobilization of methylalumoxane on cellulose support on ethylene polymerization behaviors.

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จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2018

ผลของการตรึงเมทิลอะลูมอกเซนบนตัวรองรับเซลลูโลสต่อพฤติกรรมของเอทิลีนพอลิเมอร์ไรเซชัน

น.ส.พราวนภา ทุมาวงศ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2561

Thesis Title   Effects of immobilization of methylalumoxane on cellulose support on ethylene polymerization behaviors.

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พราวนภาทุมวงศ์ : ผลของการตรึงเมทิลอะลูมอกเซนบนตัวรองรับเซลลูโลสต่อ
พฤติกรรมของเอทิลีนพอลิเมอร์ไรเซชัน. (Effects of immobilization of
methylalumoxane on cellulose support on ethylene polymerization
behaviors.) อ.ที่ปรึกษาหลัก : ศ. ดร.บรรเจิดจงสมจิตร

การปรับปรุงคุณสมบัติทางกายภาพของพอลิเอทิลีนนั้นทำได้โดยการเติมสารปรับปรุงที่มี
ขนาดระดับนาโนลงไปในระหว่างการทำการสังเคราะห์ซึ่งการเตรียมการสังเคราะห์สามารถทำได้
โดยการทำอินซิทูพอลิเมอร์ไรเซชันในการศึกษานี้ได้แบ่งออกเป็นสองส่วนในการวิจัยส่วนแรกศึกษา
ผลของชนิดและปริมาณของตัวเร่งปฏิกิริยาร่วมและตัวกำจัดสิ่งปนเปื้อนของตัวเร่งปฏิกิริยาเซอร์โค
โนซีนต่อพฤติกรรมของเอทิลีนพอลิเมอร์ไรเซชันในความเป็นจริงเมทิลอะลูมอกเซน (MAO) และ
ไตรเอทิลอะลูมินัม (TEA) จะใช้เป็นตัวเร่งปฏิกิริยาร่วมและตัวกำจัดสิ่งปนเปื้อนตามลำดับ
อัตราส่วนของ $[Al]_{MAO}/[Zr]_{cat}$และ $[Al]_{TEA}/[Zr]_{cat}$ที่แตกต่างกันใช้ในระหว่างการเกิดปฏิกิริยาอินซิทู
พอลิเมอร์ไรเซชันของเอทิลีนปฏิกิริยาถูกดำเนินการในเครื่องปฏิกรณ์แบบกึ่งกะภายใต้การทำงาน
แบบแอเดียแบติกที่อุณหภูมิ 70 ° C เป็นเวลา 15 นาทีภาวะที่ดีที่สุดที่ให้ความว่องไวของปฏิกิริยา
สูงสุดพบได้ที่อัตราส่วนของ $[Al]_{MAO}/[Zr]_{cat}$เท่ากับ 2000 ด้วยเหตุนี้เราจึงใช้ภาวะนี้ในส่วนถัดไปใน
ส่วนที่สองส่วนนี้เน้นที่การสังเคราะห์พอลิเอทิลีนโดยกระบวนการอินซิทูพอลิเมอร์ไรเซชันด้วย
วิธีการตรึงแบบต่างๆโดยใช้เมทิลอะลูมอกเซน/ตัวเร่งปฏิกิริยาเซอร์โคโนซีนที่รองรับเซลลูโลสเราทำ
การตรึงตัวเร่งปฏิกิริยาร่วม /ตัวเร่งปฏิกิริยาลงบนเซลลูโลสด้วยวิธีที่ต่างกันสามวิธีได้แก่ (i) ตรึง
ตัวเร่งปฏิกิริยาร่วม / เซลลูโลส (ii) ตรึงตัวเร่งปฏิกิริยา / เซลลูโลสและ (iii) ตัวเร่งปฏิกิริยา / ตัวเร่ง
ปฏิกิริยาร่วม/ เซลลูโลสจากผลการทดลองพบว่าความว่องไวของปฏิกิริยาที่สูงที่สุดพบใน PE-MAO
/ MCC เนื่องจากตัวรองรับ MCC กับการตรึงของเมทิลอะลูมอกเซนนั้นสามารถทำให้ประจุลบ
เสถียรซึ่งช่วยป้องกันการหยุดปฏิกิริยาได้

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต ....
ปีการศึกษา	2561	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

6070250721 : MAJOR CHEMICAL ENGINEERING

KEYWORD: Polyethylene Metallocene Cellulose Immobilization Scavenger

Praonapa Tumawong : Effects of immobilization of methylalumoxane on cellulose support on ethylene polymerization behaviors.. Advisor: Prof. BUNJERD JONGSOMJIT, Ph.D.

The way to improve the physical properties of polyethylene is done by adding nano-sized filler during the synthetic process. These can be commonly achieved by *in situ* polymerization. These studies are divided into two parts in this research. Firstly, it investigated the effect of types and amounts of cocatalyst and scavenger of zirconocene catalyst on ethylene polymerization behaviors. In fact, methylalumoxane (MAO) and triethylaluminum (TEA) were used as cocatalyst and scavenger, respectively. The ratios of $[Al]_{MAO}/[Zr]_{cat}$ and $[Al]_{TEA}/[Zr]_{cat}$ were varied during the *in situ* polymerization of ethylene. The polymerization was performed in a semi-batch autoclave reactor under adiabatic operation at 70 °C for 15 minutes. The best condition which reached the maximum catalytic activity was found at the ratio of $[Al]_{MAO}/[Zr]_{cat}$ equals to 2000. For this reason, we used this condition in the next part. The second part focused on synthesis of polyethylene by *in situ* polymerization with different immobilization methods using cellulose-supported MAO/zirconocene catalyst. We performed the immobilization of cocatalyst/catalyst onto cellulose with three different methods including (i) immobilized cocatalyst/cellulose, (ii) immobilized catalyst/cellulose and (iii) immobilized catalyst/cocatalyst/cellulose. From the experimental results, it was found that the highest catalytic activity was obtained in PE-MAO/MCC because the MCC support with immobilization of MAO can stabilize the anion, which prevent termination.

Field of Study: Chemical Engineering   Student's Signature ....

Academic Year: 2018   Advisor's Signature ....

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CHULALONGKORN UNIVERSITY

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CHAPTER 1

INTRODUCTION

1.1 Introduction

It is widely recognized that polyethylene plastics have a role to play in our daily lives. Through their interesting properties such as light-weight, toughness, durability, excellent chemical resistance and other properties that can be applied to a variety of applications as the producer needs, it makes polyethylene being the popular plastic in the world. Polyethylene is used in applications including films, tubes, plastic parts, laminates, foam, geomembranes and in several markets (packaging, toy, automotive, electrical, etc.). Polyethylene is polyolefin family of polymers and classified by its density and branching. The most common types of polyethylene are: low density polyethylene (LDPE), high density polyethylene (HDPE), and linear low-density polyethylene (LLDPE). The use of polyethylene in each type depends on the application for materials[1, 2].

It is well known that chemical catalysts such as Ziegler-Natta and metallocene catalysts have been used for ethylene polymerization to produce polyethylene. The polyethylene polymer, which is produced from Ziegler-Natta catalysts, is broad molecular weight distribution (MWD) and chemical composite distribution (CCD), while the polymers produced by metallocene catalysts give a narrow molecular weight distribution (MWD) and chemical composite distribution (CCD) because metallocene catalyst is a single-site catalyst. It has only one type of active site that is a revolution in the polymer industry for producing polyolefins. The advantage of metallocene catalysts compared to Ziegler-Natta catalysts is that they exhibit higher catalytic activity than Ziegler-Natta catalysts for homogeneous system

[3-5].For this reason, it is interesting for the development of ethylene polymerization by using metallocene catalysts.

Metallocene catalysts are sensitive to various polymerization conditions, such as the concentrations of catalyst, cocatalyst and their ratios, polymerization temperature and time, monomer concentration, the nature of solvent, etc. [6]. The interesting factor influencing the catalytic activity of metallocenes for α-olefin polymerizations is the different types and amount of alkylaluminum. Aluminum alkyls, added to the reactor during slurry or gas-phase polymerization with MAO/metallocene and conventional Ziegler-Natta catalysts, are used to activate the catalyst acting as cocatalyst and also scavenge impurities, which contaminate in materials during the reaction [7, 8].

Other factor to improve the physical properties of polyethylene is done by adding nano-sized filler enhancers during the synthetic process which produces the product called polymer composites by *in situ* polymerization, which is the most popular way due to its good efficiency and good distribution. In fact, *in situ* polymerization can be performed by immobilizing the catalyst onto the surface of the nano-particle fillers, also known as the support. There are various kinds of supports such as inorganic supports and organic supports. According to the concern in environmental problems, we are more interested in using natural cellulose than other synthetic substances. Apart from that reason, natural cellulose has numbers of suitable properties to be a support; for example, a high porous property, high sorption capacity, stability of metal anions, and physical and chemical versatility, which make them proper and attractive to be used as supports for metallocene catalyst in *in situ* polymerization that produces polyethylene-polymer composites[9, 10].

This research was divided into two parts. The first part was to investigate the effect of cocatalyst amounts and scavenger of zirconocene catalyst for ethylene

polymerization. This was done by adding two types of alkylaluminum consisting of methylaluminoxane (MAO) and triethylaluminum (TEA). The molar ratios of $[Al]_{MAO}/[Zr]_{cat}$ and $[Al]_{TEA}/[Zr]_{cat}$ were varied during the *in situ* polymerization of ethylene. In the final part, the effect of different methods for immobilization of catalyst and MAO onto cellulose on the ethylene polymerization behaviors was further investigated. In addition, the obtained polymers were also characterized by different techniques including, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) in order to determine the morphology and the quantity of elements, which were distributed on the cellulose supports. The bulk crystalline phases were investigated by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Fourier transform infrared spectroscopy (FT-IR) was used to determine the functional group of catalysts and X-ray photoelectron spectroscopy (XPS) was used to measure the interaction between MAO and cellulose. The catalytic activity and polymer properties are discussed in more detail.

1.2 Research Objective

1.2.1   To investigate effect of types and amounts cocatalyst and scavenger of zirconocene catalyst on ethylene polymerization behaviors.

1.2.2   To synthesize polyethylene by *in situ* polymerization with different immobilization methods using cellulose-supported MAO/zirconocene catalyst.

1.3 Research Scopes

1.3.1   Commercial cellulose is used as support for MAO in *in situ* ethylene polymerization reaction.

1.3.2   Cellulose-supported MAO was prepared by *in situ* immobilization compared with homogeneous system.

1.3.3   Cellulose and cellulose-supported MAO are characterized by SEM-EDX, XRD, TGA-DSC, and FT-IR method.

1.3.4   Alkylaluminum was divided into 2 types consisting of methylaluminoxane (MAO) and triethylaluminum (TEA), which are used as cocatalyst and scavenger for zirconocene catalyst.

1.3.5   The molar ratios of $[Al]_{MAO}/[Zr]_{cat}$ were varied at 1000,1500, 2000 and $[Al]_{TEA}/[Zr]_{cat}$ molar ratios were at for 500,1000,1500 with $[Al]_{MAO}/[Zr]_{cat}$ molar ratio of 1000.

1.3.6   Performance of the immobilization of cocatalyst/catalyst onto cellulose for ethylene polymerization with three different methods including (i) immobilized cocatalyst/cellulose (ii) immobilized catalyst/cellulose and (iii) immobilized cocatalyst/catalyst/cellulose.

1.3.7   Ethylene polymerization was carried out to measure the catalytic activity and it was performed in a 100 mL of stainless steels reactor equipped with a magnetic stirrer. Polymerization temperature is 70 $^{\circ}$C, while stirring at 600 rpm under 3.5 bar of ethylene pressure in slurry process.

1.3.8   Polyethylene obtained is characterized by XRD, SEM, TGA, and DSC.

1.4 Research Benefits

1.4.1   To understand the effects of the different immobilization methods for cellulose-supported MAO on the catalytic activity of metallocene catalyst for ethylene polymerization and polyethylene properties.

1.4.2   To understand the effects of different alkylaluminums on the catalytic activity of metallocene catalyst for ethylene polymerization.

1.5 Research Methodology

Study information of PE
and polymerization by metallocene catalyst

Study 100ml slurry ethylene
polymerization process and laboratory skills

Part 1

Study effect of molar ratios of different types

of alkylaluminum on ethylene

polymerization by metallocene catalyst

- $[Al]_{MAO}/[Zr]_{cat}$
- $[Al]_{TEA}/[Zr]_{cat}$

Part 2

To investigate effect of different methods of

immobilization on ethylene polymerization by

metallocene catalyst

Prepared supports

- Commercial cellulose (MCC)

Characterization

- Supported => SEM, XRD, DSC, IR

In situ **immobilized**
- MAO/MCC
- Zirconocene/MCC
- Zirconocene/MAO/MCC

Characterization

- Cellulose before immobilization
=>SEM-EDX, XRD, DSC, IR

Ethylene Polymerization

Polymer

Characterization

- Polymer => SEM, XRD, TGA-DSC

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Polyethylene [11-13]

There are several materials produced from polyethylene. Polyethylene production is widely expanding in each day around the world, due to the development of plastic industry and their interesting properties such as light-weight, toughness, durability, excellent chemical resistance and other properties that can be applied to a variety of applications as the producer needs, it makes polyethylene being the popular plastic in the world. Polyethylene is used in applications, which can be found in household durable goods, toys, consumer packaging, beverage caps, trash bags, and can liners. It is also widely used in industrial packaging systems, storage tanks, foam, reusable pallets, composite decking materials, sealants for solar panels, and artificial turf, and in several markets (automotive, electrical, etc.).

Normally, Polyethylene is made from the polymerization of ethylene monomer. Polyethylene molecule consists of a long backbone of covalently linked carbon atoms with a pair of hydrogen atoms attached to each carbon then chain ends are terminated by methyl groups. Polyethylene chemical formula is $(C_2H_4)_n$ that shown schematically in Figure 1[13].

Figure1 Polyethylene structure.

Polyethylene has a number of different forms with different mechanical properties example branching, crystallinity, density and most of all molecular weight.

Industrial polyethylene is commonly classified by based on density or molecular weight. On the other hand, IUPAC names are not typically used. Density is measured using density gradient columns and hydrostatic methods. Density is directly related to crystalline content, in fact can be used to estimate % crystallinity in polyethylene.

The Society of the Plastics Industry (SPI), that is an industry of trade association founded in 1937, identifies three main categories of polyethylene based on density:

• Low density: 0.910-0.925 g/cm3

• Medium density: 0.926-0.940 g/cm3

• High density: 0.941-0.965 g/cm3

The American Society for Testing and Materials (ASTM) has also defined various types of polyethylene, which provides the following classifications based upon density:

• High density polyethylene (HDPE): >0.941 g/cm3

• Linear medium density polyethylene (LMDPE): 0.926-0.940 g/cm3

• Medium density polyethylene (MDPE): 0.926-0.940 g/cm3

• Linear low density polyethylene (LLDPE): 0.919-0.925 g/cm3

• Low density polyethylene (LDPE):0.910-0.925 g/cm3

SPI and ASTM classifications are not enough to describe the wide range of polyethylenes available in the industry. Classifications have been further subdivided to additional information, such as molecular weight or comonomer employed. The various classifications of polyethylene in common use in industry are provided below: [12]

- Low Density Polyethylene (LDPE)

LDPE is produced only by free radical polymerization of ethylene initiated by organic peroxides or other reagents. Density is typically from 0.915-0.930 g/cm^3. LDPE is the easily processed of major types of polyethylene that often blended with linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). LDPE is highly branched and contains relatively high amorphous content, that carbon atoms are attached to three carbon atoms instead of two, because a branch on which other polyethylene chains are attached. These branches are relatively long and link with other molecules which results in outstanding clarity in film for food packaging, a major application.

- High Density Polyethylene (HDPE)

HDPE is produced by ethylene polymerization using Ziegler-Natta or supported chromium ("Phillips") catalysts. Density is typically range from 0.94-0.97 g/cm^3. HDPE has high modulus, yield, crystallinity and tensile properties. HDPE is a more linear molecule that regularly shorter compared to LDPE. There are very few side chains caused by branching, and these side chains. HDPE is widely used in important applications such as extruded pipe for potable water/gas and in blow molded packaging for industrial chemicals (HIC) example bottle, detergent, shampoo, etc.

- Linear Low Density Polyethylene (LLDPE)

LLDPE is produced by ethylene copolymerization using Ziegler-Natta, supported chromium or metallocene catalysts with α-olefins and common comonomer such as 1-butene, 1-hexene and 1-octene. Density is typically range from 0.915-0.930 g/cm^3. The structure of LLDPE has a linear backbone with short uniform branches that unlike longer branches of LDPE. These short branches are able slide against each other elongation without form entangled like LPDE. Properties of LLDPE are very flexible, high impact strength, good chemical resistance, good stress crack and impact resistance. LLDPE suitable for a variety of film application such as general purpose film, garment packaging, stretch film, agricultural film and etc.
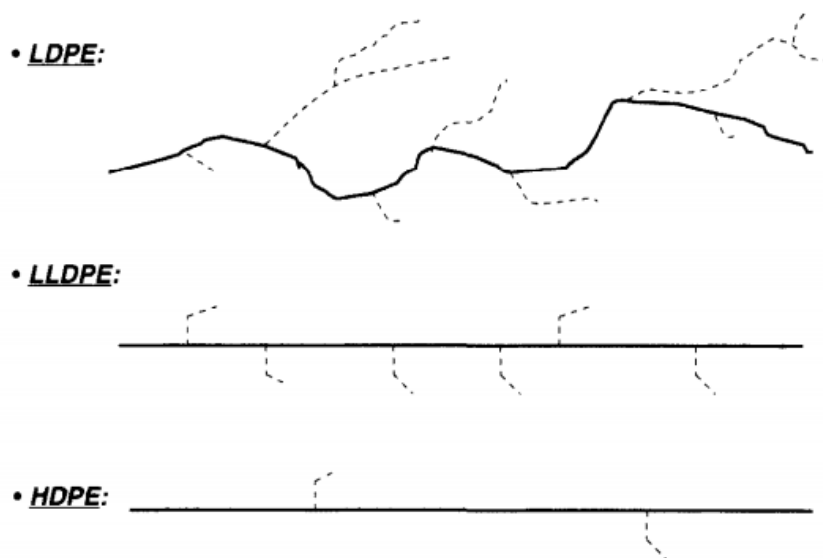
Figure2 Schematic molecular structure of three types of polyethylene A) Low-density polyethylene, B) Linear low-density polyethylene, C) High-density polyethylene [12].

Conditions for polymerization vary widely and polyethylene compositions also differ substantially in structure and properties. In addition, Single-site catalysts or metallocene catalysts also involve transition metal catalysts to produced polyethylene.

2.2 Metallocene catalytic systems

All these catalytic systems can be conveniently divided into two components. First, is a metallocene complex of a transition metal. In the second component, an aluminoxane, an alkylaluminum, or a combination of aluminoxanes and alkylaluminums, are used to activate the metallocene catalyst as known as cocatalyst. Normally, these metallocenes have poor or no activity when used alone. It is now generally accepted that the catalytic active species for metallocene/aluminoxane/alkylaluminum systems that also form cationic metallocene catalyst [14, 15].

2.2.1 Metallocene catalysts

Metallocene catalysts represent to development for polyolefin polymerization. Their properties are soluble in hydrocarbons and have only one type of active site. These catalysts are mostly used for the synthesis polyethylene such as LLDPE with a narrow molecular weight distribution (MWD) and chemical composite distribution (CCD). The history of metallocene catalysts has begun in Germany since 1976, when Kaminsky and Sinn discovered highly active catalystic systems based on zirconocene complexes. These catalysts are applied as solutions or supported on inert carriers. The structure of the catalyst used to control the resulting molecular weight and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions. In addition, their catalytic activity is 10 to 100 times higher than the classical Ziegler-Natta systems [14, 16].

Metallocenes are π-bonded organometallic compounds, are complexes of metals that the group 4B transition metallocenes (titanocenes, zirconocenes and hafnocenes), with between aromatic ligands, such as dicyclopentadienyl (cp) or indenyl groups creating a structure like sandwich (Fig. 3). The cyclopentadienyl ring ligands of a metallocene are singly bonded to the central transition metal atom by a π-bond. The nature and number of the rings and substituents (S); the type of transition metal (M) and its substituents (R); the type of the bridge, if present. The types of cocatalyst determine the catalytic behavior of these organometallic compounds towards the polymerization of linear and cyclic olefins. These polymerization catalysts have been used for the production of polymers. The first characterized metallocene was ferrocene, bis(cyclopentadienyl) iron. The simple examples of these metallocenes are shown in Fig. 4 [12, 17, 18].

M : transition metal of groups 4b, 5b or 6b

R : hydrocarbyl, alkylidene, halogen radicals

S: hydrogen, hydrocarbyl radicals

B: alkylene, alkyl radicals, heteroatom groups
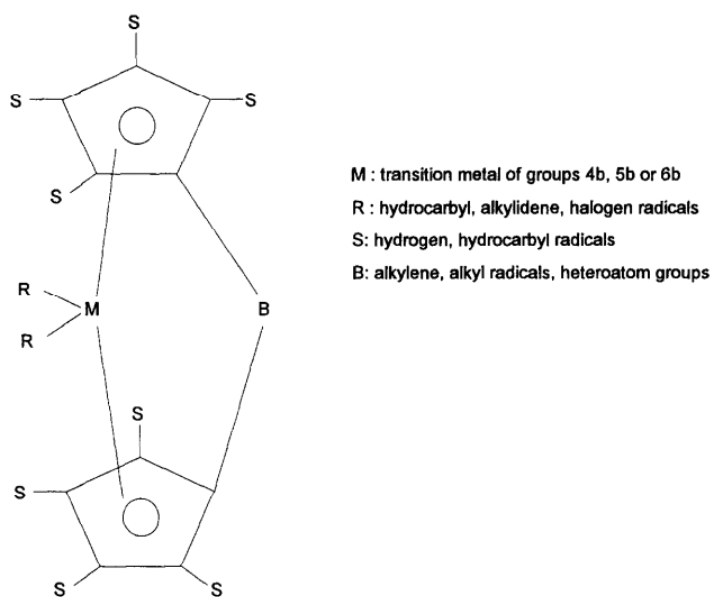
Figure3 Generic structure of a metallocene catalyst.

1 R = H
2 R = neomenthyl

4

8 X = C_2H_4, $R^1 = R^2 = R^3$ = Me
11 X = Me_2Si, $R^1 = R^2 = R^3$ = Me
12 X = Me_2Si, R^1 = Me, R^2 = Ph, R^3 = H

13

5 M = Zr, X = C_2H_4
6 M = Hf, X = C_2H_4
9 M = Zr, X = Me_2Si

7 X = C_2H_4
10 X = Me_2Si

14 X = Me_2C
18 X = Ph_2C

15 M = Zr, X = Me_2C, R = H
16 M = Hf, X = Me_2C, R = H
17 M = Zr, X = Ph_2C, R = H
19 M = Zr, X = Me_2C, R = Bu^t
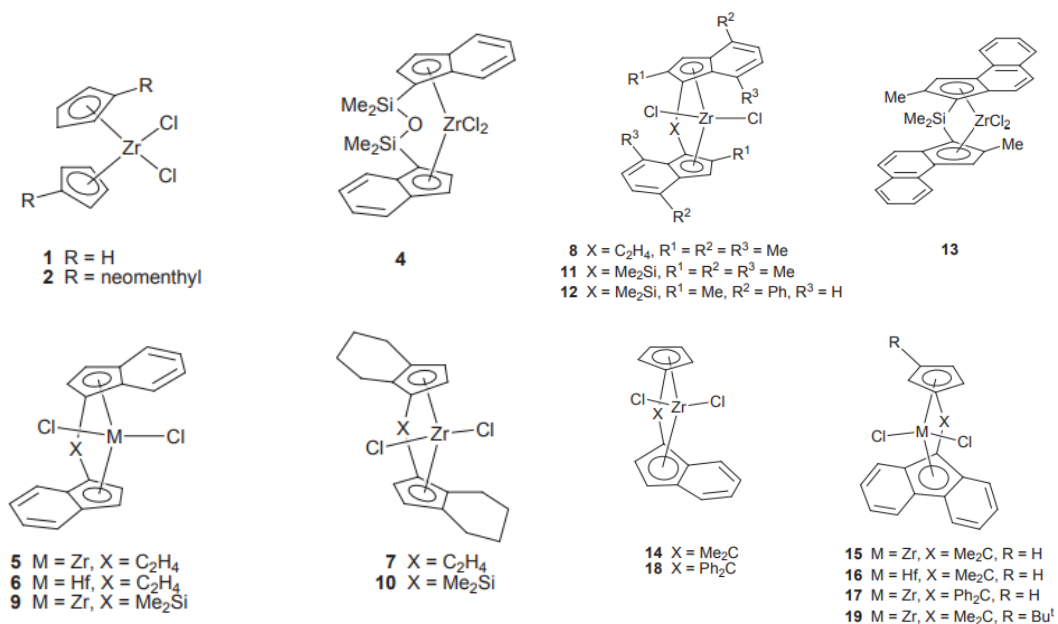
Figure 4 Structure of metallocenes are used in the polymerization of olefins [15].

Using metallocene catalyst, it was possible for the first time to produce [12].

- polyethylene, polypropylene and copolymer with narrow molecular weight distributions.
- cycloolefin copolymers (COC) with high catalytic activity
- optically active oligomers
- composite materials of biomass, powdered metals with polyolefin

2.2.2 Aluminum alkyls [19]

Aluminum alkyls include any compound that contains a direct carbon–aluminum σ-bond and encompasses R_3Al, R_2AlCl, $R_3Al_2Cl_3$, $RAlCl_2$, R_2AlOR', and R_2AlH that R is commonly refer to C_1 - C_4 alkyl. In addition, methyl (CH_3) and ethyl group (C_2H_5) are important for commercial aluminum alkyls.

Aluminum alkyls have been produced commercially using technology licensed by Nobel laureate Karl Ziegler since 1959. Aluminum alkyls are pyrophoric that have the ability to ignite spontaneously in the air and harshly reactive with water or moisture[20, 21]. Considering these properties, it is remarkable that large of aluminum alkyls are produced and have been supplied to the polyolefins industry worldwide with relatively safety proceedings. Principal aluminum alkyls available in the market and their common acronyms are shown in Table 1.

Table 1 Commercially available aluminum alkyls [19].

Product	Acronym	Formula	CAS number	Theoretical wt% Al
Trimethylaluminum	TMA	$(CH_3)_3Al$	75-24-1	37.4
Dimethylaluminum chloride	DMAC	$(CH_3)_2AlCl$	118-58-3	29.2
Methylaluminumsesquichloride	MASC	$(CH_3)_3Al_2Cl_3$	12542-85-7	26.3
Triethylaluminum	TEA	$(C_2H_5)_3Al$	97-93-8	23.6
Diethylaluminum chloride	DEAC	$(C_2H_5)_2AlCl$	96-10-6	22.4
Diethylaluminum iodide	DEAI	$(C_2H_5)_2AlI$	2040-00-8	12.7
Ethylaluminumsesquichloride	EASC	$(C_2H_5)_3Al_2Cl_3$	12075-68-2	21.8
Ethylaluminum dichloride	EADC	$C_2H_5AlCl_2$	563-43-9	21.3
Isobutylaluminum dichloride	MONIBAC	$i\text{-}C_4H_9AlCl_2$	1888-87-5	17.4
Tri-n-butylaluminum	TNBA	$(C_4H_9)_3Al$	1116-70-7	13.6
Triisobutylaluminum	TIBA	$(i\text{-}C_4H_9)_3Al$	100-99-2	13.6
Diisobutylaluminum hydride	DIBAL-H	$(i\text{-}C_4H_9)_2AlH$	1191-15-7	19.0
Tri-n-hexylaluminum	TNHAL	$(C_6H_{13})_3Al$	1116-73-0	9.6
Tri-n-octylaluminum	TNOAL	$(C_8H_{17})_3Al$	1070-00-4	7.4
Di-n-octylaluminum iodide	DNOAI	$(C_8H_{17})_2AlI$	7585-14-0	7.1
Diethylaluminumethoxide	DEAL-E	$(C_2H_5)_2AlOC_2H_5$	1586-92-1	20.7
Ethylpropoxyaluminum chloride	EPAC	$(C_2H_5)(C_3H_7O)AlCl$		17.9

Commercial aluminum alkyls are generally clear, colorless, low viscosities at ambient temperatures and are miscible in aliphatic hydrocarbons (HC). Large quantities of aluminum alkyls are supplied as solutions in HC for safety. Purity of aluminum alkyls used in manufacture of polyolefins varies. To illustrate, R_3Al compounds commonly contain small amounts of other trialkylaluminum compounds (R'_3Al, $R'{\neq}R$). This is usually a consequence of the purity of precursors materials or of side reactions during process, such as addition of an ethylaluminum in TEA across ethylene to produce an n-butylaluminum group (Figure 5).

$$\diagdown \diagup \text{AlCH}_2\text{CH}_3 + \text{CH}_2=\text{CH}_2 \longrightarrow \diagdown \diagup \text{AlCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$
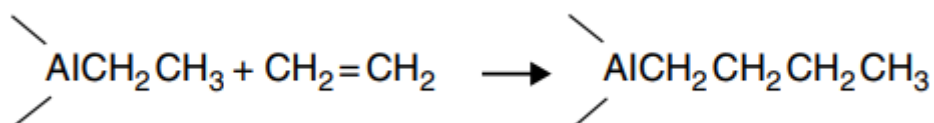
Figure5 Insertion of ethylene into an ethyl-aluminum bond to form an n-butylaluminum group.

Products from reaction of aluminum alkyls with water (eq. 2.1) and oxygen that will also contain ppm amounts of aluminoxanes and alkoxides. However, water, oxygen, nitrogen, olefins and hydrogen act as contaminants in process materials. Aluminoxanes and alkoxides are usually undetectable (below 500 ppm) that no problems in polyolefin catalystic systems at these levels [19].

$$2(C_2H_5)_3 Al + H_2O \rightarrow (C_2H_5)_2 Al-O-Al(C_2H_5)_2 + 2C_2H_6 \uparrow \qquad \text{(eq. 2.1)}$$
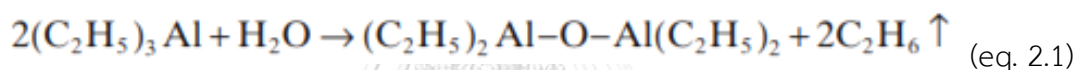
- Hydride content: R_3Al compounds (most commercially) also contain little amounts of R_2AlH (R=ethyl or higher). Hydride content is expressed as AlH_3 by among major suppliers and ranges from about 0.02% (wt.) in TEA and to about 0.5% in TIBA. However, TMA does not ordinarily contain hydride. In the major of ZN catalytic systems, hydride content and small amounts of other trialkylaluminum compounds (R'_3Al) are not damaging to catalytic performance.

- Compatibility with organic solvents: Aluminum alkyls are compatible with commonly hydrocarbon (HC) solvents such as toluene and heptane.

- Reactivity with CO_2 and CO: R_3Al are reactive with CO_2[22].The reaction of TMA with CO_2 has been used to produce MAO cocatalysts for metallocene catalysts. However, R_3Al are unreactive with CO at moderate pressures and

temperatures. Aluminum alkyls containing halogen or oxygen (DEAC, diethylaluminumethoxide, etc.) are not reactive with CO_2.

- Thermal stability: Aluminum alkyls indicate moderate to superior thermal stability, depending on ligands.

Aluminum alkyls are as raw materials for catalyst synthesis and as activators for the transition metal catalyst called "cocatalysts".

These key functions are illustrated below [19].

➢ Aluminum alkyls as cocatalysts

Alkylation of the reduced transition metal compound to produce active centers for polymerization. For example, reaction of triethylaluminum (TEA) with $TiCl_3$ in eq. 2.2

(eq. 2.2)
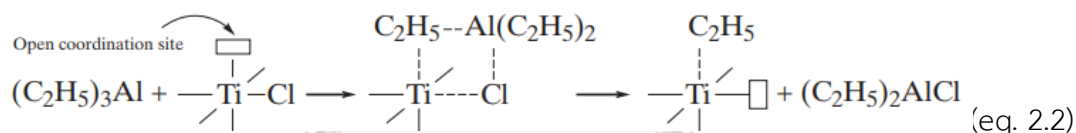
➢ Aluminum alkyls act as scavenger

The purpose of aluminum alkyls also scavenges contaminants in materials that are catalyst poisons (water, O_2, etc.), which is commonly added to the reactor during slurry or gas-phase polymerization with MAO/metallocene and conventional Ziegler-Natta catalysts. Poisons enter as ppm contaminants in materials such as monomer, comonomer, solvents, and chain transfer agents. Reaction of the aluminum alkyl with contaminants (eq. 2.3-2.4) generates alkylaluminum derivatives that do not affect to catalytic performance. On the other hand, reaction between water and TEA produce small amounts of ethylaluminoxane (EAO) that can be used as cocatalyst, so this improve catalytic performance (eq. 2.1).

$$(C_2H_5)_3Al + \tfrac{1}{2}O_2 \rightarrow (C_2H_5)_2AlOC_2H_5$$

(eq. 2.3)

$$(C_2H_5)_3Al + CO_2 \rightarrow (C_2H_5)_2AlO\overset{\overset{\textstyle O}{\|}}{C}C_2H_5$$

(eq. 2.4)
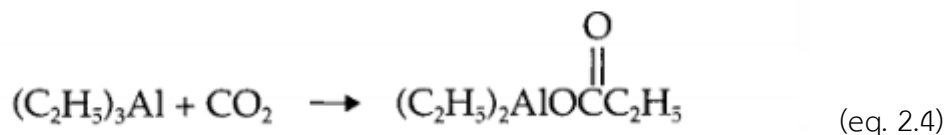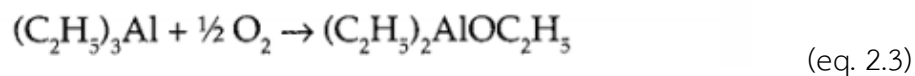
➢ Aluminum alkyls are also concerned in chain transfer, which a minor function. Other metal alkyls are either too expensive or too toxic or perform poorly.

For this reason, aluminum alkyls are preferred as cocatalyst or scavenger. For instance, magnesium alkyls as cocatalysts may completely deactivate ZN catalysts. The reason may stem from blockage of active centers caused by strong coordination of magnesium alkyl or overreduction of the transition metal.

As usual in commercial operations, cost and performance are the key factor in selecting an aluminum alkyl based on aluminum content. Moreover, prices vary by region and other considerations that depend upon product and geographical. The prices of different aluminum alkyl are illustrated below (Table 2).

Table2 Costs of different aluminum alkyl from Sigma Aldrich supplier.

Aluminum alkyl	Amount(g)	Price (USD)
TMA	100	244.00
TEA	100	148.00
TIBA	100	122.00

TMA has a high cost more than other aluminum alkyl due to conventional MAO,which is excellent cocatalyst for metallocene, produced by partial hydrolysis of TMA in toluene. Hence, TMA translates to very high costs for MAO such as 315.83 USD for 100mlof MAO.In addition, TIBA was less expensive than TEA. However, TEA contains amount of molar of aluminum than TIBA. So, TEA is the most cost-effective than TIBA that being selected in this research.

2.2.3 The role of the aluminoxane cocatalyst [17].

Metallocenes, in combination with the aluminium alkyl cocatalysts used in metallocene systems, are indeed capable of ethylene polymerization. On the contrary, using only metallocene catalyst results in a very low activity. The first olefin was ethylene polymerized by using metallocene/aluminoxane catalysts. The activity of metallocene system derivatives could be increased by the addition of small amounts of water[23]. This increased activity is related to the reaction between alkylaluminum and water to form aluminoxanes cocatalyst (eq. 2.1).

Aluminoxane component influences in catalytic performance that besides acting as an alkylation agent and an impurity scavenger. Aluminoxanes are involved in the formation of active sites and the prevention of their deactivation by contaminates. Chien and Wang [24] obviously demonstrated that the functions of the aluminoxane component go beyond alkylation of the metallocene.

The type of aluminoxane influences on the efficiency of the metallocene/aluminoxane catalytic system. methylaluminoxanes (MAO) are also aluminum alkyls and have become important in recent years as cocatalysts for metallocene catalysts. methylaluminoxane(MAO) discovery and application of MAO in institute at Hamburg in 1977,that seems to be more effective as a cocatalyst than

other aluminoxanes such as ethylaluminoxane (EAO) and isobutylaluminoxane (IBAO) [25]. Moreover, the catalytic activity of the metallocene system is directly proportional to the degree of oligomerization of the aluminoxane. For mostly homogeneous metallocene catalystic systems, a large excess of aluminoxane is required for the polymerization to reach its optimum value, commonly used aluminum/transition metal ratios varying from 1,000 to 50,000.

MAO is a compound between aluminium and oxygen atoms that are arranged alternately and free valences are saturated by methyl substituents. It is gained by partial hydrolysis of trimethylaluminium(TMA) (Eq.2.5) [26] and, according to investigations by Sinn[27] and Barron[28], it consists mainly of units of the basic structure $[Al_4O_3Me_6]$, which contains four aluminium, three oxygen atoms and six methyl groups. As the aluminium atoms in this structure are co-ordinatively unsaturated, the basic units (mostly four) join together forming clusters and cages (Fig. 6). These have molecular weights from 1200 to 1600 and are soluble in hydrocarbons [23, 29].
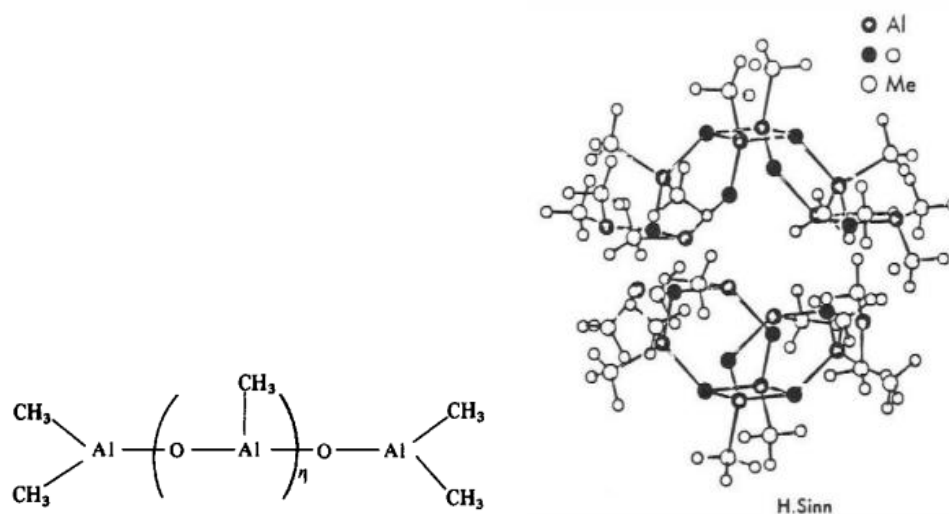
$$nAl(CH_3)_3 + nH_2O \rightarrow [-Al(CH_3)O-]_n + 2nCH_4$$

(eq.2.5)

Figure6 Structures of methylaluminoxane (MAO).

2.3 Supported metallocene catalysts

Since, most of the polyolefin industrial plants with metallocene catalysts are designed to use heterogeneous system, due to major disadvantages of the homogeneous catalysts are the lack of morphology control and reactor fouling. One way of solving this problem is by supporting the metallocene catalyst on an inert carrier, without the loss of catalytic activity and ability to make polymer with narrow molecular weight distribution and chemical composition distributions and when desired, long chain branches. Because supported catalysts allow control of morphology, it may be applied in cheaper gasphase processes, and may permit the use of less MAO, whilst still offering facile control of polymer properties by ligand variation [17, 30]. Metallocenes can be effectively supported on several inorganic oxides. The most commonly used supports are SiO_2, $MgCl_2$, Al_2O_3, MgF_2 and CaF_2. Polyolefin particles and natural polymers such as cellulose have also been used to support metallocene catalysts.

The types of support and the synthetic preparations for supporting the metallocene catalyst and MAO cocatalyst have a critical influence on catalytic behavior. Synthetic preparations can be conducted by three methods: melt-mixing, solution blending, and *in situ* polymerization. *In situ* polymerization is the most popular way due to its good efficiency and good distribution, which can be prepared by immobilizing the catalyst onto the surface of the nano-particle fillers, also known as the support. Several *in situ* polymerization technique for supporting metallocenes and MAO have been proposed:(Fig.7)[14]

(A) immobilized cocatalyst/support: Initial adsorption of MAO cocatalyst on the support followed by addition of the metallocene is mostly used.

(B) immobilized cocatalyst/catalyst/support: immobilization of the mixture of metallocene and MAO is adsorbed on the support.

(C) immobilized catalyst/support: immobilization of the metallocene on the support, followed by addition with MAO in the polymerization reactor.

By supporting the metallocene catalysts, the energy bonds are raised up to a higher level. This means that in most cases, it decreases activity.
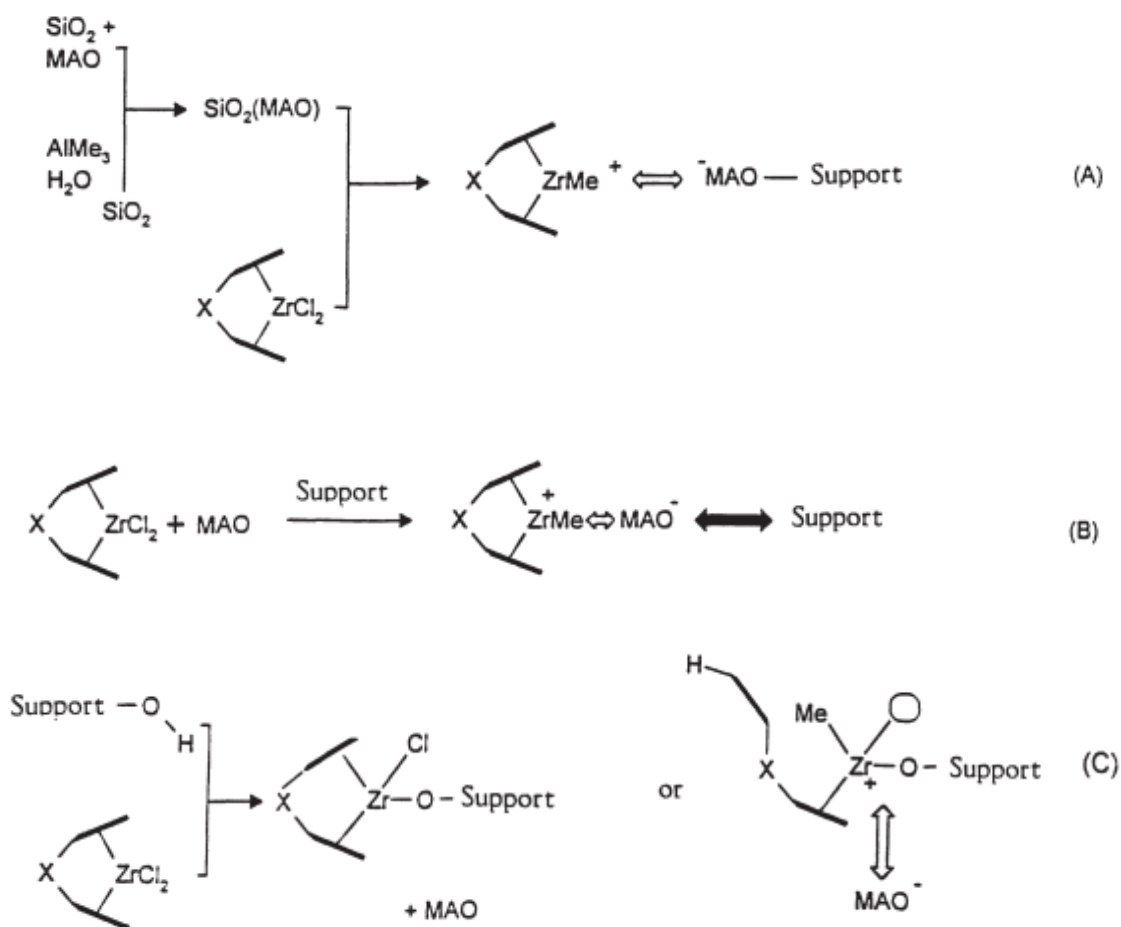
Figure7 Methods for supporting metallocenes.

There are various kinds of supports such as inorganic supports and organic supports. According to the concern in environmental problems, we are more interested in using natural cellulose than other synthetic substances. Apart from that reason, natural cellulose has numbers of suitable properties to be a support; for example, a high porous property, high sorption capacity, stability of metal anions, and physical and chemical versatility, which make them proper and attractive to be used as supports for metallocene catalyst in *in situ* polymerization that produces polyethylene-polymer composites.

2.4 Microcrystalline cellulose (AVICEL[®])

Microcrystalline cellulose (MCC), which is a purified form of subunits of poly-α-cellobiose derived from cellulose by acid hydrolysis of cotton or wood-past that provides hydroxylfor distinctive surface chemistries(Figure 8)[31], was discovered by Battista and Smith in 1955 and was first commercialized under the brand name "Avicel". In 1966, MCC was first registered in the supplement to the National Formulary, twelfth edition. This cellulose consists of linear chains of β-1,4-D anhydroglucopyranosyl units. Chemical structure of MCC shown in (Figure 9)[32-34].
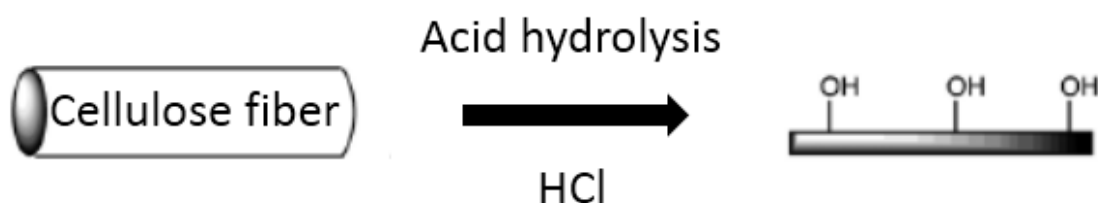

Figure8 Synthesis of cellulose nanoparticles provide for distinctive surface chemistries by HCl treatment provides hydroxyl.
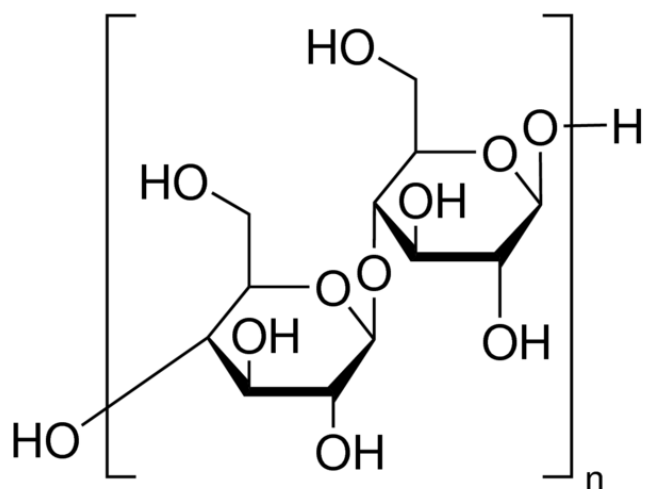
Figure 9 Chemical structure of microcrystalline cellulose (MCC).

MCC has been widely used as an additive for direct compression because of its good flowability, compactibility, and compressibility. Moreover, MCC is used vastly in the manufacture of pharmaceuticals, cosmetics, food, paper, and composite materials [12]. Over the last few decades, interest in producing polymer composite materials with cellulose materials that can be obtained from many sources [33, 35].

Polymer composites with MCC are materials with unique properties. Application of MCC to thermoplastic composites is used as composite polymer such as polyethylene(PE), polypropylene(PP), polyethylene terephthalate(PET) and poly(trimethylene terephthalate) (PTT) .The main advantages of cellulose are its renewable nature, biodegradable, high specific strength and modulus, excellent mechanical properties, low density compared to inorganic substances, advanced performances, lower cost, reliable, adaptable properties and the possibility of recycling.In addition, for polyethylene-cellulose composite had expanded to enhance the mechanical properties of cellulosic composites through improved compatibility between hydrophilic of cellulose and hydrophobic of thermoplastic materials[35, 36].

In this research, the cellulose was used as support for metallocene catalyst by commercial cellulose named "Avicel PH101" that consists of hemicellulose sugar and lignin. This white powder has particle size~50 μm. Its property is porous, odorless, tasteless, fine, crystalline powder and insoluble with organic solvent and water[37].

2.5 Polymerization reaction

Polymerization is a process of reacting small molecule, called "monomer", together in a chemical reaction to form large network molecule or polymer chains. For ethylene polymerization used ethylene for monomer molecules. Active homogeneous olefin polymerization catalysts are obtained on mixing bent metallocene catalyst with MAO cocatalyst in inert solvents such as toluene.

Mechanism of the polymerization of olefins by zirconocenes[15, 30].

Three roles in polymerization (Fig 10).

➢ Initiation step: the formation of an alkylated cation of the transition metal. The MAO cocatalyst converts the zirconocene after complexation into the active species which has a free co-ordination position for the monomer and stabilizes the latter, followed by the insertion of the ethylene (monomer) into the zirconium alkyl bond that allocated to the complex.

➢ Propagation step: insertion of the ethylene into the zirconium complex and provision of a new free co-ordination position then repeat of insertion of the ethylene in a very short period of time, hence rendering a polymer chain.

➢ Termination step: Three major chain transfer/termination mechanisms
-β-H elimination, proceeding via an agostic, β C-H. . .Zr interaction.

-β-Me elimination is favored for crowded metallocenes.

-σ-Bond metathesis between the Zr-alkyl bond and ethylene C-H bond.

a) Initiation

$$Cp_2MX_2 \quad + \quad \left[O-\underset{Me}{\overset{|}{Al}}\right] \quad \longrightarrow \quad Cp_2MMe_2$$

$$Cp_2MMe_2 \quad + \quad \left[O-\underset{Me}{\overset{|}{Al}}\right] \quad \longrightarrow \quad Cp_2\overset{+}{M}Me \quad + \quad \left[O-\underset{Me}{\overset{|}{Al}}\overset{X}{}\right]^{-}$$

$$Cp_2\overset{+}{M}Me \quad + \quad CH_2{=}\underset{R}{CH} \quad \longrightarrow \quad Cp_2\overset{+}{M}-CH_2-\underset{R}{CH}-Me$$
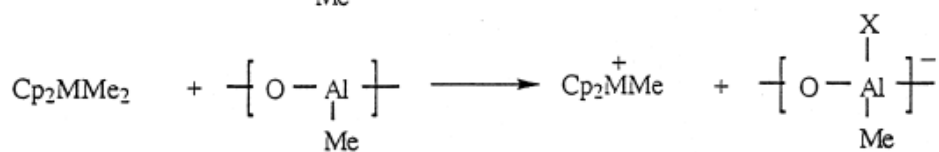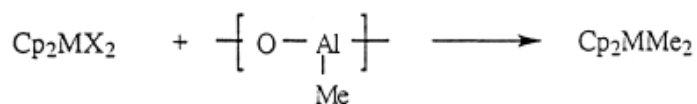
b) Propagation (repeated insertion)

$$Cp_2\overset{+}{M}-CH_2-\underset{R}{CH}-Me \ + \ m\ CH_2{=}\underset{R}{CH} \longrightarrow Cp_2\overset{+}{M}\left(CH_2-\underset{R}{CH}\right)_m CH_2-\underset{R}{CH}-Me$$

c) Chain transfer (β-hydrogen transfer)

$$Cp_2\overset{+}{M}-CH_2-\underset{R}{CH}\sim\sim\sim \longrightarrow Cp_2\overset{+}{M}-H \ + \ CH_2{=}\underset{R}{CH}\sim\sim\sim$$
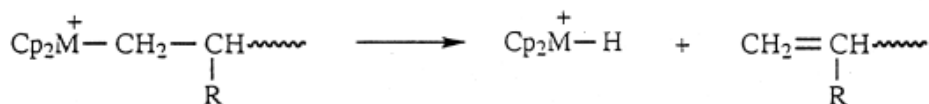
Figure 10 Mechanism of the olefins polymerization by zirconocenes catalyst.

2.6 Literature reviews

Kaminsky (1994)[38] gives an overview on different metallocene-alumoxane catalysts for ethylene polymerization. Especially at polymerization temperature above 50°C the zirconium catalyst is more active than the hafnium or titanium system. Furthermore, the titanium complex is decomposed at such temperatures. Of the cocatalysts, methylalumoxane(MAO) is much more effective than the ethylaluminoxane(EAO) or isobutylalumoxane(IBAO).For this reason, we interested to used zirconocene/MAO catalystic system for ethylene polymerization.

Hammawa et al.(2003) [39] has studied the effects of aluminum alkyls on the kinetic behavior and polyolefin properties for gas-phase ethylene and ethylene/1-hexene polymerization with $(n\text{-}BuCp)_2ZrCl_2$/MAO supported(Poly(DVB/HEMA)). A 2-L semi batch reactor typically run at 80°C and ethylene pressure 1.4 MPa for 1 to 5 h was used for the gas-phase polymerization. Results with triisobutylaluminum (TIBA), and triethylaluminum (TEA) showed that both type and amount of aluminum alkyl influenced the polymerization activity profiles and to a lesser extent the polymer molar masses. The effectiveness of the aluminum alkyls in inhibiting the initial polymerization activity increases with increasing size of the alkyl group, TEA >TIBA.

Wu et al.(1997) [40] studied the effect of free alkylaluminium in the titanocene catalyst system on the syndiotactic polymerization of styrene. By addition of external alkylaluminium(TMA) or triisobutylaluminium (TIBA), into the catalyst system with the MAO originally containing less retained TMA, the styrene polymerization was more efficiently promoted than without the external alkylaluminium. The result is contrary to the case of ethylene polymerization in

which high content of retained TMA in MAO decreased the catalytic activity. The difference in the effect of alkylaluminium on the catalytic activity between ethylene and styrene polymerization may be concerned with the dissimilarity in the oxidation state of the catalytic species for these polymerizations. It has been suggested that the Ti^{3+} species are active for styrene syndiotactic polymerization, whereas the active species for ethylene polymerization are Ti^{4+} (or Zr^{4+}). Based on this consideration, a higher concentration of free alkylaluminium, which is a strong reducing agent in the catalyst system, favors the reduction of Ti^{4+} to Ti^3, resulting in an enhanced catalytic activity in the styrene polymerization

Charpentier et al.(1998) [41] has explored different types of commercial and developmental aluminoxanes of ethylene polymerization using bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2)in the semi-batch polymerization. The structure and type of aluminoxane co-catalyst were found not to influence the molecular weight distribution (MWD) of polyethylene (PE) although to influence the activity of the zirconocene catalyst. The type of aluminoxane influenced the activity of the catalyst with generally, MAO ≥ MMAO >> IBAO for polymerization activity. By increasing the MAO concentration (increasing Al/Zr molar ratio), the polymerization activity was found to increase up to a maximum at an Al/Zr ratio of 2400, after which further increase of Al/Zr molar ratio decreased the catalyst activity. The results of MWs and PDIs polyethylene were found not to vary with MAO type or concentration. Use of TMA, along with MAO, gives lower activity than MAO by itself for a given Al/Zr molar ratio, but has no effect on MWs or PDIs of the formed PE. Results of studying the MWD and catalytic activity of PE, agree with the hypothesis of a single active cationic metallocene site-type for the simple metallocene system Cp_2ZrCl_2/MAO/TMA. For the polymerization of ethylene with zirconocene dichloride, the aluminoxane was found to function solely as a co-catalyst in activating the catalyst and was not found to be involved in the catalyst site-type having no effect on the termination to propagation ratio.

Mubarak and Abdulsamad (2019)[42]have studied the effect of microcrystalline cellulose (MCC) on the mechanical properties of low-density polyethylene (LDPE). The impact resistance and the tensile properties of low-density LDPE/MCC composites were investigated. The weight fraction of MCC was varied at (0, 0.5, 1, 2.5, 5, 10, 20, and 30 wt %). The tensile and impact testing of obtained blends was characterized by hot compression molding technique. It has been found that MCC has a strong influence on the mechanical properties of LDPE. At a low MCC weight fraction, there was a little improvement in the ultimate strength, fracture stress, and elongation at break. While at a high MCC weight fraction, the tensile properties were deteriorated and reduced significantly. The addition of 1 wt% MCC to LDPE enhanced the mentioned properties by 10, 25, and 6%, respectively. However, at 30 wt% MCC, these properties were lowered by 36, 25, and 96%. The elastic modulus of LDPE composites was improved on all MCC weight fractions used in the study. At 20 wt% MCC, an increase in the elastic modulus by 12 folds was achieved. On the contrary, with the impact strength of pure LDPE, the addition of MCC particles enhanced the impact strength, the highest value obtained was for LDPE composites filled with 10 wt% MCC where the impact strength enhanced by two folds.

Suttivutnarubet et al.(2016) [43] has explored the synthesized polyethylene/coir dust hybrid filler with zirconocene/MAO catalyst by using *in situ* polymerization. Under an argon atmosphere, the amount of coir dust was calcined at 150 °C for 4 h with a heating rate of 10 °C/min prior to use. The amount of zirconocene (Et(Ind)$_2$ZrCl$_2$) was 1.5 mL (5×10^{-5} M) of toluene solution and methylaluminoxane (MAO) of 1.1 ml. The zirconocene/MAO catalyst on coir dust support ([Al]$_{MAO}$/[Zr]$_{cat.}$ = 1135) were mixed and stirred for 30 min aging at room temperature. The *in situ* polymerization process was using 100 ml semi-batch stainless steel autoclave reactor with a magnetic stirrer at 70°C.The reaction was deactivated by acidic methanol (0.1% HCl in methanol), then polymer was filtrated by vacuum filter system, washed by using methanol, and dried at room temperature. The obtained polymer was white powder. The results and discussion identified that the catalytic activity was decreased while the number coir dust was increased, that was due to supporting effect.

Eberhardt et al.(2004)[44] has studied the ethylene polymerization with different biomass supported for metallocene /MAO catalyst. The various biomass supported were cellulose, starch and chitosan for zirconocene catalyst with Al$_{(MAO)}$/Zr equal 2000 up to 3000 in heterogeneous system were compared to homogeneous system. Polymerization of ethylene was conducted in a glass reactor equipped with a magnetic stirrer at 45°C for 30 minutes under nitrogen atmosphere. The polymers obtained with the zirconocene supported on chitosan or cellulose pretreated with MAO exhibited a higher molecular weight than those obtained with a homogeneous system. High activity in ethylene polymerization was obtained when supports used were chitosan and cellulose. Polymer particles obtained with these supported metallocene catalysts showed a good replication of the original support particles.

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals

Table3 The chemicals used in metallocene catalystic system and the polymerization reaction

Chemicals	Formulation	Supplier	Purification
rac-ethylenebis(indenyl) zirconiumdichloride	[Et(Ind)$_2$ZrCl$_2$]	Aldrich Chemical Company, Inc	Used as received
Methylaluminoxane (MAO)	(Al(CH$_3$)O)$_n$	Tosoh FinechemCo., Ltd., Japan	10wt% in toluene
Triethylaluminium (TEA)	(C$_2$H$_5$)$_3$Al	Thai polyethylene Co., Ltd	Used as received
Microcrystalline cellulose (Avicel PH101)	(C$_6$H$_{10}$O$_5$)$_n$		Used as received
Ethylene gas	C$_2$H$_4$	National Petrochemical Co., Ltd.	99.99%
Toluene	C$_6$H$_5$-CH$_3$	S.M.Chemical Supplies Co.,Ltd.	99.5% Soaked in molecular sieve
Hydrochloric acid	HCl	Aldrich Chemical Company	Fuming 36.7%
Methanol	CH$_3$OH	S.R. lab	Used as received
Ultra high purity argon gas	Ar	Thai Industrial Gas Co., Ltd.	99.999%

3.2 Equipment

The metallocene catalytic systems are always prepared and handled under an inert atmosphere due to this catalystis pyrophoric**,**whichhas to be used without moisture and oxygen. Hence, there are a lot of equipments that are used for ethylene polymerization.

3.2.1 Schlenk line

The Schlenk line is a commonly used to control and eliminate moisture and oxygen in overall operation in this research. The Schlenk line is a chemistry apparatus developed by Wilhelm Schlenk, including vacuum line and nitrogen gas line with several stopcocks.Schlenk lines are useful for safely and successfully operating air-sensitive compounds. Basically, gas and solvent vapors from evacuation were trapped by liquid nitrogen cold trap for preventing the vacuum pump contamination. This operation was conductedunder vacuum.

3.2.2 Schlenk tube

Schlenk tube isa tube with a ground glass joint and side arm having three-way glass valve. Their sizes are 50, 100 and 200 ml. These were used to store cellulose materials and prepare the immobilization of MAO and metallocene on cellulose. This tube is shown in (Figure 11).

Figure 11 Schlenk tube

3.2.3 Vacuum pump

Vacuum pump model 195 supplied from Labconco Corporation was used to remove oxygen from the system with the pressure of 10^{-1} to 10^{-3} mmHg for the vacuum supply to the vacuum line in the Schlenk line.

3.2.4 Glove box

MRBAUN LABstar Glove boxprovided an inert surrounding for handling high moisture and oxygen sensitive materials,and used to control moisture and oxygen for inert atmosphere.There are 2 parts to produce inert atmosphere consisting of gas purification system and closed loop gas recirculation to remove water and oxygen. Furthermore, investigating moisture and oxygen concentration in Glove box system also were applied by moisture and oxygen analyzer including MB-MO-SE1 and MB-OX-SE1, respectively.

3.2.5 Polymerization reactor

A 100 ml of stainless steel autoclave with a magnetic stirrer wasused in polymerization process.

3.2.6 Magnetic stirrer and heater

The magnetic stirrer and heater model RTC basis from IKA Labortechnik were used to mix solution and control heat of reaction during polymerization process.

3.3 Preparation of support

3.3.1 Calcination

Commercial cellulose (Avicel PH101)was calcined under vacuum at $150^{\circ}C$ with heating rate of $10^{\circ}C/min$ for 4 hours. After that, cooled down at room temperature and stored in bottle under inert atmosphere.

3.3.2 Immobilization

Several techniquesof immobilization for metallocene /MAO catalyst on cellulosesupport wereused in this research (Figure 12-13).

(A) Immobilized cocatalyst/support:

Immobilization of MAO cocatalyst on the support

(B) Immobilized catalyst/ support:

Immobilization of the metallocene on the support

(C) Immobilized cocatalyst/catalyst/support:

Immobilization of the mixture of metallocene and MAO is adsorbed on the support

The ratio of cellulose materials and MAO or metallocene catalyst or the mixture of catalyst and MAO, in toluene was 1:10 with the magnetic stirrer at room temperature. Then, cellulose-supportedcatalystic systems were dried by vacuum system at room temperature. The solid powders of cellulose-supported catalytic systemswere achieved.
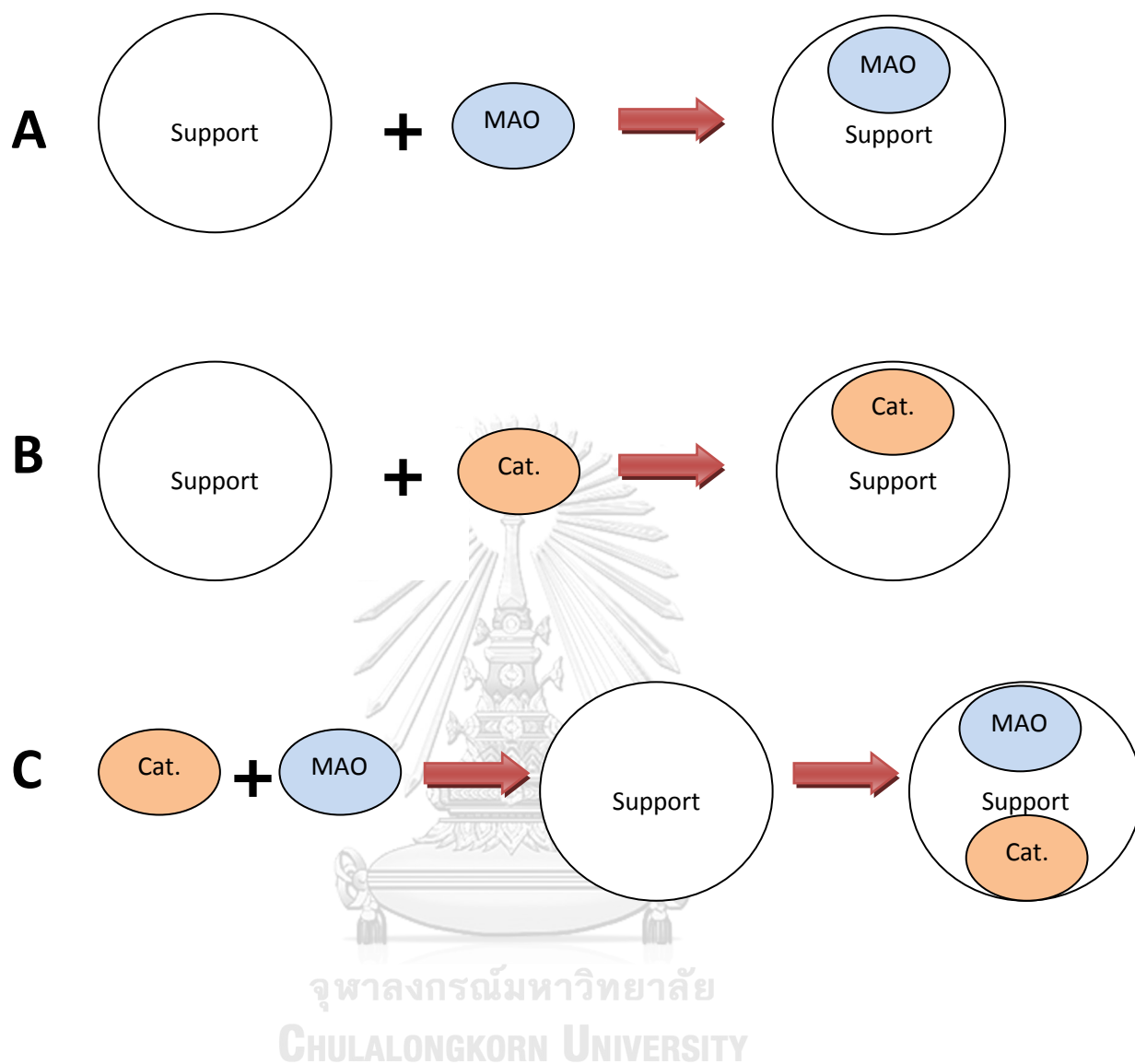
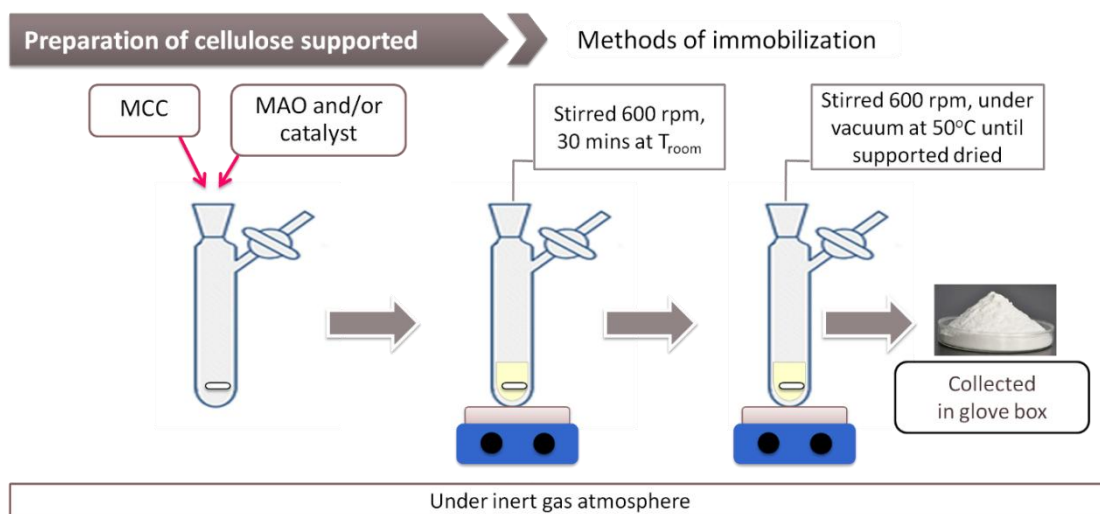**Figure 12**Methods of immobilization for metallocene/MAO catalyst with cellulose support.

Figure 13 Preparation of cellulose supported by immobilizations

3.4*In situ* polymerization

The ethylene polymerization reaction was performed in a 100 ml semi-batch stainless steel autoclave reactor with magnetic stirrer(Figure 14). Cocatalyst and/or scavenger with various molar ratios of $[Al]_{MAO}/[Zr]_{cat}$ and $[Al]_{TEA}/[Zr]_{cat}$ were added into reactor. Then, 1.5 ml of $Et(Ind)_2ZrCl_2$ (5×10^{-5} M) of catalyst solution was added for homogeneous system. Moreover, heterogeneous polymerization used cellulose-supported catalytic systems instead,that added into reactor followed by catalyst or cocatalyst, which was controlled total molar ratio of $[Al]_{MAO}/[Zr]_{cat}$ at same2000molar ratio,was added.Toluene acting as solvent was added into the reactor to fill a total volume of reactor as 30 ml. The reactor was stirred,while heated up to polymerization temperature (70 °C). Polymerization reaction was started,while ethylene gas was fed under 3.5 bar. Polymerization reaction was operated until 15 minutes. Then, it was terminated by acidic methanol and stirred around 30 minutes. The polymer obtained was filtrated and dried at room temperature.
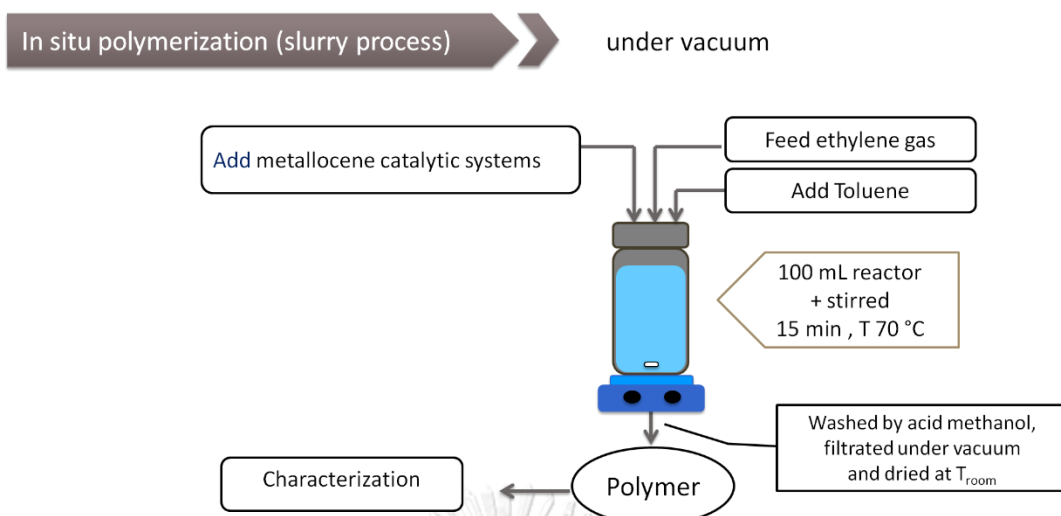
Figure 14*In situ* polymerization

3.5 Characterization of supports and polymers

3.5.1 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The morphology of cellulose material, cellulose supports after immobilization, and polymerswere investigated by using JEOL mode JSM-6400 model of SEM. The elemental distributions of Al and Zr were observed by EDX using Link Isis series 300 program to confirm the modification of celluloses after immobilization by MAO and/or zirconocene catalyst.

3.5.2 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline of cellulose material, cellulose supports after immobilization, and polymers.It was proceeded using a SIEMENS D-5000 X-ray diffractometer with CuK$_\alpha$radiation (λ = 1.54439x10^{-10} m) with Ni filter. The spectrum was scanned in the 2θ range of 10 to 80 degrees at scan rate of2.4 degree/min.

3.5.3 Thermal gravimetric analysis-differential scanning calorimetry (TGA-DSC)

TGA-DSC was used to analyze melting temperature (T_m) of cellulose materials and polymers by using TA Instruments SDT Q600 analyzer and crystallinity (χ_c) of polymers following by DSC *204 F1 phoenix*. The analyses were operated at a heating rate of 10 °C/min in the temperature range of 10 to 150°C.

3.5.4 Fourier transform infrared spectrophotometer (FTIR)

FTIR was used to determine functional group or molecular structure of cellulose materials and cellulose supports after immobilization. The small amount of samples of IR was casted as thin film on NaCl plates under inert gas, so that protection from moisture and oxygen. The analyzed samples were investigated by ATR mode with Nicolet 6700 FTIR spectrometer. The FTIR spectra were in the scanning range from 400-4000 cm^{-1} with 100 scans at resolution of 4 cm^{-1}.

3.5.5 X-ray photoelectron spectroscopy (XPS)

The surface chemical composition and the binding energy (BE) of surface element on the cellulose supports after immobilization, was investigated by XPS technique. It was evaluated by the AMICUS photoelectron spectrometer (KRATOS VISION 2 software). The condition was operated at 0.1 eV/step of resolution and 75 eV pass energy with the operating pressure approximately 1×10^{-6} Pa.

3.6 Research plan

Table 4 The research plan

Research plan	Year 2018							Year 2019						
	6	7	8	9	10	11	12	1	2	3	4	5	6	7
Study the theory of metallocenecatalyst,scavenger, cellulose as support and experiment	←———————————————————————————————————————→												
Schedule an experimental duration		←———→												
Prepare scavenger and cellulose materials			←———→											
Characterize the cellulose supports					←———→									
Determine the variables associated with this experiment				←———————→										
Run polymerization							←———————————→							
Characterize obtain polymer							←———————————————→							
Analyze results and discussion					←———————————————————→									
Prepare report and presentation								←———————————————→						

CHEPTER 4

RESULTS AND DISCUSSION

This chapter is described about the results and discussion relevant to this research. There are divided into two parts in this research; part 1 focuses on the effect of types and amounts cocatalyst and scavenger of zirconocene catalyst on ethylene polymerization behaviors and part 2 describes to synthesize polyethylene by in situ polymerization with different immobilization methods using cellulose-supported MAO/zirconocene catalyst. All contents as mentioned are provided in this chapter.

4.1To investigate effect of types and amounts cocatalyst and scavenger of zirconocene catalyst on ethylene polymerization behaviors.

4.1.1 Characterization of polymer with scanning electron microscopy (SEM)

The morphologies of polyethylene samples are shown in Figure 15. It was found that morphologies of all polymers were irregular shape. The polymers obtained from the MAO/zirconocene catalytic systems exhibited larger size than those obtained from the MAO/TEA zirconocene catalytic systems with poor morphology due to the agglomeration from fine particle that can be seen in threads attached with particles. It is known that MAO exhibits higher catalytic activity than TEA resulting in more difficulty in controlling polymer morphology. So, different types and various molar ratios of alkylaluminum apparently affected the morphologies of the resulting polymer.
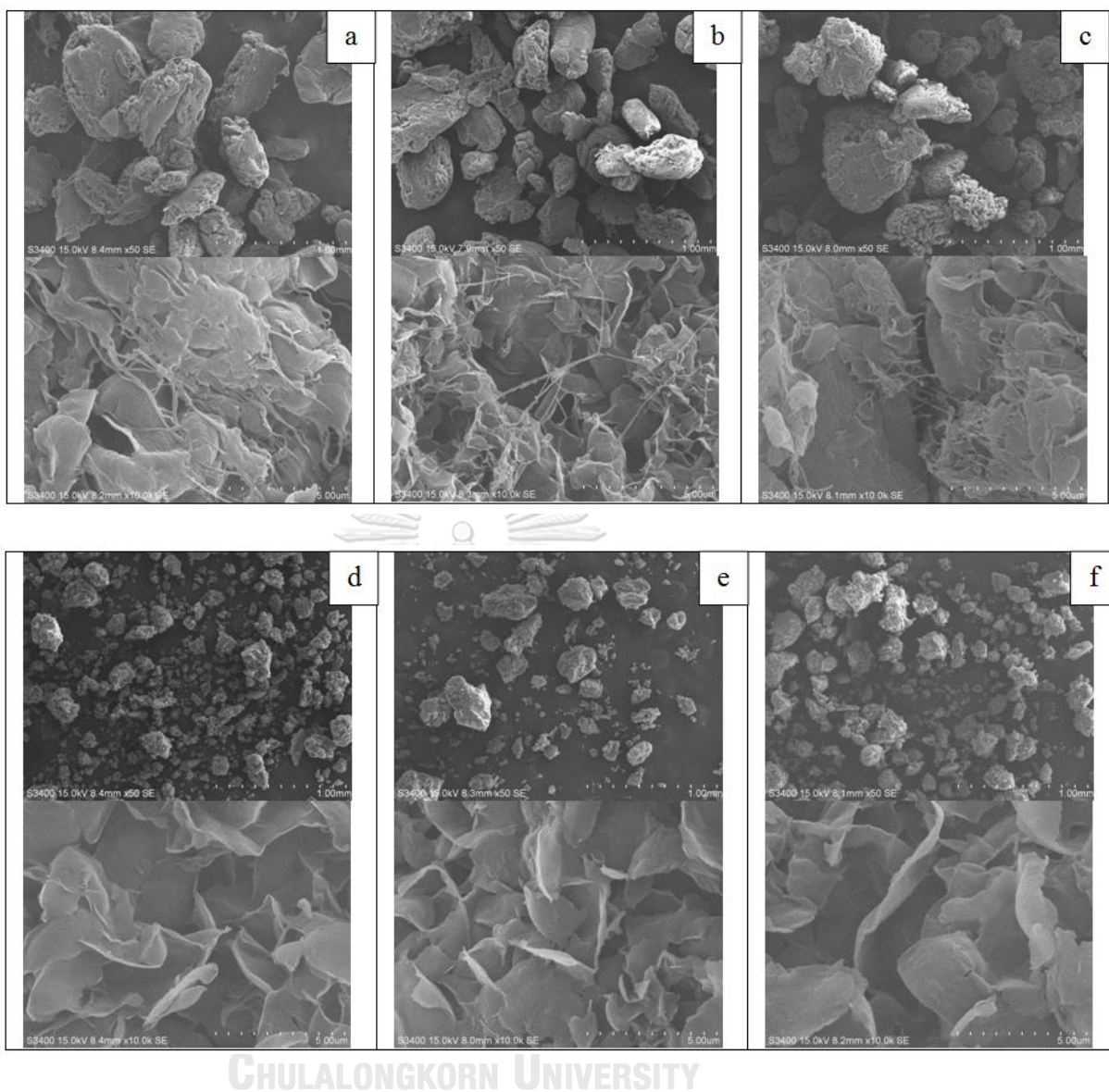
Figure 15. The morphologies of polymer obtained from various molar ratios of $[Al]_{MAO}/[Zr]_{cat}$ and $[Al]_{TEA}/[Zr]_{cat}$; (a) PE/1000-0, (b) PE/1500-0, (c) PE/2000-0, (d) PE/1000-500, (e) PE/1000-1000and (f) PE/1000-1500 at 50X and 10.0kX magnification

4.1.2 Characterization of polymer with X-ray diffraction (XRD)

The obtained polymers were characterized by XRD technique. Figure 16 shows the XRD patterns of polyethylenes synthesized with different types and various molar ratios of alkylaluminum. It was observed that the XRD patterns for all obtained polyethylene were similar that exhibited two sharp peaks of 2θ at 21.3° and 23.7°, which is assigned to the orthorhombic crystalline form in polyethylene[45].
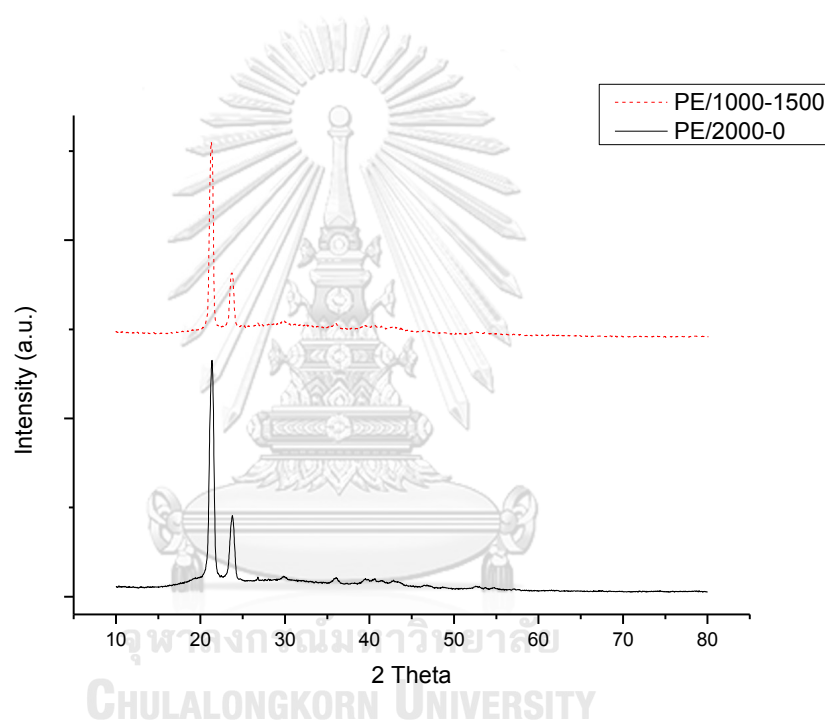
Figure 16. XRD patterns of polymers produced from various molar ratios of $[Al]_{MAO}/[Zr]_{cat}$ and $[Al]_{TEA}/[Zr]_{cat}$; (a) PE/2000-0 and (b) PE/1000-1500

4.1.3 Characterization of polymer with thermal gravimetric analysis-differential scanning calorimetry (TGA-DSC)

The thermal properties of obtained polymer are also shown in Figure 17 and Table 5. It can be seen that all samples had the melting temperature ranging between 121 and 123 °C, thus no significant change in T_m was observed. Moreover, increasing molar ratios $[Al]_{MAO}/[Zr]_{cat}$ with MAO/zirconocene catalyst tend to increase crystallinity(χ_c) as well. Crystallinity of the polymer from the addition of TEA into MAO/zirconocene catalyst increased when compared with that obtained from pure MAO/zirconocene catalyst. However, the crystallinity tended to decrease with increasing the molar ratios of $[Al]_{TEA}/[Zr]_{cat}$. This is perhaps due to MAO as the cocatalyst gave higher catalyst activity than TEA. This will cause the polymer from addition of TEA catalyst systems takes longer time to form crystal structure of polyethylene than the MAO catalytic systems. This suggests that different types and various molar ratios of alkylaluminum influenced on crystallization enthalpy (ΔH_{exp}) and crystallinity, but they did not affect the melting temperature.
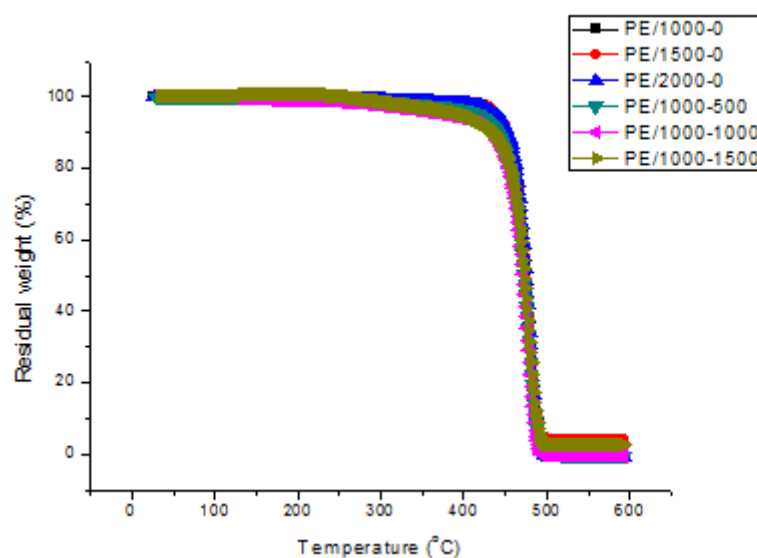
Figure 17 TGA profiles of obtained polymer

Table 5 Melting and crystallization behaviors

Polymer sample	Melting temperature[a] (°C)	ΔH_{exp}[b] (J/g)	Crystallinity[a] (% χc)
PE/1000-0	122.10	224.0	78.3
PE/1500-0	121.23	234.3	81.9
PE/2000-0	121.76	237.0	82.9
PE/1000-500	122.92	281.8	98.5
PE/1000-1000	122.51	265.9	93.0
PE/1000-1500	121.73	239.3	83.7

[a] Melting temperature (T_m) measured by DSC measurement.

[b] Heat of fusion (ΔH_{exp}) measured by DSC measurement.

[c] Crystallinity (χ_c)was calculated from the equation; %crystallinity = ($\Delta H_{sample}/\Delta H_{100\%}$ crystallinity)x100, the $\Delta H_{100\%}$ crystallinity of polyethylene is 286 J/g.

4.1.4 Ethylene consumption

The ethylene consumption rates (ml/min) during ethylene polymerization from heterogeneous system were recorded as shown in Figure 18. All polymers exhibited rapid activation (with very short induction period) in first minute. After that, consumption rate still slightly increased since the first minute to the last minute in the interval time of 15 minutes. No deactivation of catalytic systems was observed in all runs. It was seen that there was no significant change in the ethylene consumption rates for all polyethylene polymerization systems.
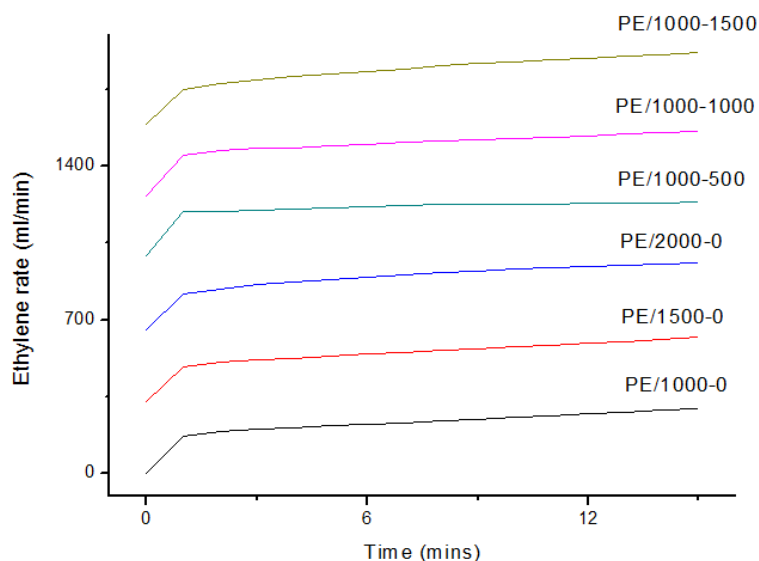
Figure 18 The ethylene consumption of polyethylene

4.1.5 Catalytic activity

The effect of various molar ratios $[Al]_{MAO}/[Zr]_{cat}$ and $[Al]_{TEA}/[Zr]_{cat}$ with zirconocene catalyst for ethylene polymerization is shown in Table 6.It reveals that different types and molar ratios of cocatalyst and/or scavenger of zirconocene catalyst influenced on catalytic activity. The catalytic activity shows a tendency to increase with increasing both $[Al]_{MAO}/[Zr]_{cat}$ and $[Al]_{TEA}/[Zr]_{cat}$ molar ratios. Moreover, methylaluminoxane (MAO) /zirconocene catalysts with the addition of triethylaluminum (TEA) for scavenger gave higher catalytic activity than MAO/zirconocene catalysts with the absence of TEA due to alkylaluminum also scavenging catalyst poisons (water, O_2, etc.) in polymerization processes. In addition, the MAO/zirconocene catalysts gave slightly higher activity than MAO /TEA zirconocene catalysts at equal [Al] /$[Zr]_{cat}$ molar ratios.

Table 6 Catalytic activities of various molar ratios of $[Al]_{MAO}/[Zr]_{cat}$

and $[Al]_{TEA}/[Zr]_{cat}$ zirconocene catalysts via ethylene polymerization.

$[Al]_{MAO}/[Zr]_{cat}$	$[Al]_{TEA}/[Zr]_{cat}$	Total $[Al]/[Zr]_{cat}$	Polymerization yield (g)	Catalytic activity $(g_{polymer}/g_{Cat}*h)$
1000	-	1000	0.2378	114.6
1500	-	1500	0.3666	177.1
2000	-	2000	0.6265	301.93
1000	500	1500	0.3346	161.25
1000	1000	2000	0.4157	200.34
1000	1500	2500	0.4635	223.37

Activities were measured at polymerization temperature of 70 °C, [ethylene] = 0.018

mole, $[Zr]_{cat}$ =5 x 10^{-5} M.and polymerization time was 15 min.

4.2 Synthesis of polyethylene by *in situ* polymerization with different immobilization methods using cellulose-supported MAO/zirconocene catalyst.

Part 2 aimed to investigate the effect of different immobilization methods using cellulose-supported zirconocene/MAO catalyst on the characteristics and activity of catalytic system. This part is divided into 3 portions. Firstly, cellulose support was characterized using different techniques. Secondly, the effect of different immobilization methods using cellulose-supported zirconocene/MAO catalyst is presented. Finally, the obtained polyethylene was characterized in terms of morphology, crystallization, thermal properties and activity of catalytic system.

4.2.1 Characterization of support

4.2.1.1 Characterization of support with scanning electron microscopy (SEM)

The morphology of commercial cellulose support (MCC) obtained by scanning electron microscopy (SEM) is shown in Figure 19. It can be seen that the particles have a size ranging from 10 to 50 μm. The MCC exhibited non-uniform shape composing of small micron-sized rod-like, flake-like shape and smooth layer surface
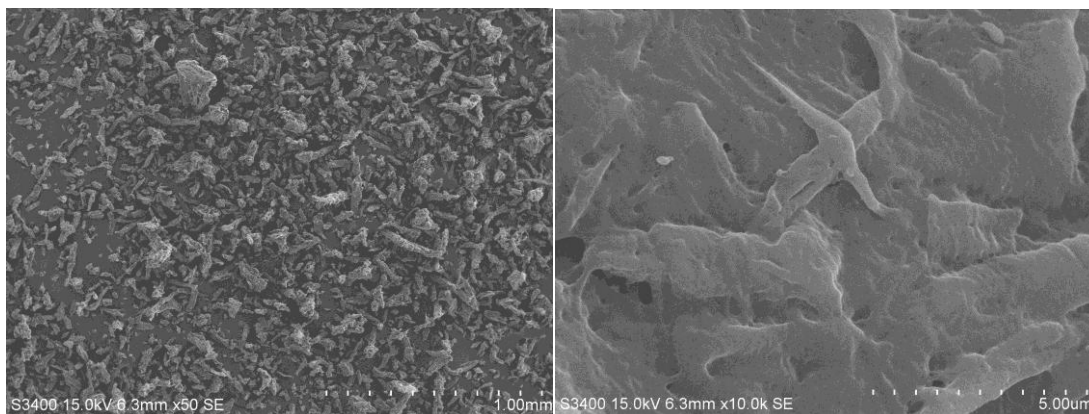
Figure 19SEM micrographs of cellulose material MCC at 50X and 10.0kX magnification before immobilization

4.2.1.2 Characterization of support with X-ray diffraction (XRD)

The crystalline structure of microcrystalline cellulose (MCC) support after calcination at 150 °C was investigated by X-ray diffraction (XRD) as shown in Figure 20. The XRD patterns of MCC support presents the characteristic peaks at 2θ equal to 14.8, 16.2, 22.5, and 34.5°corresponding to the cellulose sample with Miller indices (101) (002) (040)[46, 47].
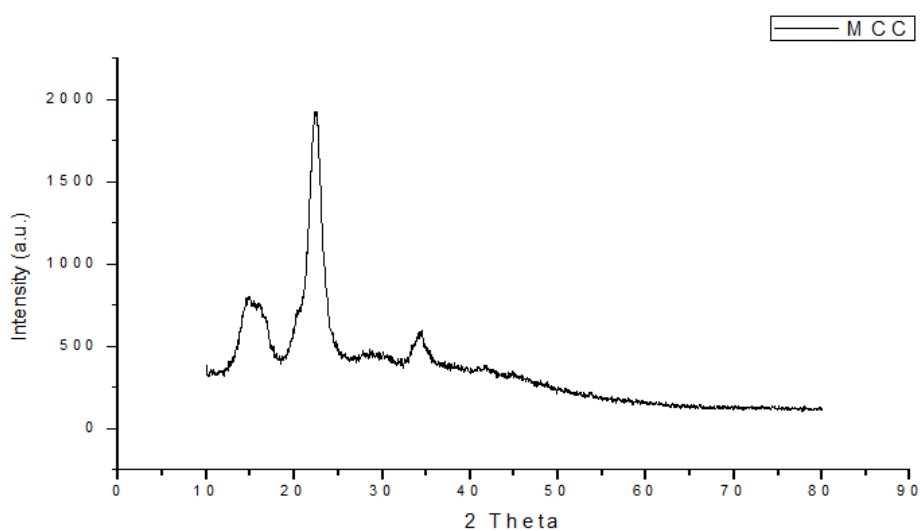
Figure 20XRD pattern of MCC support

4.2.1.3 Characterization of support with Fourier transform infrared

spectrophotometer (FT-IR)

The functional groups of MCC support were characterized by Fourier transform infrared spectroscopy (FT-IR). The FTIR spectrum of the MCC support is shown in Fig. 21. The broad band in the range 3000 to 3600 cm^{-1} was an indication of the stretching vibration of boned hydroxyl group on the cellulose. The broad absorption peak at 2912 cm^{-1} was assigned to the C–H stretching vibrations in methyl and methylene groups. Moreover, the peaks at 2160, 2024 and 1975 cm^{-1} were appeared due to ATR-diamond crystal of FTIR instrument. The peaks at 1315 and 1427cm^{-1} were attributed to the asymmetric CH$_2$ bending vibration. In addition, it was observed that the peak at 1023 cm^{-1}, which was corresponded to the –C—O—C— stretch of the β-1,4-glycosidic linkage and C-O stretching in cellulose[48].
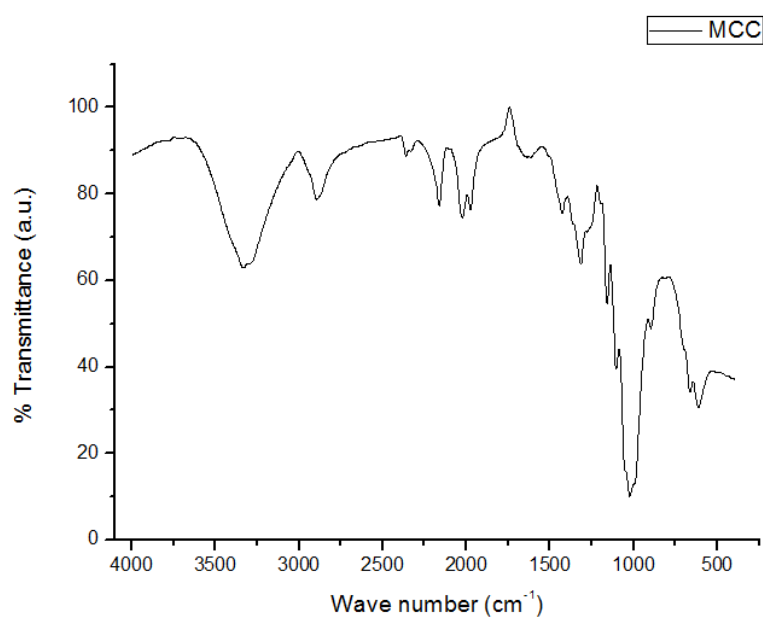
Figure 21 FTIR spectrum of MCC support

4.2.2 Characterization of MCC support after different immobilization methods

4.2.2.1 Characterization of MCC support after different immobilization methods with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Morphologies of the MCC supports after immobilization using different methods were compared to the pristine MCC supports using a SEM measurement as shown in Fig. 22. It was observed that there are lots of the adhesion of small particles on support surface in MAO/MCC and Zr/MAO/MCC samples, indicating the presence of MAO and/or catalyst (Zr) onto the supports surface. However, Zr/MCC exhibited slightly small particle adhesion on a smooth surface of MCC support when compared to other different methods of immobilization.

The elemental distribution of aluminium (Al) from MAO and zirconium (Zr) represent for zirconocene catalyst of supports was investigated using EDX in Fig23-25. All samples show the good distribution of Al and/or Zr covered on the external support surface after immobilization of MAO. Moreover, it can be observed that MCC supports had higher amount of Al than amount of Zr over the scanned area. It reveals that different methods of immobilization on MCC supports influenced on morphologies and elemental distribution on surface supports.
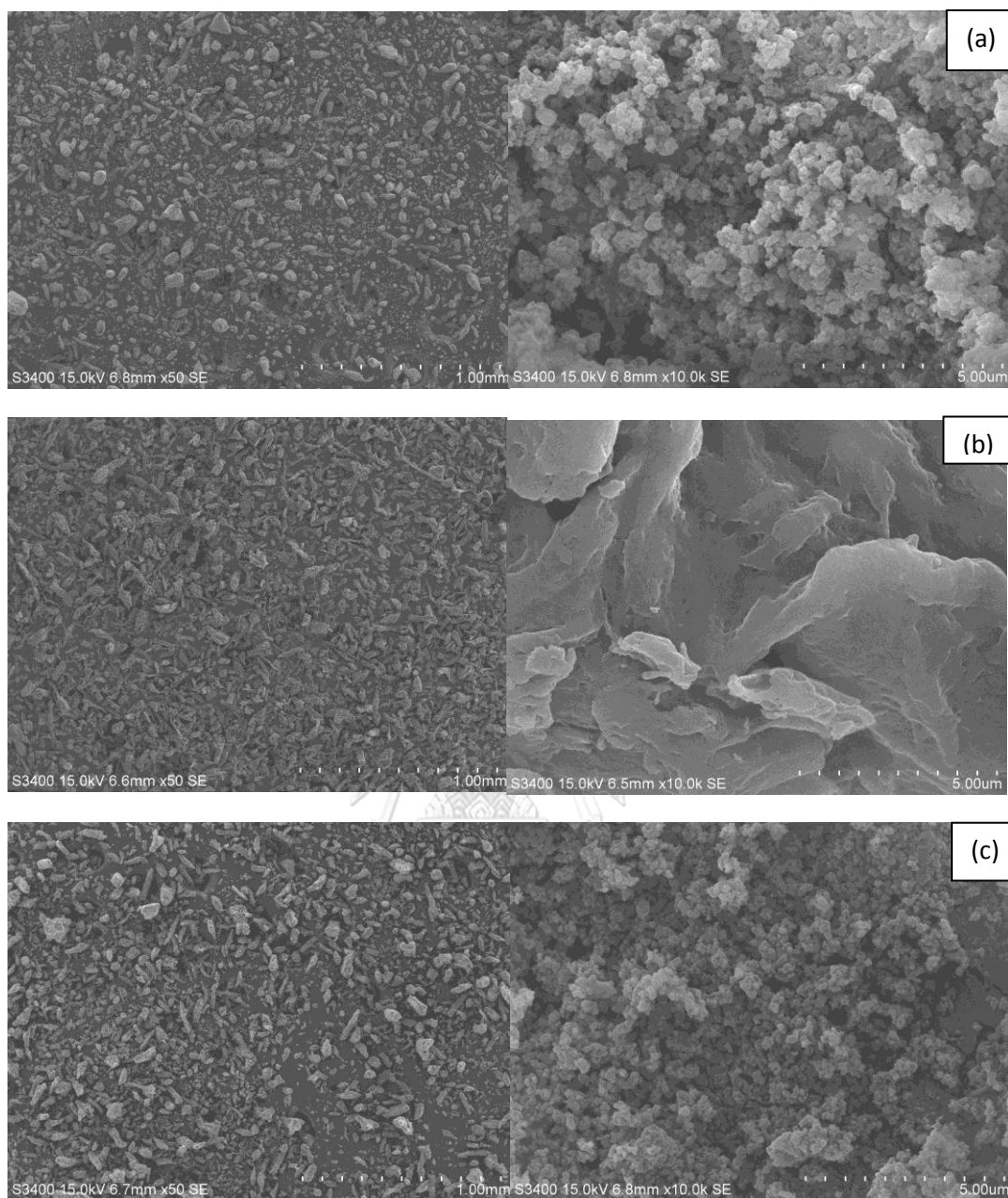
Figure 22 SEM micrographs of cellulose material (a) MAO/MCC, (b) Zr/MCC, and (c)
Zr/MAO/MCC at 50X and 10.0kX magnification after immobilization
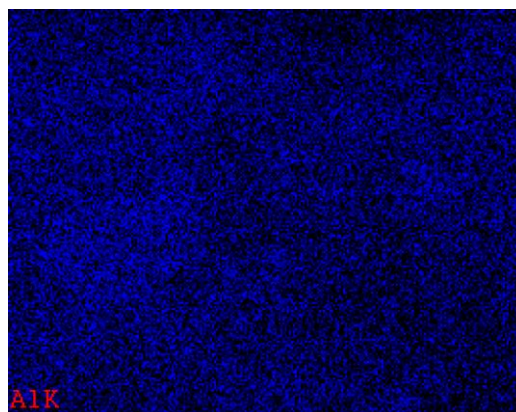
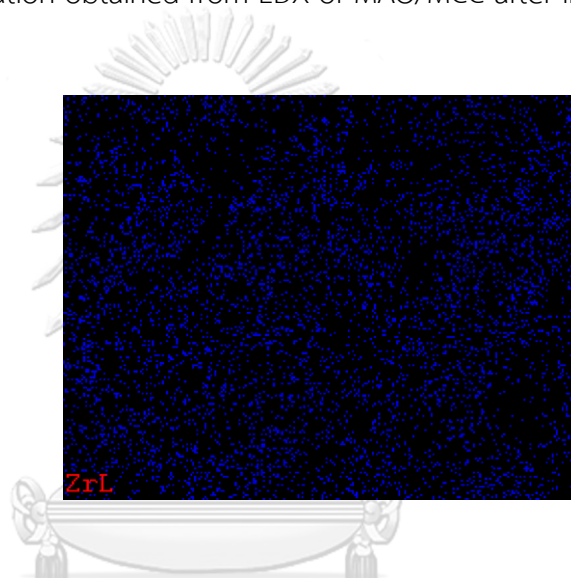**Figure 23**Al distribution obtained from EDX of MAO/MCC after immobilization

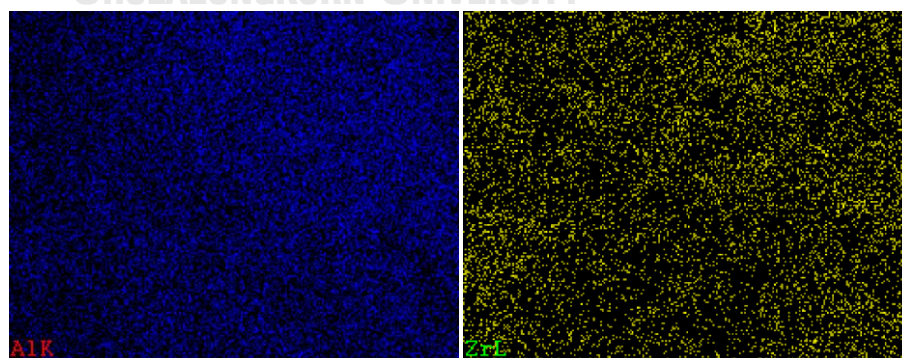**Figure24**Zr distribution obtained from EDX of Zr/MCC after immobilization

Figure 25 Al and Zr distribution obtained from EDX of Zr/MAO/MCC after

immobilization

4.2.2.2 Characterization of MCC supports after immobilization of different methods with X-ray diffraction (XRD)

XRD patterns of MCC support after the different methods of immobilization are shown in Figure 26. It was seen that after the immobilization of MAO and/or catalyst, all MCC supports presented the broad peak of XRD, which is probably due to lower crystallinity of the MCC supports after immobilization. The broad peak of XRD at 2θ equals to 22.5 that was similar to the one of characterized XRD peak of MCC support before immobilization, for MAO/MCC following by Zr/MAO/MCC. It indicated that Al from MAO and Zr from catalyst were in the highly dispersed form on MCC support. Moreover, the crystal structures of Zr/MAO/MCC presented the broad peak of XRD at 2θ equals to 14.8, 16.2, 22.5, and 34.5°, which is similar to pattern of XRD peak of cellulose before immobilization. Thus, this probably indicated that Zr from zirconocene catalyst did not disperse on the entire surface of MCC support[49].
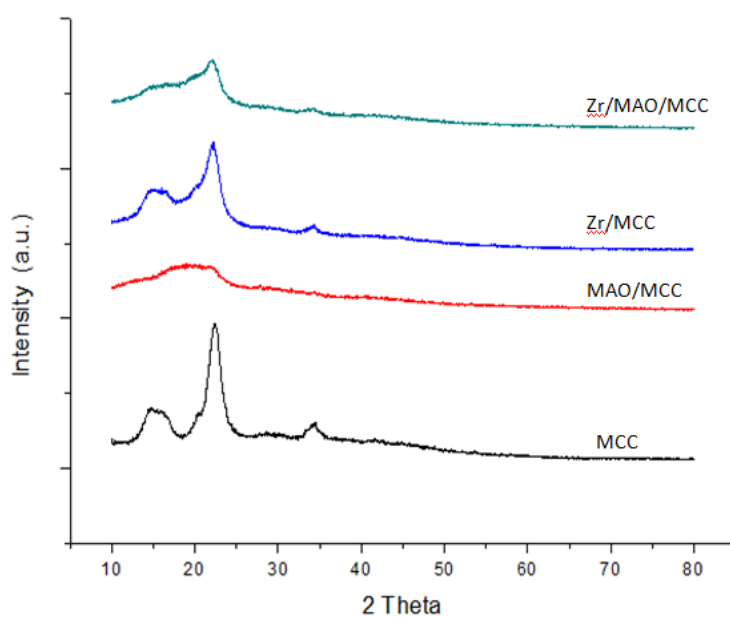
Figure 26 XRD patterns of MCC supports before and after

different immobilization methods

4.2.2.3 Characterization of MCC support after different immobilization methods with Fourier transform infrared spectrophotometer (FT-IR)

The MCC supports after immobilization with MAO and zirconocene catalyst were characterized using FT-IR to determine the bonding form and functional group. The FT-IR spectra of samples are shown in Figure 27, presenting the broad band at the range of wave number between 3600-3200 cm^{-1} that was ascribed to the stretching of hydrogen-bonded –OH groups. The broad absorptions at 2900, 1430 and 1320 cm^{-1} were attributed to C—H stretching. The broad peak at 1100 cm^{-1} was appeared due to C–O– stretching. The highest intensity of all broad peaks was obtained in Zr/MAO/MCC, following by MAO/MCC and Zr/MCC, respectively. They also indicated the FT-IR spectra of all samples that they still had the amount of hydroxyl group suggesting that no reaction occurred between MCC support and catalytic systems, in their structures after immobilization that was varied according to intensity of FT-IR peak.
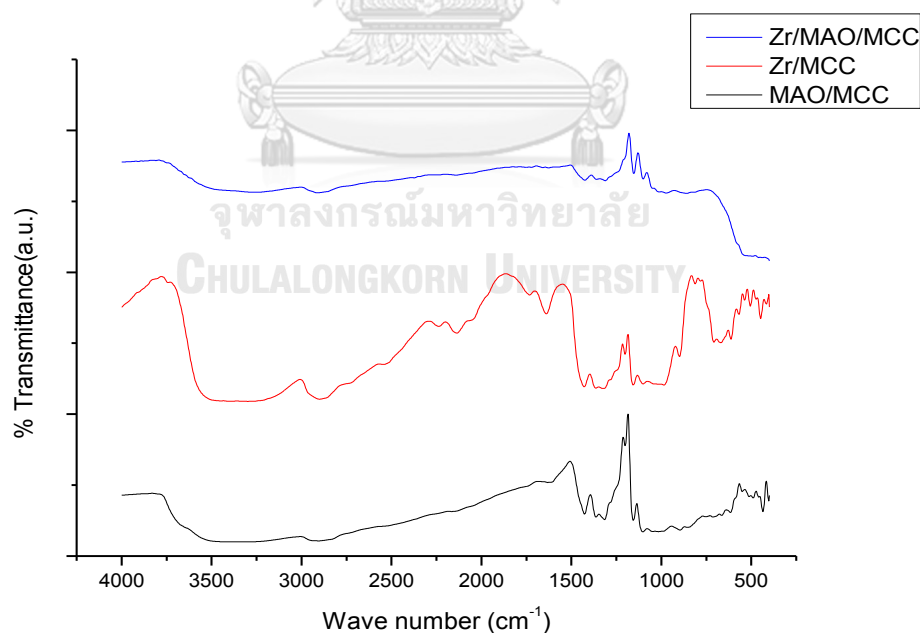
Figure 27 FT-IR spectra of MCC after immobilization

4.2.3 Characterization of polymer

4.2.3.1 Characterization of polymer with scanning electron microscopy (SEM)

SEM micrographs of the obtained polyethylene samples from homogeneous and heterogeneous systems are shown in Fig. 28. As seen, the obtained polyethylene from homogeneous system show irregular shapes and poor morphology with the agglomeration of fine particles and gave smaller particle sizes than that obtained from heterogeneous system. On contrary, all polymers produced from heterogeneous systems under different immobilization methods exhibited the similar morphologies showing good morphology and larger particle sizes with irregular shapes than polymer obtained from homogeneous system. This is because the advantage of the heterogeneous system over the homogeneous system that can reduce reactor fouling during polymerization and easily handle during processing [30].
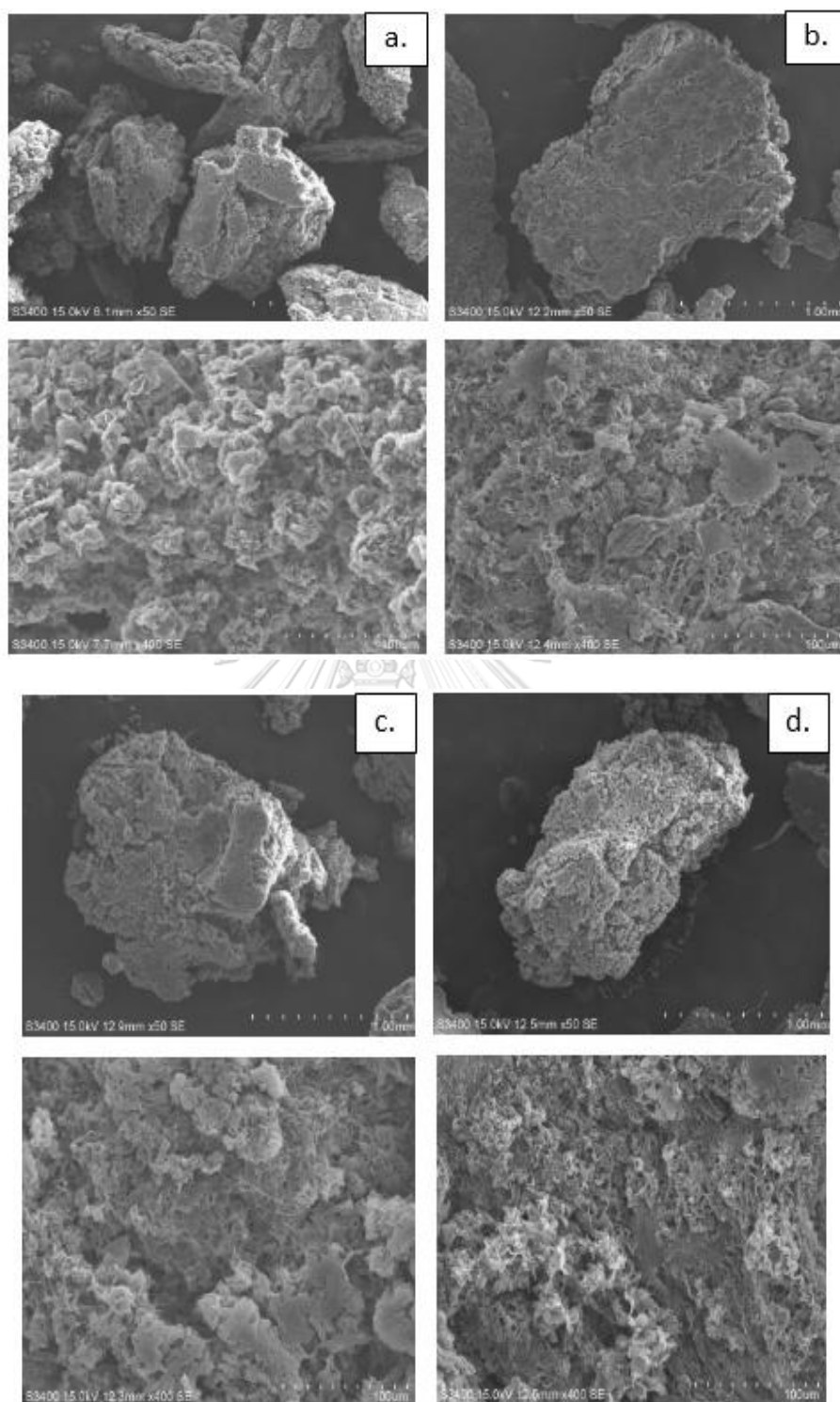
Figure 28SEM micrographs of polyethylene produced via homogeneous system and heterogeneous system (a) PE-HOMO, (b) PE-MAO/MCC, (c) PE- Zr/MCC, and (d) PE-Zr/MAO/MCC at 50X and 400X magnification

4.2.3.2 Characterization of polymer with X-ray diffraction (XRD)

Crystal structures of all obtained polymers were characterized by XRD technique as shown in Fig. 29.The XRD patterns of all polyethylenes from different methods of immobilization also confirmed that the MCC was used as a support for zirconocene/MAO catalytic system in ethylene polymerization. It was observed that the XRD patterns for all obtained polyethylene were similar showing two sharp peaks of 2θ at 21.3° and 23.7°, which is assigned to the orthorhombic crystalline form in polyethylene[45].
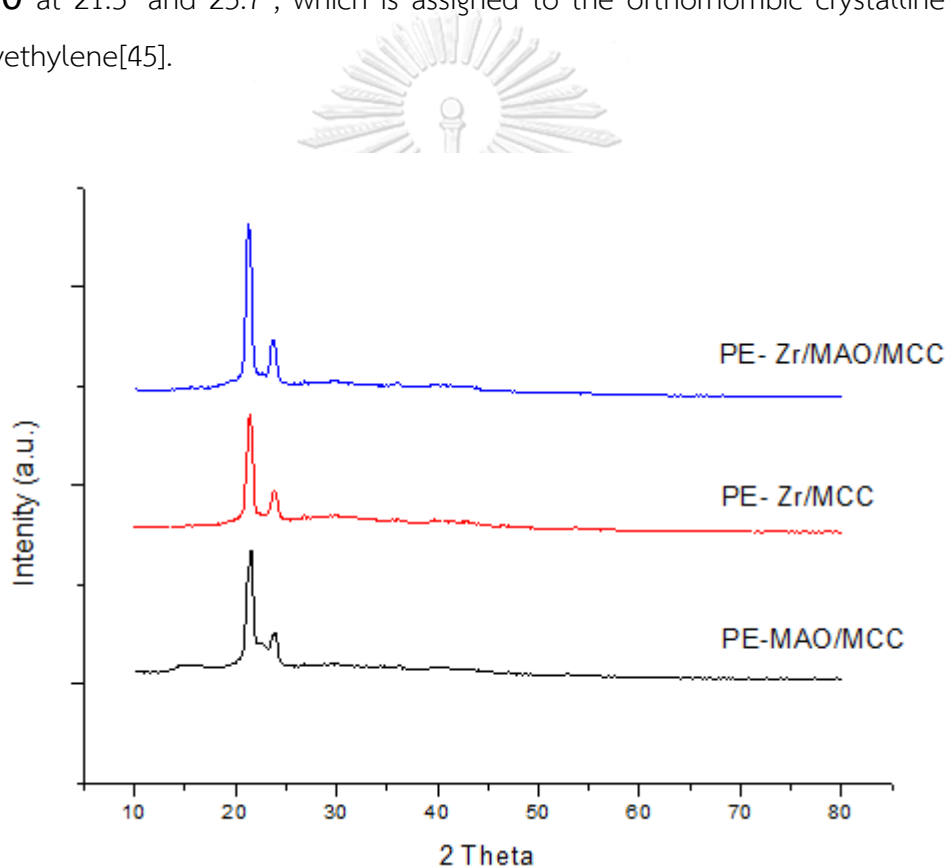
Figure 29 XRD patterns of polyethylene from different methods of immobilization

4.2.3.3 Characterization of polymers with thermal gravimetric analysis-differential scanning calorimetry (TGA-DSC)

To investigate the melting temperature (T_m) and crystallinity (χ_c) of obtained polyethylenes from different methods of immobilization, TGA-DSC technique was used for this purpose as shown in Table7. It can be seen that the melting temperature of obtained polyethylenes was in the range between 119 and 120 $^{\circ}$C. Thus, there was no significant change in the melting temperature for all polymers. On the contrary, it was observed that their crystallinity values varied with different methods of immobilization. The highest crystallinity was obtained in PE-Zr/MCC followed by PE-Zr/MAO/MCC and PE-MAO/MCC, respectively. It suggested that the different methods of immobilization influenced the crystallization of the polymers.

Table 7 Melting temperature and crystallization behaviors of polyethylenes produced from different methods of immobilization

Sample	Melting temperature[a] (°C)	ΔH_{exp}[b] (J/g)	Crystallinity[a] (% χ_c)
PE-MAO/MCC	120.1	111.0	38.8
PE-Zr/MCC	119.8	161.0	56.3
PE-Zr/MAO/MCC	120.0	149.3	52.2

[a] Melting temperature (Tm) measured by DSC measurement.

[b]Heat of fusion (ΔHexp) measured by DSC measurement.

[c] Crystallinity (Xc) was calculated from the equation; %crystallinity = ($\Delta H_{sample}/\Delta H_{100\%}$ crystallinity)x100, the $\Delta H_{100\%}$ crystallinity of polyethylene is 286 J/g.

4.2.3.4 Ethylene consumption

The ethylene consumption rates (ml/min) during ethylene polymerization from heterogeneous system were recorded as shown in Figure 30.All polymers exhibited rapid activation (with very short induction period) in first minute. After that, consumption rate still slightly increased since the first minute to the last minute in the interval time of 15 minutes. No deactivation of catalytic systems was observed in all runs. It was seen that there was no significant change in the ethylene consumption rates for all polyethylene polymerization systems.
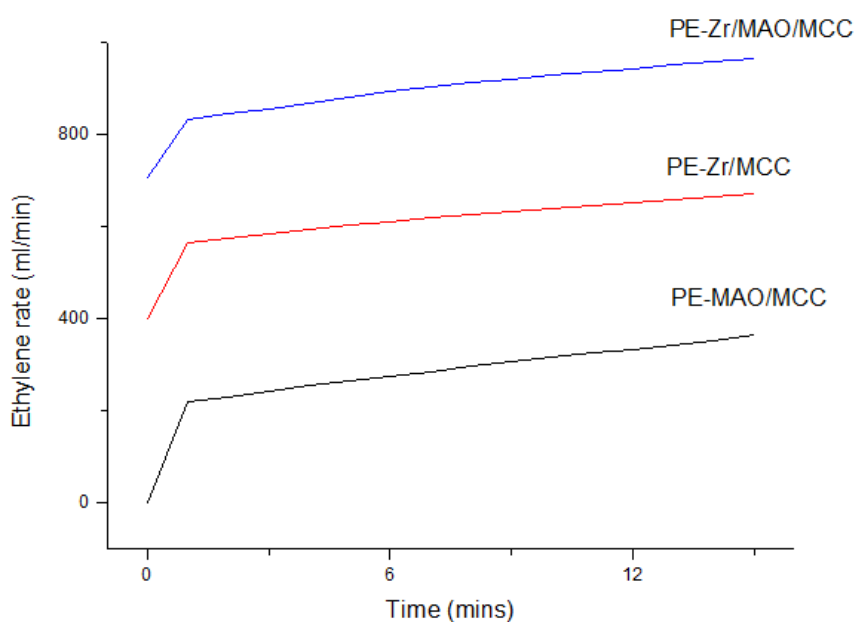
Figure 30 Ethylene consumption during ethylene polymerization from heterogeneous system using commercial cellulose (MCC) supports.

4.2.3.5 Catalytic activity

The effect of different methods of immobilization with zirconocene/MAO catalyst for ethylene polymerization is shown inTable 8. It can be seen from the results that the polymerization systems with the immobilization of MAO and zirconocene catalyst exhibited lower catalytic activities and polymer yield compared to the polymerization system without MCC support due to negative supporting effects arising from the interaction between MCC support and catalytic system resulting in lower active sites for the polymerization process [50]. Another reason may be caused by impurities inside the MCC support. Moreover, considering the heterogeneous system, it can be seen that the highest catalytic activity and polymer yield was obtained in PE-MAO/MCC, following by PE-Zr/MCC and PE-Zr/MAO/MCC, respectively. Mechanisms of different methods of immobilization with zirconocene/MAO catalyst are shown in Scheme 1-3[51-53].In addition, MAO is involved in the formation of cationic active sites for metallocene catalyst and also formation of a "crown-alumoxane complex"(as shown in Scheme 4) by immobilization with MAO to stabilize the anion [51], which can prevent anion that attacks the metallocene cation nucleophilically, that termination process in cationic ethylene polymerization. Moreover, the mechanisms of immobilization with catalyst/support (Zr/MCC) can be speculated that Zr^+ cations are more difficult to formation and stabilizationin the case of supports with weak Lewis acid character. For this reason, MCC support with immobilization of MAO presented high activity and polymer yield than other immobilization methods. It reveals that different methods of immobilization of zirconocene catalyst influenced on catalytic activity.

Table 8 the catalytic activity of catalysts via homogeneous

and heterogeneous systems

Run	Polymer sample	Support (g)	Polymer obtain (g)	Yield (g)	Activity (kg $_{PE}$ g$^{-1}_{catalyst}$ h^{-1})
1	Homogeneous	-	-	0.6265	301.9
2	MAO/MCC	0.0930	0.2548	0.1608	77.5
3	Zr/MCC	0.0210	0.1804	0.1593	76.8
4	Zr/MAO/MCC	0.0128	0.1658	0.1530	73.7
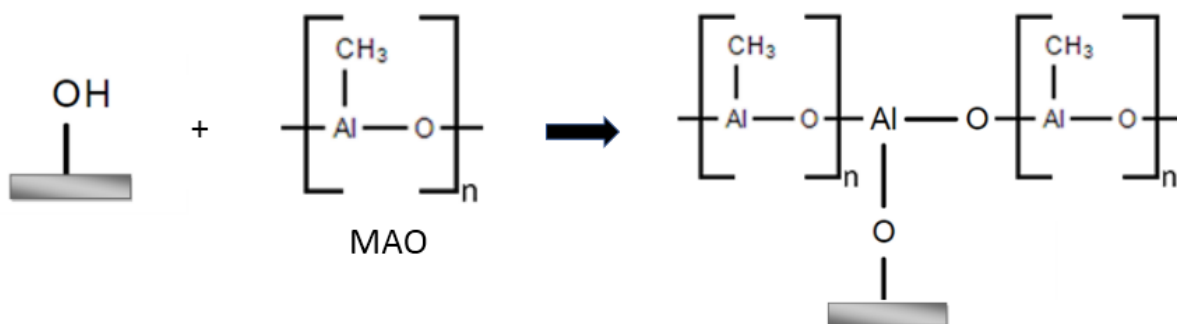
Scheme 1 Mechanisms of immobilization with cocatalyst/support (MAO/MCC):

Initial adsorption of MAO cocatalyst on the support.
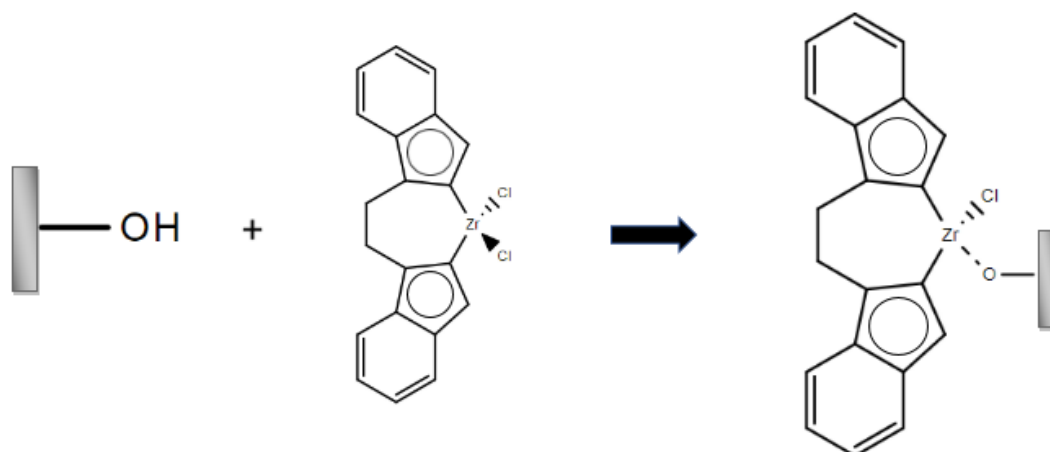
Scheme 2 Mechanisms of immobilization with catalyst/support (Zr/MCC) :
immobilization of the metallocene on the support.
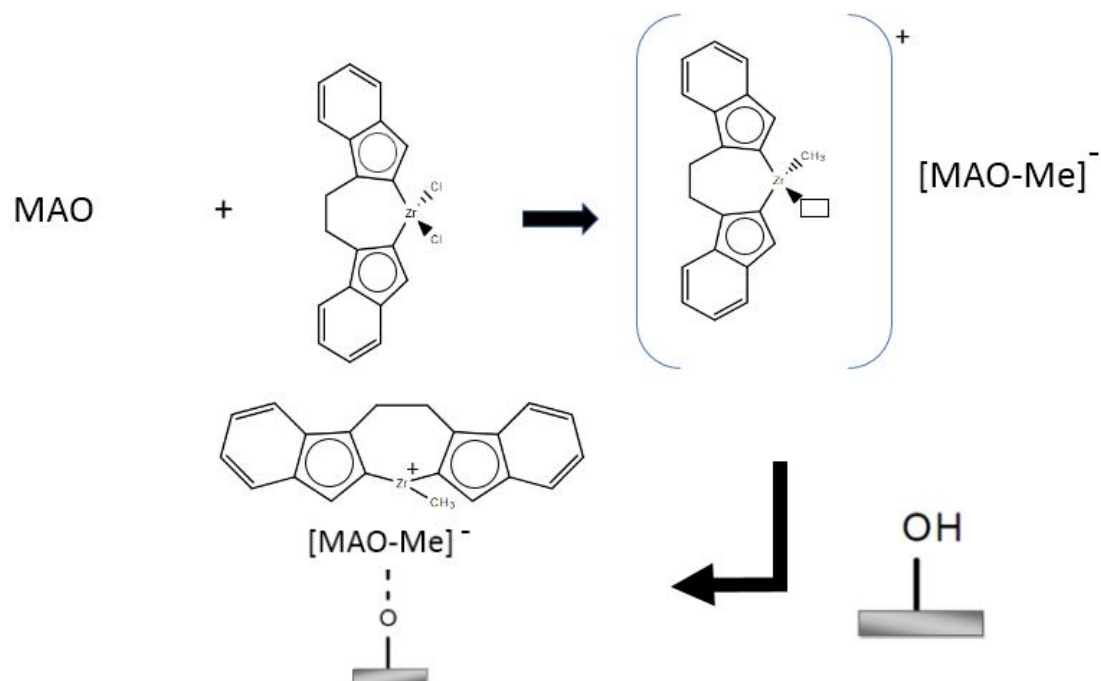
Scheme 3 Mechanisms of immobilization with catalyst/cocatalyst/support
(Zr/MAO/MCC): immobilization of the mixture of metallocene
and MAO is adsorbed on the support.
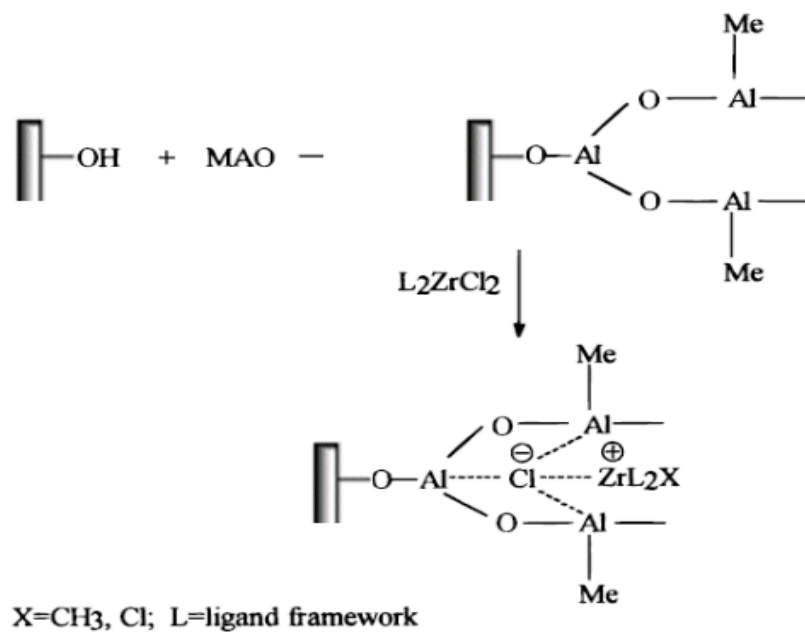
Scheme 4 Formation of a "crown-alumoxane complex" by immobilization with MAO

CHEPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In the first part, Aluminum alkyls used as cocatalyst and scavenge impurities during ethylene polymerization with zirconocene catalysts were investigated. It was found from the obtained polymer that different types and amount of alkylaluminum influenced on morphologies, crystallinity and catalytic activity. The activity of MAO/zirconocene catalysts increased with increasing $[Al]_{MAO}/[Zr]_{cat}$ molar ratios. Therefore, addition of TEA to MAO /zirconocene catalysts slightly increased catalytic activity, but lower activity at same total $[Al]/[Zr]_{cat}$ molar ratios of MAO/zirconocene. For this reason, we can added TEA to increase catalytic activity to compensate MAO which is higher cost than TEA. However, MAO catalyst systems gave higher catalytic activity than TEA catalyst systems that cause poor morphologies and larger size than the obtained polymers from TEA catalyst systems due to the agglomeration from fine particle. Moreover, addition of TEA into MAO/zirconocene resulted in increased crystallinity compared to MAO catalyst systems. However, the crystallinity tended to decrease with increasing the molar ratios of $[Al]_{TEA}/[Zr]_{cat}$ catalytic systems. The melting temperature of all polymers obtained is between 122-123°C. Thus, it can be summarized that proper types and molar ratios of cocatalyst and/or scavenger of zirconocene catalyst can be altered depending on the applications for manufacturer wants.

In the second part, the immobilization of cocatalyst/catalyst onto microcrystalline cellulose (MCC) for ethylene polymerization with three different methods including (i) immobilized cocatalyst/cellulose (MAO/MCC) (ii) immobilized catalyst/cellulose (Zr/MCC) and (iii) immobilized catalyst/cocatalyst/cellulose (Zr/MAO/MCC). It was found that all methods achieved to the dispersion and adhesion of MAO and/or catalyst onto MCC surface, which was confirmed by SEM-

EDX, FT-IR, XPS and XRD. Furthermore, all the methods achieved to produce polyethylene having melting temperature(T_m) of all samples in range between (119-120 $^{\circ}$C). Moreover, the highest catalytic activity and polymer yield were obtained in PE-MAO/MCC followed by PE-Zr/MCC and PE-Zr/MAO/MCC, respectively. The MCC support with immobilization of MAO can form a "crown-alumoxane complex" to stabilize the anion, which prevent termination process[51]. For this reason, MCC support with immobilization of MAO presented high activity and polymer yield than other immobilization methods.

5.2 Recommendation

- Effect of another cocatalyst and scavenger should be studied.
- Effect of calcination temperature should be investigated
- Investigating of the other type of organic support, such as starch should be applied.

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APPENDIX A: FOURIER TRANSFORM INFRARED SPECTROSCOPY
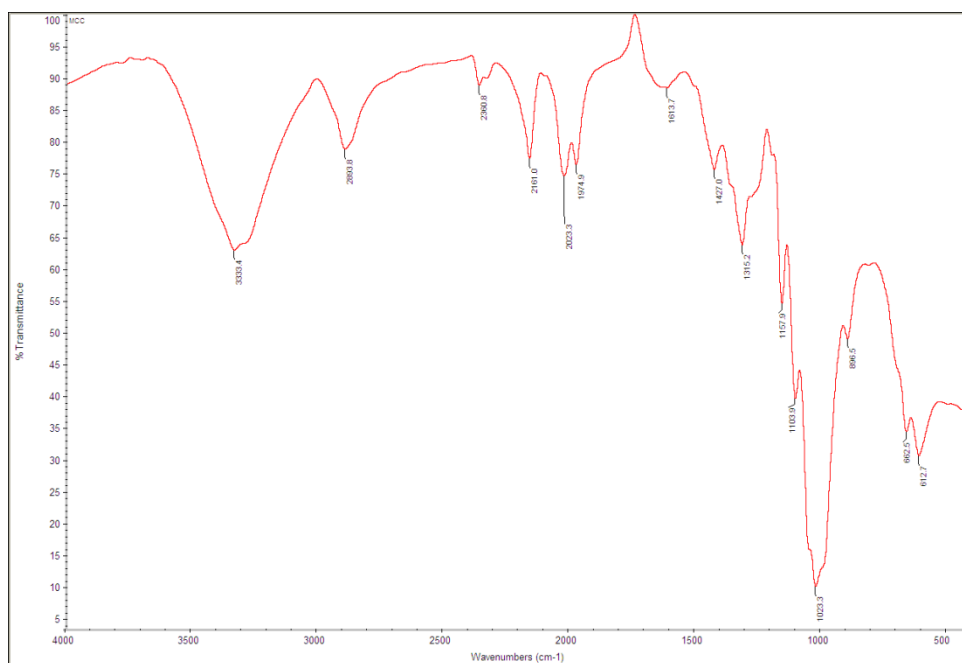
Figure A-1 FT-IR of MCC support
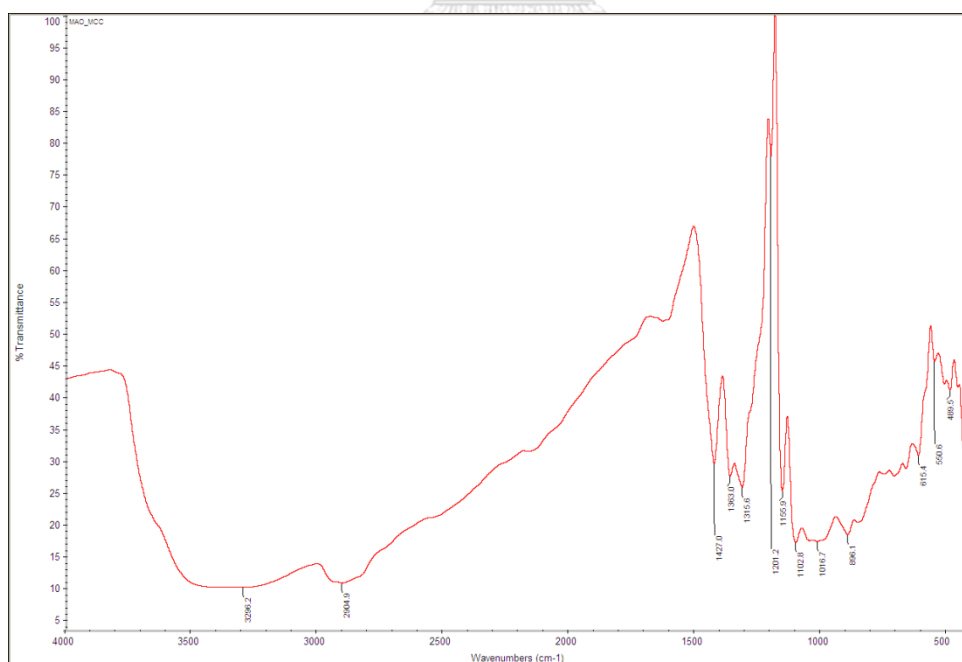
Figure A-2 FT-IR of MCC after immobilization with MAO
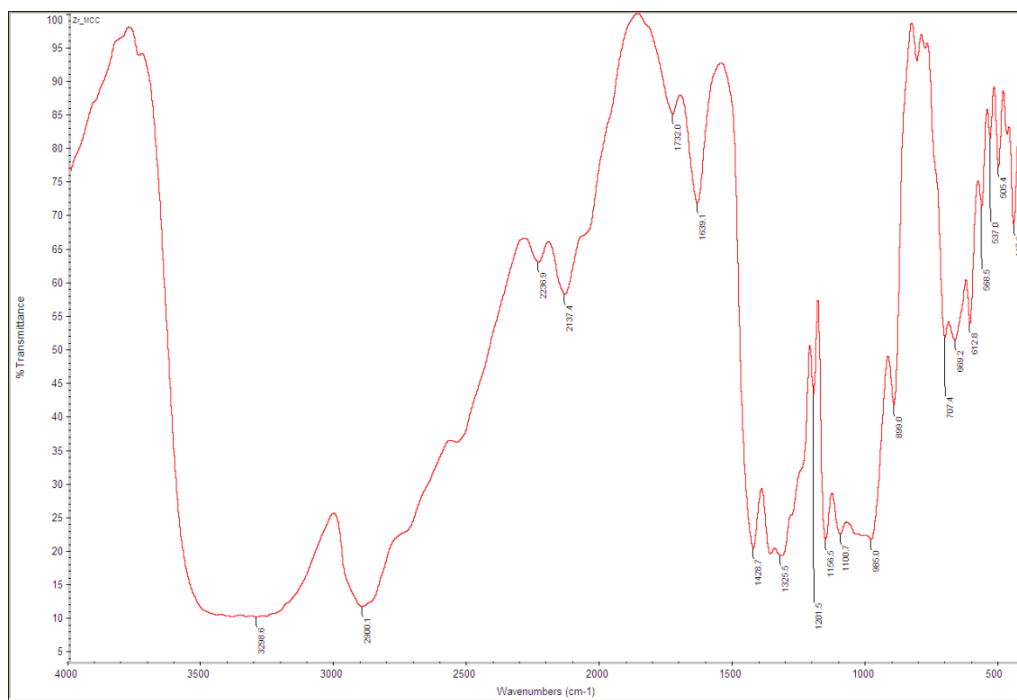
Figure A-3 FT-IR of MCC after immobilization with catalyst
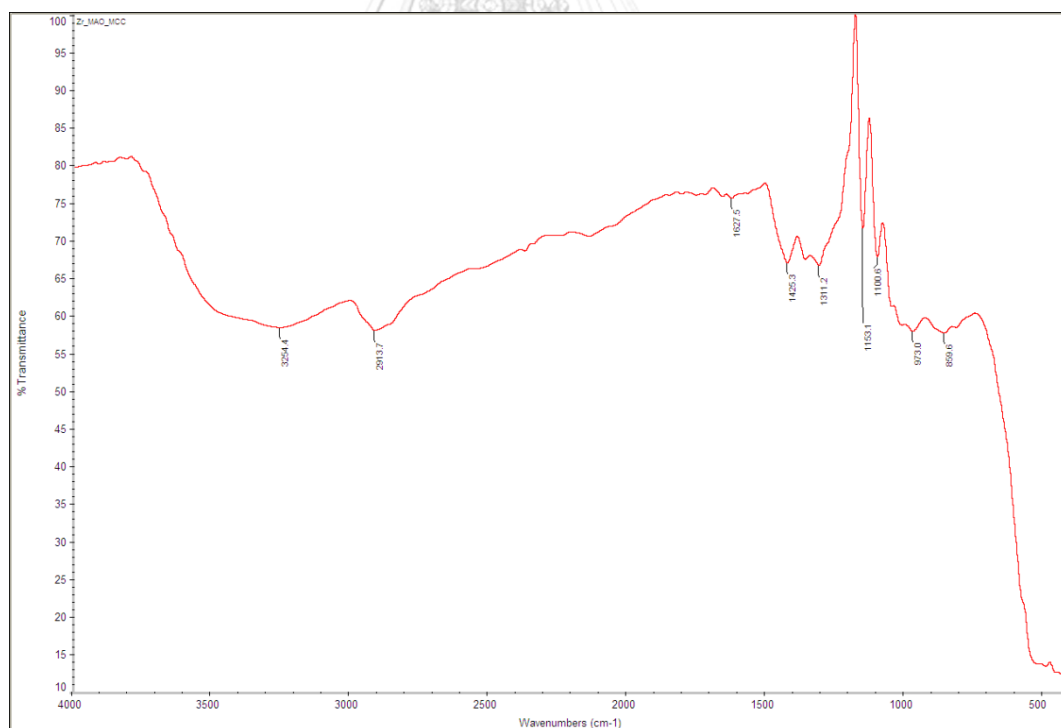
Figure A-4 FT-IR of MCC after immobilization with catalyst and MAO

APPENDIX B : THERMAL GRAVIMETRIC ANALYSIS
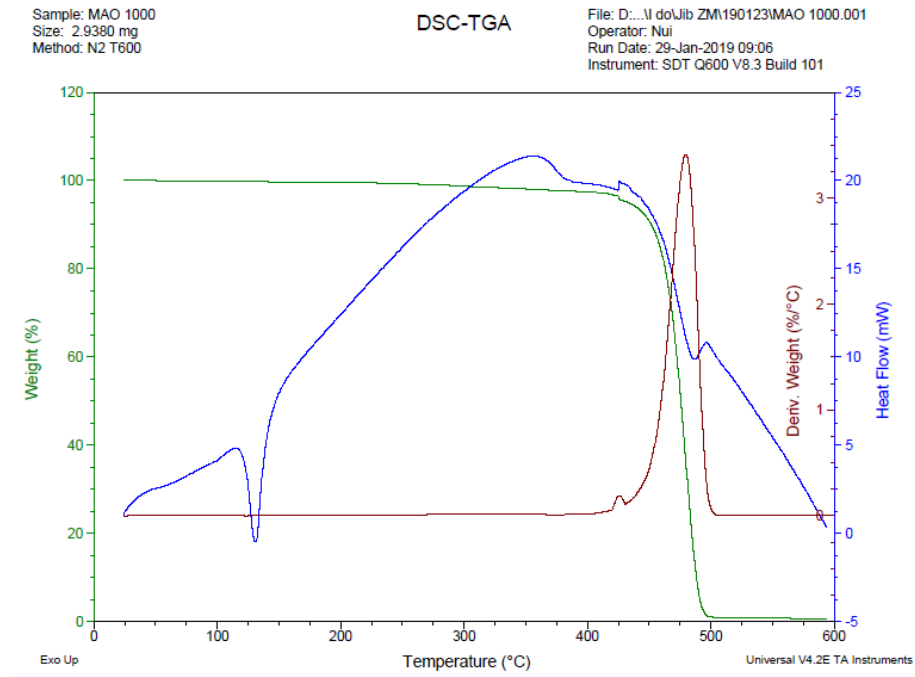
Figure B-1 TGA of PE/1000-0
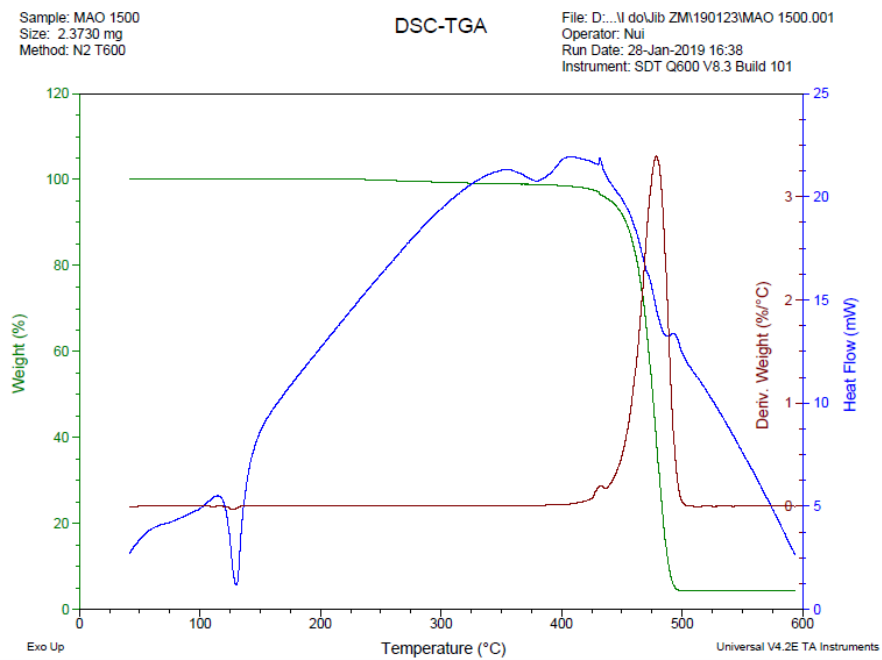
Figure B-2 TGA of PE/1500-0
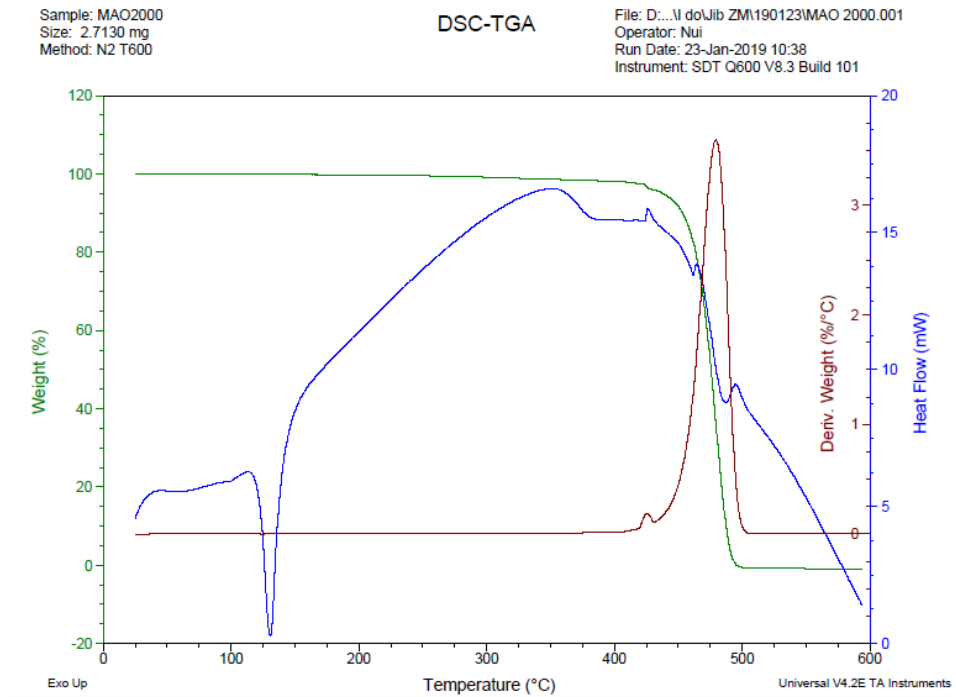
Figure B-3 TGA of PE/2000-0
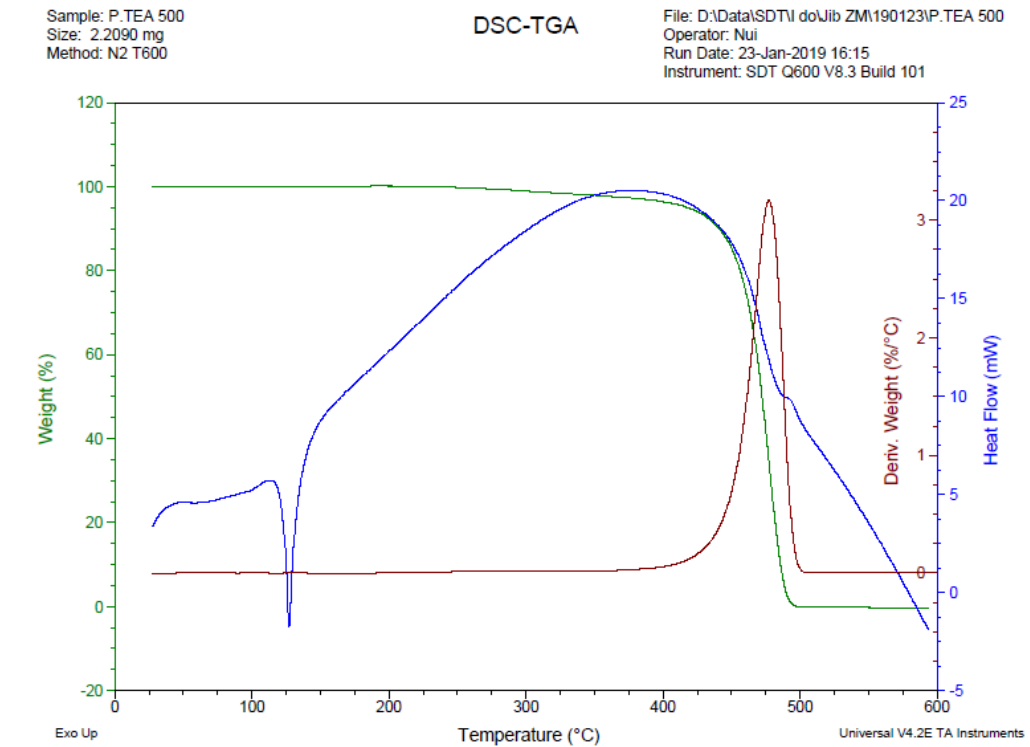
Figure B-4 TGA of PE/1000-500

Sample: P.TEA 1000
Size: 2.2130 mg
Method: N2 T600

DSC-TGA

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Run Date: 28-Jan-2019 13:53
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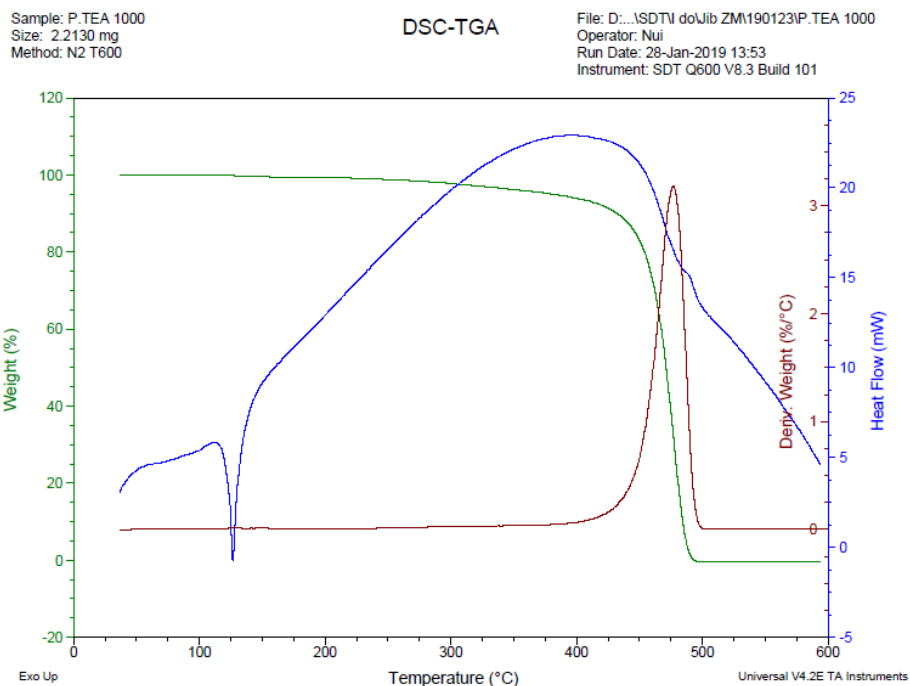
Figure B-5 TGA of PE/1000-1000

Sample: P.TEA 1500
Size: 2.0970 mg
Method: N2 T600

DSC-TGA

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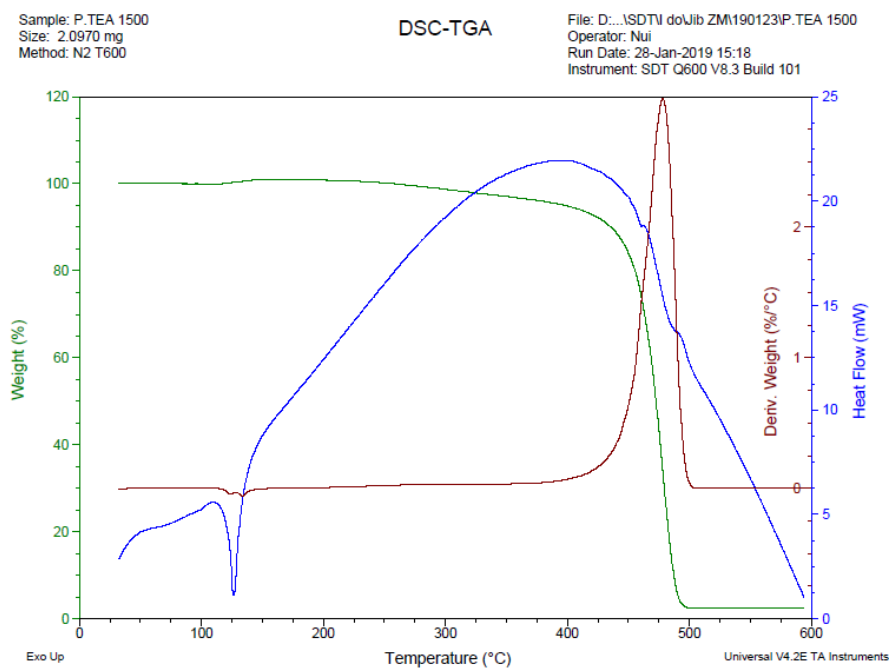
Figure B-6 TGA of PE/1000-1500
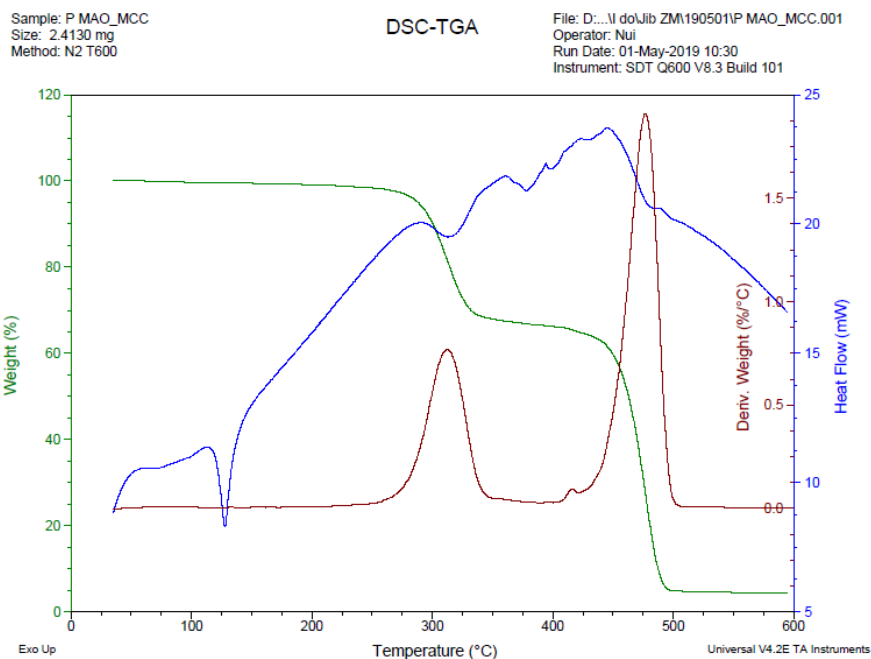
Figure B-7 TGA of PE-MAO/MCC
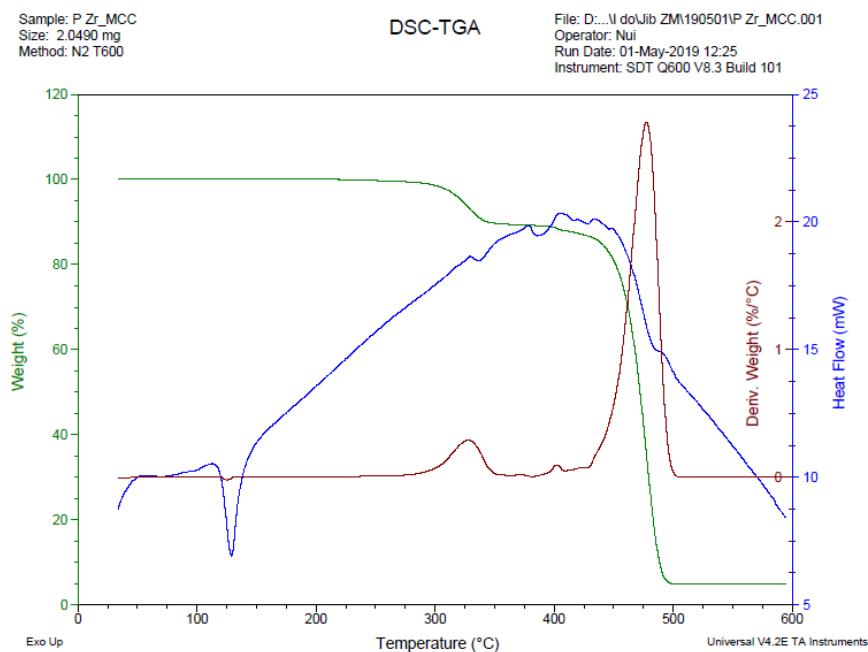
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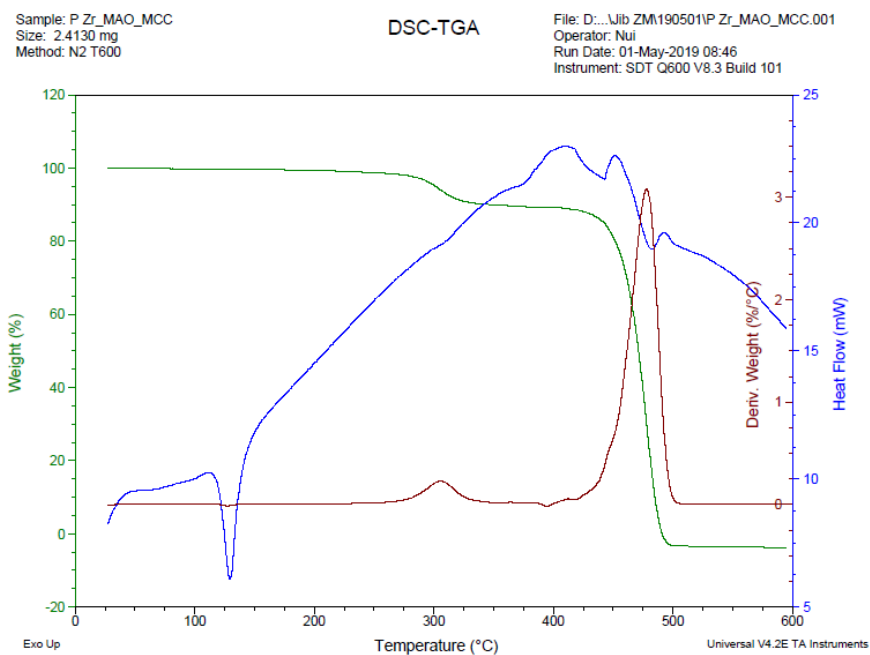
Figure B-9 TGA of PE-Zr/MAO/MCC

APPENDIX C : DIFFERENTIAL SCANNING CAROLIMETRY
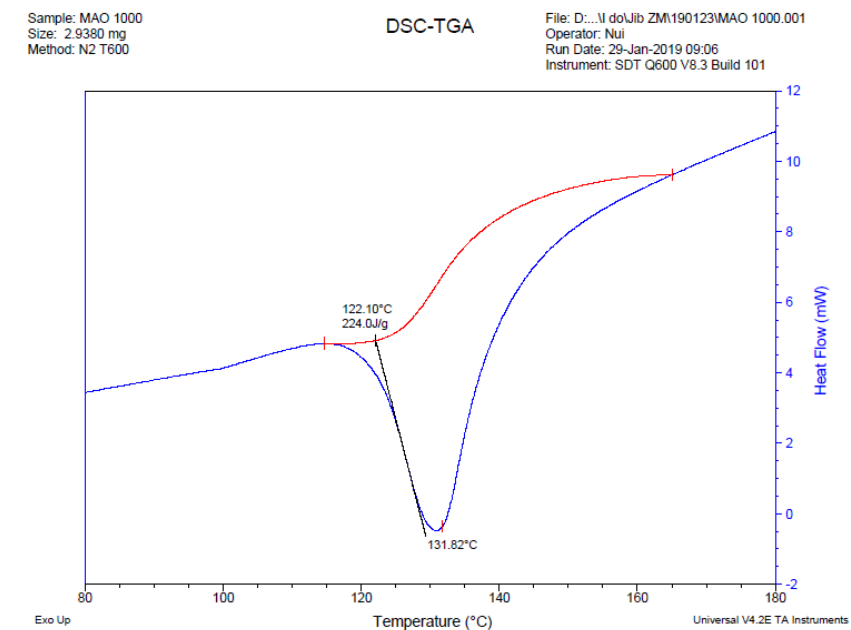
Figure C-1 DSC of of PE/1000-0
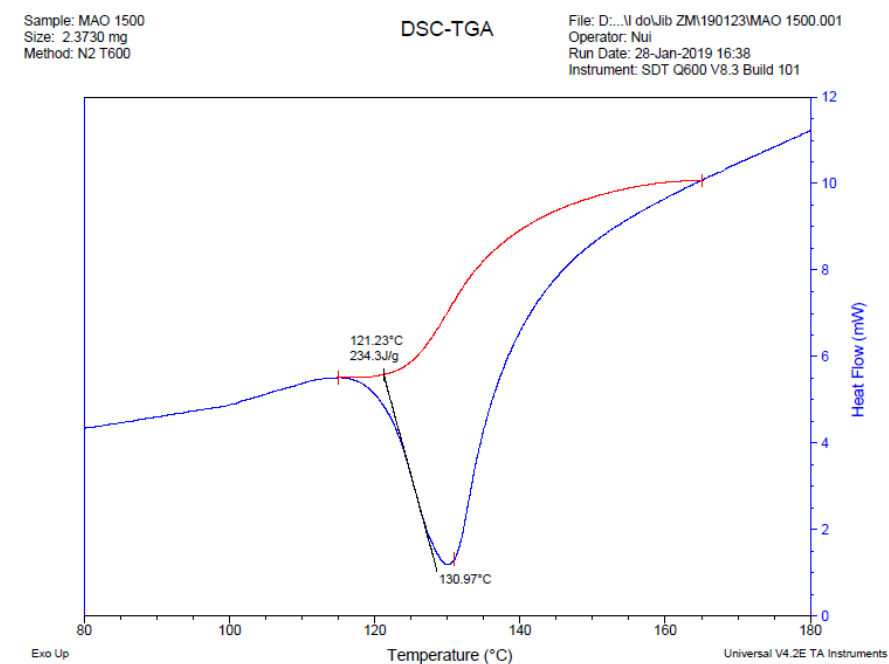
Figure C-2 DSC of of PE/1500-0
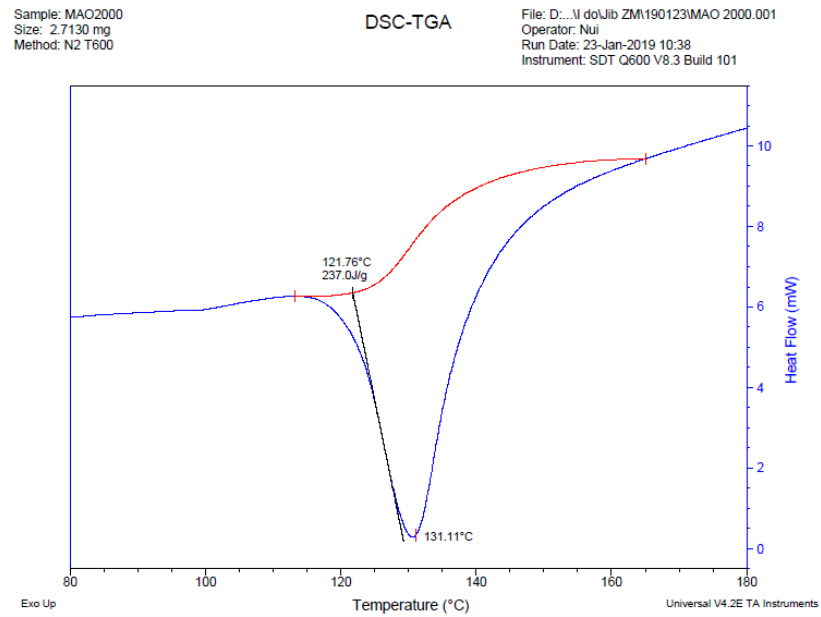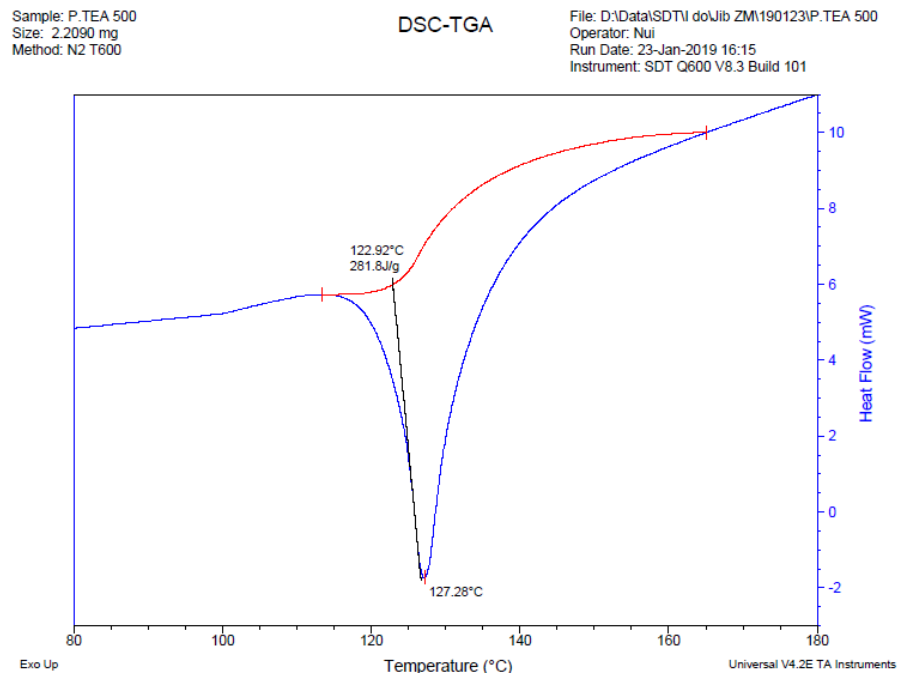
Figure C-3 DSC of of PE/2000-0
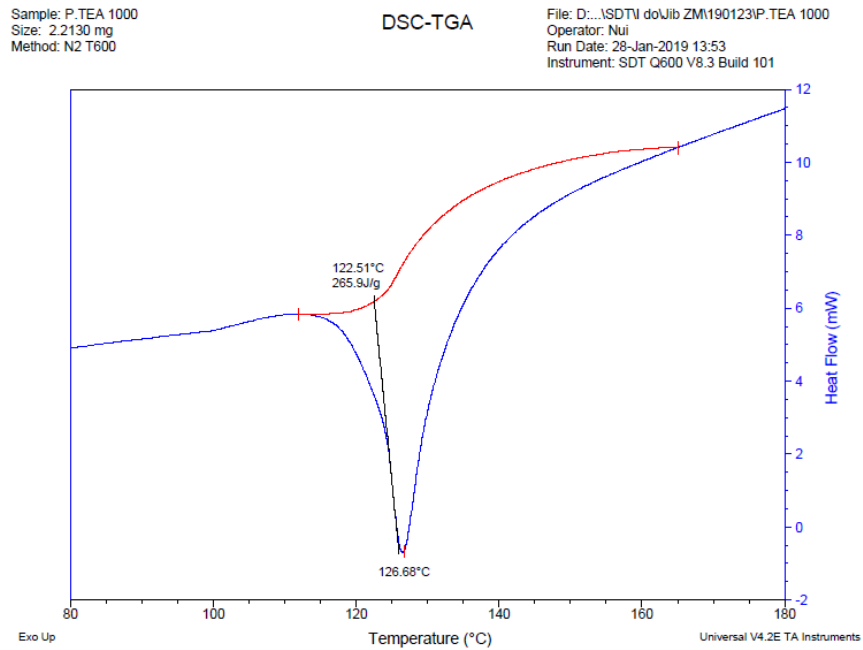

Figure C-4 DSC of of PE/1000-500

Figure C-5 DSC of of PE/1000-1000
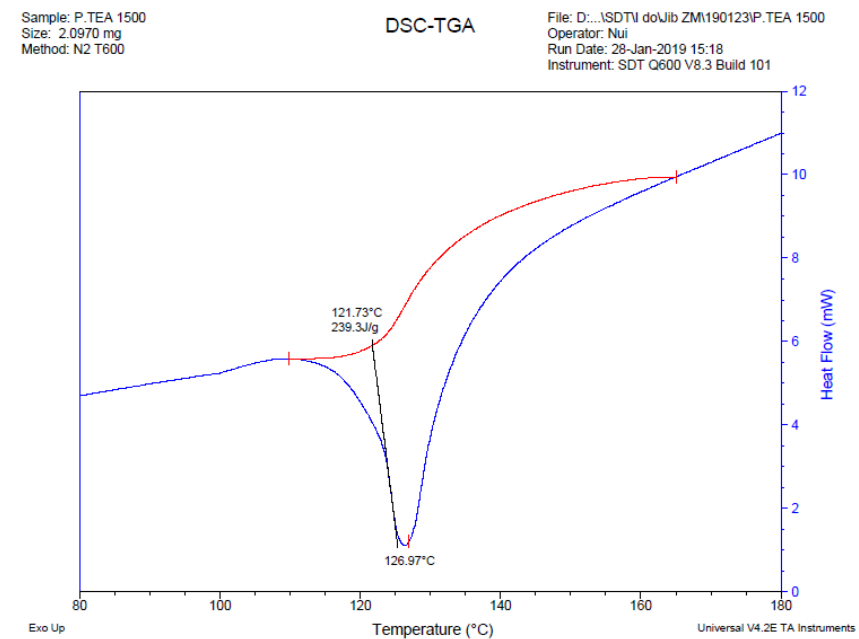
Figure C-6 DSC of of PE/1000-1500
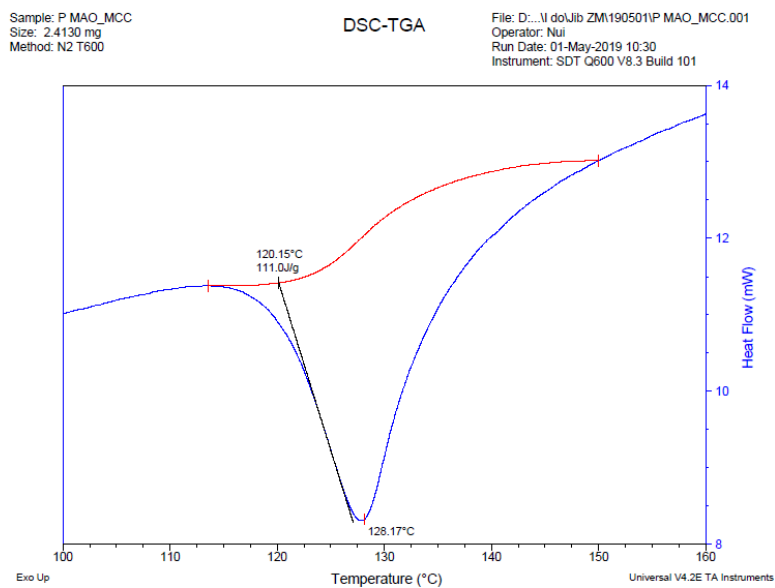
Figure C-7 DSC of PE-MAO/MCC
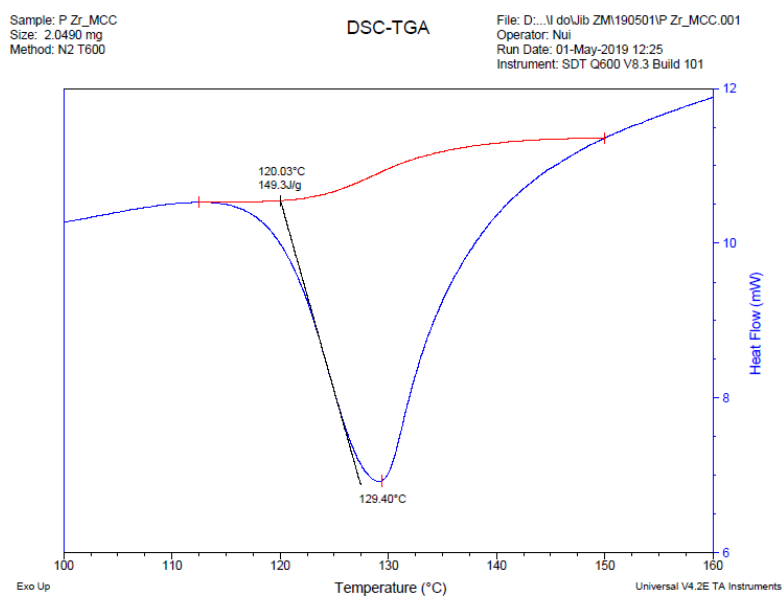
Figure C-8 DSC of PE-Zr/MCC
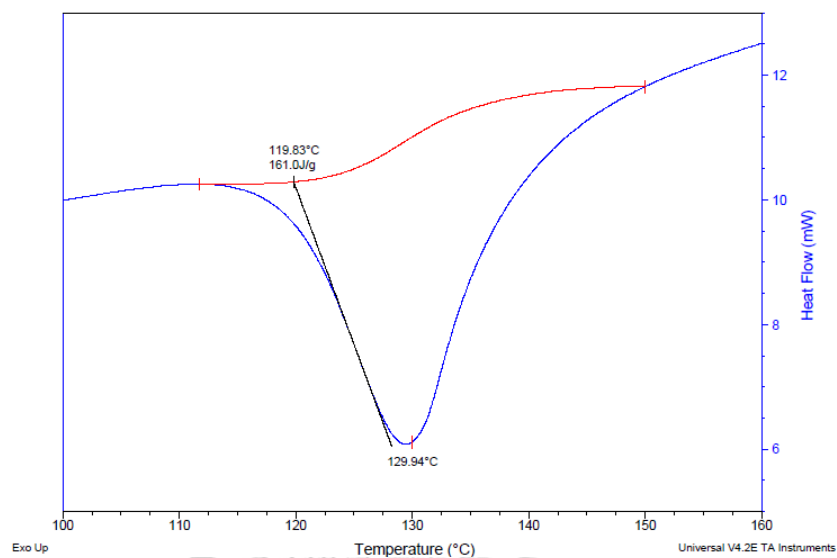
Figure C-9 DSC of PE-Zr/MAO/MCC

APPENDIX D : CALCULATION

Calculation of stock solution for heterogeneous system (support)

For this research, vary immobilization techniques including MAO/MCC, Zr/MCC and Zr/MAO/MCC

- For example : calculation of addition support(g) for ethylene polymerization of Al/Zr = 2000

$$\text{support(g)} = \frac{\text{mmol of Al required}^1 \text{ x MW of Al (mg/mmol)}^2}{\text{amount of Al(mg of Al /g support)}^3}$$

For Zr/MCC and Zr/MAO/MCC used Zr from catalyst instant Al from MAO

[1] $\text{mmol}_{Al}/\text{mmol}_{Zr}$ = 2000

[2] MW of Al = 26.9815 (g/mol) , MW of Zr = 91.224 (g/mol)

[3] amount of Al(mg of Al/g support) = %wt from EDX technique

Homogeneous system

Yield polymer (g) = obtain polymer after run ethylene polymerization for 15 minutes with filtrated under vacuum and dried at T_{room}

Heterogeneous system

Yield polymer (g) = obtain polymer[1](g) – support[2](g)

[1] Obtain polymer after run ethylene polymerization for 15 minutes with filtrated under vacuum and dried at T_{room}

[2] support for addition in ethylene polymerization

Calculation of catalytic activity

$$\text{Activity} = \frac{\text{Yield polymer (g)}}{\text{Gram of catalyst (g) x polymerization time (hr)}}$$

APPENDIX E : LIST OF PUBLICATION

Tumawong P. et al. "Effect of cocatalyst and scavenger on catalytic properties of metallocene catalyst for ethylene polymerization"(The proceeding of Pure and Applied Chemistry International Conference 2019,PACCON 2019 ,Bangkok International Trade & Exhibition Centre (BITEC), Bangkok, Thailand)

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