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MODIFICATION OF CELLULOSE-SUPPORTED ZIRCONOCENE CATALYST WITH BORON AND GALLIUM FOR ETHYLENE COPOLYMERIZATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	MODIFICATION OF CELLULOSE-SUPPORTED ZIRCONOCENE CATALYST WITH BORON AND GALLIUM FOR ETHYLENE COPOLYMERIZATION
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ในปัจจุบันพอลิเอทิลีนเป็นพลาสติกที่มีความสำคัญและ มีความต้องการ ใช้งานมากในอุตสาหกรรมการผลิตพลาสติกประเภทถุง ในการผลิตพอลิเอทิลีนตัวเร่งปฏิกิริยาที่นำมาใช้ได้แก่ ตัวเร่งปฏิกิริยา ซีเกลอร์-แนทตาและตัวเร่งปฏิกิริยาเมทัลโลซีน โดยตัวเร่งปฏิกิริยาเมทัลโลซีนมักนำมาใช้ควบคู่กับตัวเร่งปฏิกิริยาร่วมเมทัลอะลูมินอกเซนซึ่งจะให้ความว่องไว สูงมาก สำหรับการนำตัวเร่งปฏิกิริยาไปใช้ในอุตสาหกรรมได้มีการพัฒนาและปรับปรุงตัวเร่งปฏิกิริยาเมทัลโลซีนที่มีตัวรองรับ เพื่อให้สามารถใช้ งานได้ในกระบวนการผลิตที่เป็นวัฏภาคแก๊สและวัฏภาคของเหลว และแก้ปัญหาการเกิดการยึดจับตัวของเนื้อพอลิเมอร์ในเครื่องปฏิกรณ์ แต่พบว่าผลของการใช้ตัวรองรับทำให้ความว่องไวของตัวเร่งปฏิกิริยาในระบบวิวิธพันธ์ต่ำกว่าระบบเอกพันธ์ ที่ผ่านมาจึงมีการศึกษาการปรับปรุงตัวรองรับ โดยพบว่าผลของการปรับปรุงตัวรองรับหลายชนิด ช่วยทำให้ความว่องไวเพิ่มขึ้นในระบบของตัวเร่งปฏิกิริยาเมทัลโลซีน

ซึ่งในการศึกษาจะ แบ่งงานออกเป็น 2 ส่วน ในส่วนแรกจะศึกษาการสังเคราะห์พอลิเอทิลีนโดยใช้ ขุยมะพร้าวและเซลลูโลสเป็นตัวรองรับ จากการทดลองพบว่า ตัวรองรับเซลลูโลสให้ความว่องไวของตัวเร่งปฏิกิริยาสูงกว่า ขุยมะพร้าว เมื่อศึกษาผลของการเพิ่มปริมาณของตัวรองรับในอัตราส่วน 10, 20, 30 และ 40 เปอร์เซ็นต์โดยน้ำหนัก พบว่าปริมาณ ขุยมะพร้าวที่เพิ่มขึ้นส่งผลให้ความว่องไวของตัวเร่งปฏิกิริยาลดลง ในขณะที่การเพิ่มปริมาณของเซลลูโลสกลับทำให้ความว่องไวของตัวเร่งปฏิกิริยาสูงขึ้น และพบว่าภาวะที่ตัวเร่งปฏิกิริยาใ ห้ความว่องไวสูงที่สุดในพอลิเมอร์ไรเซชันของเอทิลีนคือที่ 30 เปอร์เซนต์โดยน้ำหนักของเซลลูโลส ส่วนที่ 2 ของงานวิจัยเป็นการศึกษาตัวรองรับเซลลูโลสที่ถูกปรับปรุงด้วยแกลเลียมและโบรอน เพื่อสังเคราะห์โคพอลิเมอร์ของเอทิลีนกับหนึ่งเฮกซีน ซึ่งพบว่าการปรับปรุงด้วยแกลเลียมทำให้ความว่องไวในการเกิดพอลิเมอร์เพิ่มขึ้น โดยปริมาณแกลเลียม 2 เปอร์เซ็นต์โดยน้ำหนัก สามารถปรับปรุงความว่องไวของตัวปฏิกิริยาได้สูงที่สุด ในขณะที่ การปรับปรุงด้วย โบรอน ทำให้ความว่องไวในการเกิดพอลิเมอร์ ลดลง พอลิเมอร์และโคพอลิเมอร์ที่ได้ทั้งหมดจะนำมาวิเคราะห์เพื่อวัดคุณสมบัติด้วยเครื่องสแกนนิงอิเล็กตรอนไมโครสโคปีและเครื่องดิฟเฟอเรนเทียลสแกนนิงแคลอรีมิเตอร์

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต

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CHATUMA SUTTIVUTNARUBET : MODIFICATION OF CELLULOSE-SUPPORTED ZIRCONOCENE CATALYST WITH BORON AND GALLIUM FOR ETHYLENE COPOLYMERIZATION ADVISOR: ASSOC. PROF. BUNJERD JONGSOMJIT, Ph.D., 105 pp.

At present, polyethylene has been widely used in the industry of manufacturing plastic bags. In the production of polyethylene, Ziegler-Natta catalysts and metallocene catalysts are able to producing polyethylene. Metallocene used in associate with methylaluminoxane shows very high activity in polyethylene polymerization. For metallocene catalysts used in the industry, it has developed and improved supported metallocene because it enables their use in gas- and slurry-phase processes and prevent reactor-fouling problems. Unfortunately, owing to the supporting effect, it is found that the catalytic activity of catalysts in the heterogeneous system is usually lower than the homogeneous one. In the past, it has been studied to modification on support. The results showed that the modification on support exhibited a promising enhancement for activity in metallocene catalyst systems.

The study was divided into two parts. In the first part, study on synthesis of polyethylene using coir dust and cellulose as support was investigated. Two variables in this part are types of support and filler loading in polyethylene composites (10, 20, 30, and 40 %wt). It was found that the catalytic activity of coir dust was lower than the cellulose system. Catalytic activities can be decreased with increasing amount of coir dust while the activities increase with increasing cellulose loading. The addition of 30 % of cellulose shows that the maximal activity. In the second part, cellulose supports modified with B and Ga were employed in ethylene/1-hexene. It was found that the Ga-modified cellulose gave the higher activity than that of the non-modified one. The polymerization activities obtained from cellulose-Ga-2% exhibited the highest activity among the cellulose having Ga modification. Conversely, the B-modified cellulose gave lower activity than that of the non-modified one. All the obtained polymers and copolymers were characterized by SEM and DSC to determine the polymer properties.

Department : Chemical Engineering Student's Signature

Field of Study : Chemical Engineering Advisor's Signature

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CHAPTER I

INTRODUCTION

At the moment, polyethylene has been widely used in the plastics industry. Polyethylene has many types classified by their density. Because there are many useful properties of polyethylene such as low densicty, high strength, and chemical resistance, as well as being cost-effective, various products can be made from polyethylene; packaging food, toys, can liners, appliances, foam, film, and many others [1-3]. Normally, polyethylene has been obtained from polymerization process. There are 2 main catalyst types used in polymerization reaction; Ziegler-Natta catalysts and metallocene catalysts. The polymer using Ziegler-Natta as catalyst is a wide molecular weight distribution (MWD) and chemical composition distribution (CCD) by the reason of their multiple active sites [4]. Sinn and Kaminsky had discovered MAO activated metallocene catalysts producing polyolefin. In homogeneous system, metallocene catalysts are more active than Ziegler-Natta catalysts. Molecular weight distribution (MWD) of polymer which is produced by metallocene catalysts is narrower than using Ziegler-Natta catalyst ($M_w/M_n \approx 2$) [5].

Metallocene catalysts can be classified into 2 main systems: homogeneous and heterogeneous system. Commonly, homogeneous system is a higher activity than heterogeneous system. However, two major disadvantages of homogeneous system are the lack of morphology control of polymers produced and reactor fouling [6]. Immobilizing metallocene catalysts onto inorganic supports (heterogeneous system) is alternative employed to resolve that problem. Hence, worldwide, many researchers pay attention to develop a heterogeneous system in order to increase polymerization activity as high as homogeneous catalyst. For heterogeneous system, various inorganic supports have been utilized being supported such as silica, alumina, HY zeolite, and many other too much to mention [7]. However, a few works have been interested in organic supports to be a support choice. For instance, in the previous study, some researchers proposed using biomass (cellulose, starch and chitosan) as support for zirconocene catalysts in ethylene polymerization. The results obtained in their work show that the polymers obtained with the zirconocene supported on chitosan or cellulose pretreated with methylaluminoxane exhibited a higher molecular weight than those obtained with a homogeneous system. Polymer particles obtained with these supported metallocene catalysts showed a good replication of the original support particles [8]. Lee and Yoon had used cyclodextrin (CD) supported Cp_2ZrCl_2 in ethylene polymerization, The MW's of PE increased 30 times by using the CD as support, and the MWD present a low polydispersity index (2.3-2.5) [9].

Regularly, supported catalysts have a lower activity in the polymerization of olefins than their corresponding homogeneous metallocene systems due to the formation of inactive species between catalyst and support [10]. Thus, the modification of the support properties is required. For instance, in the previous study, some researchers focused on modified supports for improved activity. The use of gallium-modified silica-supported zirconocene/dMMAO catalyst for ethylene/α-olefin copolymerization was studied by Jongsomjit *et al.* [1]. It was found that the gallium modification of the silica support apparently resulted increasing polymerization activity. In addition, Kaivalchatchawal *et al.* [11] studied the effects of B and Ga modification of the silica support on the copolymerization. The results reveal that catalytic activity increased by adding of B and Ga modification.

In this research, coir dust and cellulose used in this study as a support for zirconocene/MAO catalyst in the ethylene polymerization was investigated. For easy understanding purpose, the investigation of those can be categorized into two parts as follows.

1) The effect of filler loading (coir dust and cellulose) on the catalytic activity and polymer properties for the ethylene polymerization

2) The effect of the acidic modification of the support on heterogeneous system

Cellulose acidic properties were modified by adding the boron metal and the gallium metal and were utilized during ethylene/1-hexene copolymerization to study and explore the efficiency of supported zirconocene catalyst.

This thesis was divided into five chapters. Chapter I involved an overview of the use of metallocene catalyst in the polyolefin industry. Chapter II provided a review of some of the literature on the metallocene catalysis for olefin polymerization. The experimental procedure as well as the instrument and techniques used for characterizing the supports, modified supports and resulting polymers were described in Chapter III.

In the chapter IV, the results on ethylene and ethylene/1-hexene polymerization with regard to two parts of investigation as mentioned above were demonstrated and discussed.

Finally, the conclusions of this work and some recommendations for future research work were provided in Chapter V.

1.1 Objectives of the thesis

1.1.1 To investigate the effect of filler loading (coir dust and cellulose) on catalytic activities and properties of polymer composites.

1.1.2 To concern the effect of acidic cellulose support modification by employing the boron metal and the gallium metal on catalyst activities and properties of polymer composites.

1.1.3 To find out the relation between activity and various amounts of Lewis acid content (1, 2, and 5 % wt the boron metal and the gallium metal)

1.2 Research scopes

1.2.1 Preparation of supports by *in situ* impregnation with methylaluminoxane (MAO).

1.2.2 Percent loading of acidic (boron metal and the gallium metal) on each supports is varied 1, 2 and 5%wt.

1.2.3 Characterization of each supports using FT-IR and SEM/EDX measurement.

1.2.4 Characterization of polymer using SEM, XRD and DSC measurement.

1.2.5 Synthesis of polymer composites (PE and LLDPE) with zirconocene /MAO catalysts by *in situ* polymerization of ethylene and ethylene/1-hexene at T = 70 °C ; [ethylene] = 0.018 mol; $[\mathrm{Al}]_{\mathrm{MAO}}/[\mathrm{Zr}]_{\mathrm{zirconocene}} = 1135$; in toluene with a volume of 30 mL.

1.3 Benefits

1.3.1 Polyethylenes were synthesized by *in situ* polymerization with metallocene catalyst and the addition of coir dust and cellulose as supports were changing the catalytic activity.

1.3.2 This thesis shows that the effect of filler loading (coir dust and cellulose) on catalytic activity and polymer characterizations.

1.3.3 Modified cellulose supported zirconocene/MAO catalyst can change and improve activities of copolymerization.

1.3.4 The data will be used as basis information for polymer industries and commercial application.

CHAPTER II

LITERATURE REVIEWS

2.1 Polyethylene Classification

Generally, the most simple of polymer is polyethylene. It consists of several repeated-CH_2-cell connections by polymerization process. Polyethylene is classified into several types. It depends on its density and molecular structure. The polyethylene properties depend on condition such as temperature, pressure and catalyst type during polymerization. These conditions affect on polyethylene shape because it can promote and break the chains of molecular branching. Thus, prepared polyethylene using different condition is main factor to produce various polyethylene types. Because of several types, Polyethylene is widely applied in many products. The products which are produced from polyethylene are trash bag packaging, containers, toys, and various house wares.

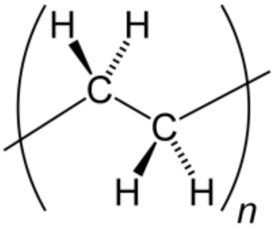


Figure 2.1 Repeating units of polyethylene [12]

In 1937, The Society of the Plastics Industry (SPI) can separate three main types of polyethylene based on density [13]:

- Low density: 0.910-0.925 g/cm^3
- Medium density: 0.926-0.940 g/cm^3
- High density: 0.941-0.965 g/cm^3

After that the American Society for Testing and Materials (ASTM) has also identified more several types of polyethylene than SPI, but also based on density as well. Polyethylene types which are classified by ASTM are shown in table 2.1

Table 2.1 Density of polymer classification

Polymer types	Density (g/cm^3)
High density polyethylene (HDPE)	>0.941
Linear medium density polyethylene (LMDPE)	0.926-0.940
Medium density polyethylene (MDPE)	0.926-0.940
Linear low density polyethylene (LLDPE)	0.919-0.925
Low density polyethylene (LDPE)	0.910-0.925

Moreover, SPI and ASTM systems are used density to classify polyethylene. It also has others systems to divide polyethylene types such as based on molecular weight or commoner employed available in the industry. An overview of the classifications of polyethylene that widely used in industry is reviewed below:

2.1.1. Low-density polyethylene (LDPE)

Low-density polyethylene (LDPE) is produced under high temperature and pressure. Its density range can be defined in 0.910-0.940 g/cm^3. LDPE highly consists of short and long chain branching. For this reason, the chains of LDPE are not press closely. Thus its structure is amorphous. The important properties of LDPE are lightweight, good impact resistance, extremely flexible, easily cleaned, thermoforming performance, no moisture absorption, chemical- and corrosion-resistant. From the properties of LDPE, it can be produced in many products such as corrosion-resistant work surfaces, plastic wrap, various containers, and parts of computer hard.

2.1.2 High-density polyethylene (HDPE)

Products which are produced from the polymerization at low temperature under low pressure are called High-density polyethylene (HDPE). HDPE cannot be produced by free radical polymerization. The structure of high-density polyethylene types consists of dense short branches, giving its stronger intermolecular forces, tensile strength and more linear than LDPE, but less flexible than LDPE. Nevertheless, due to the high crystalline structure, HDPE cannot match the clarity of LDPE or LLDPE film. The applications of HDPE are bottles for bleach, shampoo, detergent, extruded pipe for potable water and gas distribution, etc.

2.1.3 Linear low-density polyethylene (LLDPE)

LLDPE is polyethylene which was produced from 1-butene, 1-hexene, and 1-octene as comonomers. Therefore, LLDPE consists of short chain branches of ethyl, n-butyl, and n-hexyl groups. Density if this polymer is shown in 0.915-0.930 g/cm^3. LLDPE has developed and improve properties. They are employed as a film in the packaging industry. Nevertheless, the produced film from LLDPE is not as clear as from LDPE because of the lower amorphous content and heterogeneous composition distribution.

2.2 An Overview of Industrial Polyethylene Processes [13]

There are 4 main processes technologies that are widely applied to produce polyethylene are: solution, slurry, gas-phase and high pressure process. The applied conditions for polymerization process are wide. During this reaction occurs, heat of polymerization reaction is quite high. Hence, heat removal from process is very important. Process which is used in this reaction has to match catalyst properties such as kinetic profile.

2.2.1 Solution process

Solution process is homogeneous system and applied catalysts in this system are also homogeneous catalysts. The operated temperature in this reaction must be higher than melting polyethylene temperature. For these processes, polyethylene product occurs under 500-5000 psi at 160-220 °C. Under these conditions, cyclohexane or C_8 aliphatic hydrocarbon is used as solvent to dissolve the polymer. However, this process is highly cost because used solvent have to remove impurity to recover in this system again.

Features:
- Polymerization occurs in the liquid phase because of high temperature and pressure.
- Residence time using catalyst is short.
- Catalyst and catalyst which are employed in this system must be stability at high temperature.
- Morphology of the catalyst is not an important factor.
- Wide range of comonomers might be applied.

2.2.2 Slurry (Suspension) process

In the beginning, Phillips Petroleum has developed the slurry process to produce HDPE and LLDPE. That system is in slurry system. Moreover, this system is also operated in loop reactor. Thus, original name of this process has been called the "particle form loop slurry process" and the "slurry loop reactor process". This process generally operates in slurry system under pressures of 200-500 psig at temperatures from about 80 to 110 °C. Polyethylene product is precipitated at the process temperature. In slurry system, catalysts are usually utilized metallocene or Ziegler-Natta catalysts and they are suspended an inert suspension medium. Solvent in this system cannot react with catalysts. Mostly, saturated hydrocarbons such as propane, iso-butane and hexane are applied as solvent.

Selection of used catalyst in this process has to concern about leaching. Leaching is the main cause of reactor fouling that is also the main factor reducing the operability.

Features: - During the polymerization, polymer is produced as suspension in hydrocarbon solvent.
- In the slurry loop, residence time of catalyst is about 1 hour.
- Morphology of catalyst is considered factor significantly.
- Wide range of comonomers might be used.

2.2.3 Gas-phase process

Fluidized bed reactor is employed to perform gas phase ethylene polymerizations at 80-110 °C under pressure 200-500 psig. The gas phase technique does not require solvent. Moreover, energy consumption is also lower than other techniques. The polymer morphology obtains from this process is excellent. For high yield, polymerization condition in gas phase has to be closely the dew point of the monomer mixture.

Features: - Polyethylene occurs in fluidized beds.
- Residence time of catalyst in the reactor is 2-4 hours.
- Morphology of catalyst is seriously considered.
- Owing to appearance of "condensed", a wide range of comonomers might be applied.

2.2.4. High-pressure process

There are 2 reactors for using in high pressure process: autoclave and tubular reactor. The requested condition in this process is the most dangerous, applying at over 200 °C and under 15,000 to 45,000 psi. This process does not have solvent. Under severe conditions, the reaction occurs in phase with excess monomers. Both of autoclave and tubular process are nearly similar. These processes have pre-reactor to increase temperature and pressure. After the reactor, the post-reactor is also necessary for reducing temperature and pressure to ambient conditions, and then the product will be separated in the next step. Significantly, to prevent explosion, the relieve pressure system has to be designed to reduce the pressure of this system rapidly.

2.2.4.1 High-pressure autoclave process

The autoclave reactor is original reactor using in high-pressure process. Reactor residence times are very short. Heat of this process is removed by excess ethylene. High-pressure autoclave process is not required purification of ethylene monomer.

Features:
- CSTR with agitators are utilized.
- Multiple reactor zones characteristically applied.
- Polymerization occurs in liquid phase.
- Organic peroxides worked as initiators.
- Polymer has fewer branches but longer length than high-pressure process using tubular.

2.2.4.2 High-pressure tubular process

The tube reactor which is used in this process is 1000-2000 m long with an internal diameter of 25-50 mm (0.1-0.2 in). Under high pressure condition, the polyethylene which obtains from tubular reactor is not only greater molecular weight but also longer chain length than polyethylene from autoclave reactor.

Features:
- Polymerization happens in liquid phase.
- Tube is 1000-2000 m long with internal diameter of 25-50 mm (0.1-0.2 in.).
- Organic peroxides characteristically utilized as initiators.
- Generally, chain-length of polymer usually longer than product which has been produced from autoclave process, but with relatively short branches.

2.3 Background on polyolefin catalyst

Formerly, the polymerization of α-olefins can be used catalyst such as the Ziegler-Natta or Phillips catalyst systems. In the present, polyolefin catalyst pays attention to single-site catalysts mentioned to as metallocenes. The single-site characteristic of metallocenes can be improved polymer properties; control the degree of α-olefins insertion upon their stereochemistry and show higher activity than using by conventional Ziegler-Natta catalyst [14].

Ziegler-Natta catalyst systems, such as composition of $TiCl_4$ and $Al(C_2H_5)_3$, creating $TiCl_3$, were first used in 1953 for the polymerization of α-olefins [15]. Ziegler and Natta shared the Nobel Prize in 1963 for this innovation. These systems generate linear polyethylene under mild polymerization conditions, including isotactic polypropylene. Originally, the polyethylene had been produced in slurry process using $TiCl_3$ catalyst. Later, in order to increase activity, the $TiCl_3$ catalyst was replaced by $MgCl_2$-supported Ziegler-Natta catalysts in gas phase process polypropylene and polyethylene production. The appropriateness of $MgCl_2$ as support material for Ziegler-Natta catalysts is owing to a number of factors, one of which is the similarity in ionic radius between Mg^{2+} and Ti^{4+}. These catalysts are complex systems, which consist of different active species and produce polymers having relatively broad molecular weight distributions. Nevertheless, the molecular structure of the polymers cannot be controlled well for conventional Ziegler-Natta catalysts by reason of these catalysts are heterogeneous with different types of catalytic sites.

In 1957, Natta and Breslow [16] had concerned and recovered the homogeneous catalyst system (Bis(cyclopentadienyl)titanium(IV)dichloride-(titanocene)-alkyl-aluminum) which can generate similar polymerization centers. Initially, this catalyst system was not interesting because of low activity (130 g PE/g Ti). Afterwards, the first method which was discovered to increase the activity is adding of small amounts of water into the $Cp_2TiEtCl/AlEtCl_2$ catalyst system. Sinn and Kaminsky [17] succeeded to increase ethylene polymerization catalyst activity to 500,000 g PE/g Ti in a system using Cp_2TiMe_2 as catalyst precursor, in combination with TMA mixing water which are the key to produce [-O-Al(CH_3)-]n, methylaluminoxane (MAO).

2.3.1 Metallocene catalyst

Fischer [18] and Wilkinson [19] discovered Ferrocene **(Figure 2.2)**. Ferrocene can be regarded as a positively charged metal ion, sandwiched between two cyclopentadienyl anions through π-bonding.

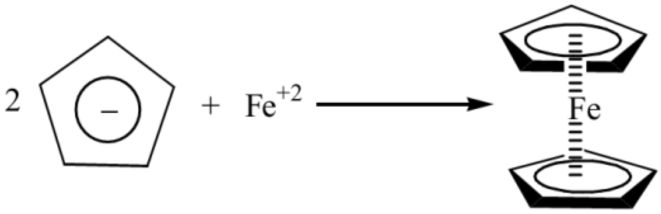


Figure 2.2 Ferrocene, the first metallocene to be synthesized [18]

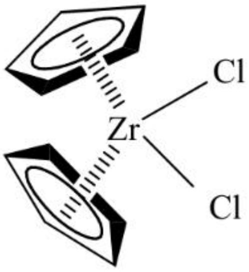


Figure 2.3 Zirconocene dichloride (inactive metallocene catalyst) [18]

Subsequently, the discovery of metallocenes in which higher charged metal ions for example zirconium (+4) would bond with two chlorine atoms to obtain a stable system **(Figure 2.3)** by Wilkinson [19]. These complexes characteristically consist of a Group IV metal that is encapsulated by two ligands. The active center is thus largely shielded against the influence of the immediate surroundings of the catalyst complex. The ligands can be either bridged or contain substituent and this gives further control over the characteristics of the resulting polymers in an olefin polymerization setup in the presence of a suitable cocatalyst.

The single site metallocene catalysts present many advantages with respect to the conventional Ziegler–Natta catalysts such as as narrow molar mass distribution ($M_w/M_n \approx 2$), control of molar mass of end groups, of stereo- and regioregularities, of comonomer incorporation, and of low residual metal content, just to mention a few. The growth of metallocene-catalyst polymerization and correlation between metallocene structure and polymer properties has been continuously reviewed in the literature [20].

2.3.2 Metallocene catalyst structure [21]

Metallocene catalysts are composed of two cyclic ligands bonded to a central transition metal atom, these compounds have been named “sandwich complexes”. The simplest structure of metallocene shows in **Figure 2.4**

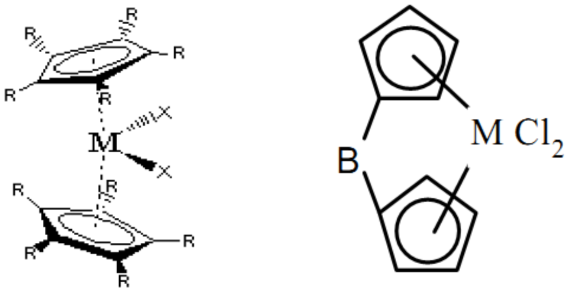


Figure 2.4 The simplest structure of metallocene [21]

When

	is Cyclopentadienyl, Indenyl, Fluorenyl (Substituted & Unsbstituted)
M	is group 4, 5, 6 transition metal (normally Ti, Zr, and Hf).
R	is alkyl group or hydrogen atom
X	is halogen atom or methyl group

B is bridge

Metallocene is a class of compounds in which cyclopentadienyl or substituted cyclopentadienyl ligands are π-bonded to the metal atom. The stereochemistry of biscyclopentadienyl (or substituted cyclopentadienyl)-metal bis (unibidentate ligand) complexes can be simply described as distorted tetrahedral, with each η^5-L group (L = ligand) occupying a single coordination position. The obtained polymer properties from polymerization using metallocene catalyst depend on metallocene characteristic such as ligand bridging, cyclic ligands, ligand substitution, transition metal type, and cocatalyst. **Table 2.2** shows the activity and molar mass of ethylene and propane when difference metallocene catalysts are applied under similar condition.

From **Table 2.2**, it clearly shows factor which affects to activity and molar mass of polymer. Thus, the each factor makes metallocene catalyst is differences that will be explained in the next part.

2.3.2.1 Ligands

Generally, cyclic has mostly been ligands of metallocene such as cyclopentadienyl (Cp), indeyl (Ind), and fluorenyl (Flu). Metallocene catalysts may consist of 1 or 2 cyclic. In addition, the ligands that are in metallocene catalysts may be different types **(Figure 2.5).** The cyclic ligands have established π-bond with metal which is center atom. According to **Table 2.2**, different ligands in metallocene structure have not only affected to polymer properties, for example, molar mass, structure, but activities of catalyst are also dissimilar.

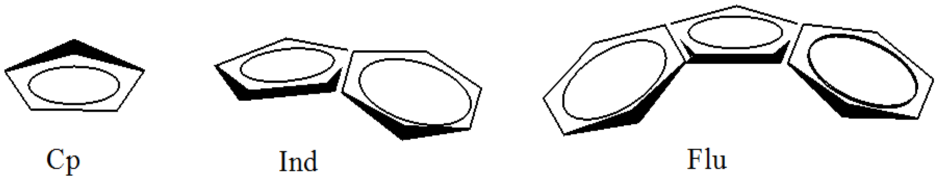


Figure 2.5 The simplest structure of cyclopentadienyl (Cp), indeyl (Ind) and fluorenyl (Flu) [21]

Table 2.2 Homopolymerization of ethene and propene at 30 °C, 2.5 bar monomer pressure, [metallocene] = 6.25×10^{-6} mol l^{-1}, and MAO/metallocene ratio = 250/1 [21]

sample	Catalyst	Ethene		Propene		
		Activity	Molar mass (10^3 g mol^{-1})	Activity	Molar mass (10^3 g mol^{-1})	Isotacticity (%)
1	Cp_2ZrCl_2	60900	620	140	2	7
2	$(C_5Me_4Et)_2ZrCl_2$	12200	1000	170	3	59
3	$(Me_4\ EtC_p)_2\ ZrCl_2$	18800	800	290	0.2	7
4	$[O(SiMe_2\ Cp)_2\ ]ZrCl_2$	57800	930	230	0.3	24
5	rac-$[En(Ind)_2\ ]ZrCl_2$	41100	140	1690	323	95
6	rac-$[En(Ind)_2\ ]HfCl_2$	29000	480	610	446	94
7	rac-$[En(IndH_4\ )_2\ ]ZrCl_2$	22200	1000	1220	24	98
8	rac-$[En(2,4,7\text{-}Me3Ind)_2\ ]ZrCl_2$	78000	190	750	418	>99
9	rac-$[Me_2\ Si(Ind)_2\ ]ZrCl_2$	36900	260	1940	79	97
10	rac-$[Me_2\ Si(IndH_4\ )_2\ ]ZrCl_2$	30200	900	7700	44	95
11	rac-$[Me_2\ Si(2,4,7\text{-}Me_3Ind)_2\ ]ZrCl_2$	111900	250	3800	192	94
12	rac-$[Me_2\ Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2\ ]ZrCl_2$	16600	730	5000	650	99
13	rac-$[Me_2\ Si(2\text{-}Me\text{-}4,5\text{-}BzoInd)_2\ ]ZrCl_2$	7600	450	6100	380	98
14	$[Me_2\ C(Ind)(Cp)]ZrCl_2$	1550	25	180	3	49
15	$[Me_2\ C(Flu)(Cp)]ZrCl_2$	2000	500	1550	159	0.6
16	$[Me_2\ C(Flu)(Cp)]HfCl_2$	890	560	130	750	0.7
17	$[Ph_2\ C(Flu)(Cp)]ZrCl_2$	2890	630	1980	729	0.4

2.3.2.2 Ligand substitution

Effect of ligand substitution to polymer properties and metallocene activity is as important as ligand type. Ligand substitution can be hydrogen atom and alkyl group. Refer to sample 15 ([$Me_2C(Flu)(Cp)]ZrCl_2$) comparing with sample 17 ([$Ph_2C(Flu)(Cp)]ZrCl_2$) in table 2.2, both of molar mass and catalyst activity under similar condition are different because of unlike ligand substitution. Beside **Table 2.2**, many researches also confirm ligand substitution effect to properties and structure of polymers and catalyst activity. Griselda *et al.* [22] had investigated ethylene/1- hexane copolymerization using silica supported $(R)ZrCl_2$ catalyst which varied ligands and substitute ligand. Influence of ligands on the cyclopentadienyl ring had been explained: when using n-Bu as ligand substitute, the Zr was immobilized less than using Me.

2.3.2.3 Ligand bridging

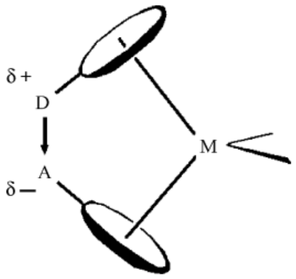


Figure 2.6 Donor/acceptor ansa -metallocene complexes [23]

Refer to **Figure 2.6**, the metallocene structure may has bridge between two ligands. Many researchers have concerned effects of ring-bridged cyclopentadienyl and indenyl to activity and the stereoselectivity of olefin polymerization reactions. The metallocene which has bridge in a structure can be called “ansa-metallocene catalysts”. Bridge of ligand protect center atom moving around itself. If the metallocene is without bridge, for example $(Ind)_2MX_2$ catalyst, the unbridged $(Ind)_2MX_2$ catalyst can rotate around the metal-Cp bond. Thus, it can the racemic structure can change into meso structure. The products from racemic structure are not as same as meso structure, for example, racemic $(C_2H_4)(IndH_4)_2MCl_2$ (M = Ti, Zr, Hf) is used for producing highly isotactic PP. Moreover, many work still pay attention to effect of different ligands, bridging groups and transition metal centers [24-25]. Kaminsky *et al.* discovered bridged cyclopentadienyl- or indenyl- ligands can increase monomer incorporation in copolymerization systems.

2.3.2.4 Transition metal type

Transition metal type is always plenty of Group 4. Industrially, Ti, Zr and Hf have been applied. For clearly, sample 5 and 6 in **Table 2.2** using Zr and Hf as center metal under similar condition demonstrates that both of activity and molar mass are difference each other. Using difference metal site in sample 15 and 16 also confirms the result as same as previous.

2.3.2.5 Cocatalyst

Originally, metallocene catalyst had been found, but it had not been applied in polymerization process widely because of low activity. After that discovering, the research was found cocatalyst (MAO), which was used to increase metallocene catalyst activity. That is the first point to be interested in metallocene catalyst again. Nowadays, many researchers still pay attention to cocatalyst because it is the key of polymerization process. Thus, cocatalyst will be discussed next main topic.

2.3.3. Cocatalyst

A main to the high polymerization activity of metallocenes is the cocatalysts. The most cocatalysts pay attention to the methytaluminoxane (MAO), this is generally used and is synthesized by controlled hydrolysis of trimethylaluminium [26]. Other bulky anionic complexes which show a weak coordination, such as tetra(perfluorophenyl)borate anions $[(C_6F_5)_4B]^-$ and $B(C_6F_5)_3$, act an increasing role too [27]. Methylaluminoxane comprises of aluminum and oxygen atoms, which both of them arranged alternately and free valences are saturated by methyl substituents. The basic structure of methylaluminoxane is shown in **Figure 2.7.**

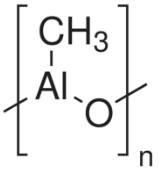
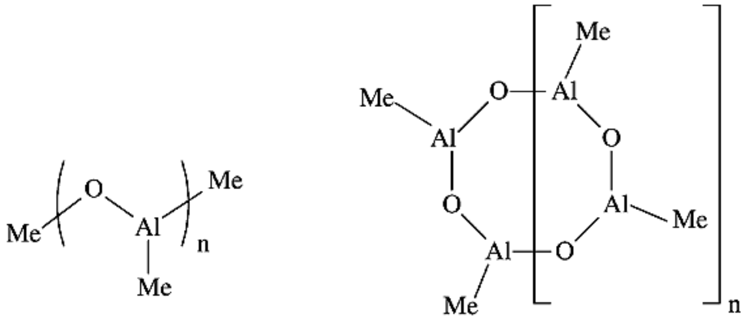


Figure 2.7 The simple structure of methylaluminoxane (MAO) [28]

The structure of MAO is complex and has been investigated by cryoscopic measurements, hydrolysis reactions, IR-, UV-, mass, and NMR-spectroscopic measurements and other methods [28-29]. There are different equilibria between the oligomers. The molecular weight determined cryoscopically in benzene lies between 1000 and 1500 g/mol [30].

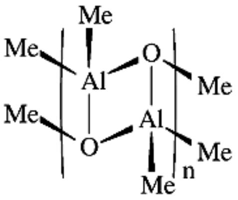
In fact, the difficulties undergone to better understand the important factors for an efficient activation are mainly due to the poor knowledge of the MAO composition and structure. Many types of macromolecular alignment, involving linear chain, monocycles, and/or various three-dimensional structures have been successively postulated. These are shown in **Figure 2.8.**

Barron and Sinn [31] investigated structure of methylaluminoxane or tert-butylaluminoxane have become known. Among the different oligomers, $(CH_3)_2A1\text{-}O\text{-}Al(CH_3)\text{-}OAl(CH_3)_2$ units are significant. These units can associate resulting in coordination of the unsaturated aluminum atoms. There are tri- and tetra-coordinated aluminium atoms, of which the trivalent show extreme Lewis acidity. Four of the $A1_4O_3(CH_3)_6$ units can form a cage structure resembling a half open dodecaeder ($Al_{16}O_{12}(CH_3)_{24}$).



chain

ring



double chain "ladder"

Figure 2.8 Early structure models for MAO [32]

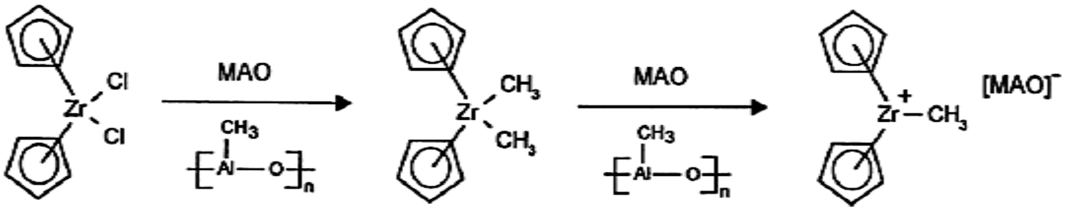


Figure 2.9 Activation of Cp_2ZrCl_2 [33]

MAO is a function to activate metallocene catalyst, for example, the activated form of bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) is shown in **Figure 2.9.** First step, dichloride(halogen group) is substituted by methyl group from MAO to give the species $Cp_2ZrMeCl$ and Cp_2ZrMe_2. Next step, MAO then plays role as a Lewis acid taking one of the methyl groups from the Zr to give. The formation of Cp_2ZrMe_2 and MAO changes into $[Cp_2ZrMe]^+$ cation and a weakly coordinating

[Me-MAO]$^-$, respectively. The last form of Cp_2ZrCl_2 becomes $[Cp_2ZrMe]^+$ as active center using in polymerization process [33].

Cam and Giannini [34] investigated the role of TMA present in MAO by a direct analysis of Cp_2ZrCl_2/MAO solution in toluene-d_8 using ^{1}H-NMR. The important roles of MAO are 1) stabilizing the cationic center by ion-pair interaction, 2) alkylation of metallocene, thus forming catalyst active species, 3) scavenging impurities in the monomer or solvent, and 4) preventing bimetallic deactivation of the active species.

2.3.4 Polymerization mechanism

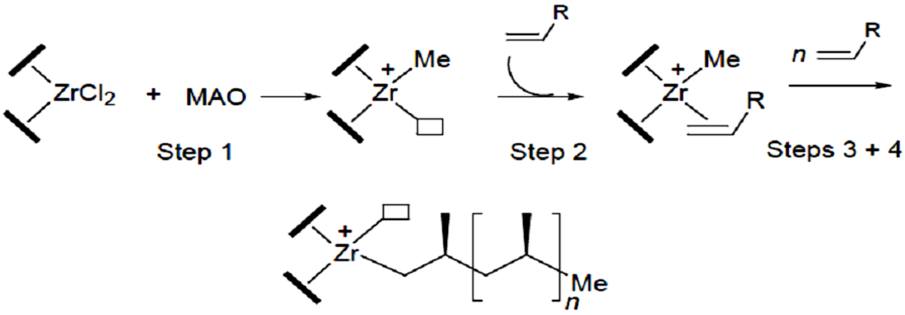


Figure 2.10 Initiation and propagation mechanism of the polymerization of olefins using zirconocenes catalyst [13]

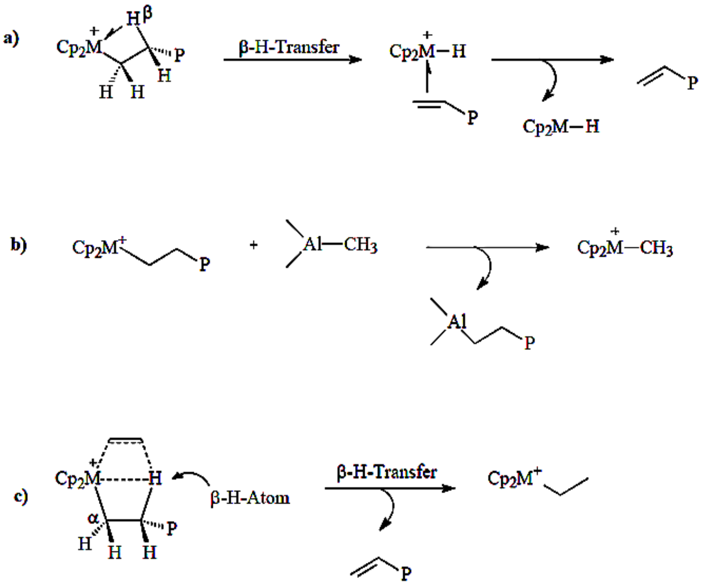


Figure 2.11 Termination mechanism of the polymerization a) β-H elimination, b) chain transfer to the cocatalyst, c) hydrogen transfer to the monomer [35]

Mechanism and kinetics of reaction is one of factor to control polymer product properties. Both of propagation and termination rates influence in molar mass distribution. Besides polymerization system, comonomer content and distribution can also resolve in copolymerization system. Kinetic of reaction depends on catalyst properties. In addition, the cocatalyst is the key which affect to general mechanism [33].

Normally, mechanism of polymerization with single site catalysts consists of 3 steps; initiation, propagation and termination.

Initiation: cocatalyst (MAO) creates metallocene catalyst into the active form. The active site generation is shown in **Figure 2.10.**

Propagation: monomer is added and repeated. Refer to **Figure 2.10**, the chain of polymer was connected by free radical and gone on.

Termination: there are 3 modes for termination step; firstly, chain transfer by β-elimination with hydride transfer to transition metal. Secondly, chain transfer to the cocatalyst. The last mode is chain transfer to hydrogen (hydrogenolysis). All modes of termination step demonstrate in **Figure 2.11.**

2.4 Heterogeneous system

2.4.1 Basic background of heterogeneous system

Normally, the polymerization using metallocene catalysts can be divided into 2 systems; homogeneous and heterogeneous system. Homogeneous system is higher cost than heterogeneous catalyst by reason of amount of MAO cocatalyst. In homogeneous catalyst, the ratio of metallocene/MAO using in the system is 1/1000 or higher, but metallocene/MAO in some heterogeneous case is as low as 1/40. One more disadvantage of homogeneous catalyst is morphology of product cannot be control as same as supported catalyst because when the products occurred, it will be cover support. Thus, morphology of polymer product depends on support structure. Nonetheless, homogeneous system activity is better than heterogeneous [9, 36].

By the reason of previous, it can conclude that many researchers have realized to develop heterogeneous system in order to increase performance (activity, stereochemical control, ability to produce co-polymers with statistical comonomer distribution, etc.) as well as homogeneous system, reduce amount cocatalyst using in the system through prevent reactor-fouling problems [37]. Moreover, the main cause which pays attention in supported catalyst is heterogeneous catalyst can apply in slurry and gas polymerization process but homogeneous cannot perform.

Kaminsky and Renner [9] had studied supported metallocene comparing with homogeneous system in PE polymerization under similar condition. When the system use silica supported $Et[Ind]_2ZrCl_2$, molecular weight of PE was higher than homogeneous system. Because zirconocene immobilization on silica prevents deactivation by bimolecular processes, molecular weights of PE increase.

Soga *et al.* [38] had improved polymerization activity using $Cl_2Si(CH_3)_2/NaHCO_3$ modified silica gel supported Cp_2ZrCl_2. Polymerization activity increased 2-3 times

Ihm *et al.* [39] had concerned many parameters as follow: active center type (Cp_2ZrCl_2, Cp_2TiCl_2, and Cp_2HfCl_2), pretreated support substances (MAO, $AlEt_3$, or $(C_2H_5)MgCl$). The catalyst was activated by MAO or a common alkylaluminum as cocatalysts. The highest activity occurred when MAO modified SiO_2 supported Cp_2ZrCl_2 was employed in the reaction. In addition, interaction between titanocene and aluminum species (MAO and $AlEt_3$) influenced molecular weight distribution of polymer.

Sacchi *et al.* [40] had also considered as same as Ihm *et al.* (1994). High activity also got from modified SiO_2/MAO-supported (Indirect method). However, activity still is not as high as homogeneous system. Nevertheless, the polyethylene molecular weight obtained with these systems remains low and nearly identical to those produced by homogeneous metallocenes. On the contrary, directly impregnated SiO2-supported systems present low activity but yield to polymers with higher molecular weights.

Satyanarayana and Sivaram [41] have prepared $MgCl_2$-supported Cp_2TiCl_2 catalysts exhibiting significant activity for ethylene polymerization after activation by $Al(i\text{-}Bu)_3$. Those supported catalysts show steady-state kinetics with no loss of activity up to 1 h, when operating at low Al/Ti ratios (<100). It was suggested that the $MgCl_2$ support provides active centers of higher stability. Much higher activity (74-141 kg of PE/(mol of Ti h)) are obtained by using $Cp_2TiCl_2/MgCl_2$ activated by MAO (Sarma *et al.* [42], Reddy and Sivaram [43]), at relatively low Al/Ti. No loss of catalyst activity is observed upon heterogenization. Unlike the soluble systems, the heterogeneous Cp_2TiCl_2 catalyst does not show any loss of activity when increasing the temperature in the 40-70 °C range.

So far, various supports have been applied in the heterogeneous system. Inorganic supports such as silica, alumina, and HY zeolite mostly have been mostly employed in polymerization process. Nonetheless, a few works used organic substances as support such as cyclodextrin or polystyrene. Lee and Yoon [9] had applied Cp_2ZrCl_2 supported on cyclodextrin (CD) and on MAO-modified CD in ethylene polymerization. This research employed TMA as cocatalyst. The molecular weight of PE earned from cyclodextrin supported catalyst is greater than with nonsupported metallocenes (30 times), and the MWD present a low polydispersity index (2.3-2.5).

Polymer-supported metallocene catalysts were recently prepared by Nishida *et al.* [44] using awell-defined polystyrene as the carrier. Preliminary results dealing with ethylene polymerization show interesting activities for these catalysts as well as good polymer morphology. Most of the research work performed in academic and industrial laboratories is focused on supporting zirconocene, titanocene, and hafnocene catalysts, and very little attention has been paid to supporting lanthanocenes. Recently, Jin *et al.* [45] described efficient catalysts for ethylene polymerization based on SiO_2-supported neodymocenes associated with suitable cocatalysts [alkylaluminum, MAO, buthyllithium (BuLi), or ethylbutylmagnesium (BuMgEt)]. BuMgEt and Al-(i-C_4H_9)$_3$ cocatalysts gave respectively the highest activity and the highest molecular weight polyethylene. The lifetimes of these supported lanthanocene catalysts are markedly improved over that of homogeneous organolanthanide catalysts.

Before developing heterogeneous catalyst, the factors affect on heterogeneous should be concerned. Basic contents of heterogeneous olefin polymerization catalyst system are; support, catalyst precursor, and cocatalyst which is agent to activate the catalyst. The interesting factor of supported catalyst performance includes; dispersion of catalyst precursor, properties of pretreated support, interaction between catalyst precursor and the support, ability of agglomeration of the catalyst precursor, impurities and poisoning of catalyst [46].

2.4.2 Supporting methods

In the case of other inorganic compounds with OH group on the surface, the resulting catalyst displayed very poor activities even combined with MAO. The reaction of metallocene complexes with the –OH groups might causes the decomposition of active species. Thus decomposition could be suppressed by fixing MAO on the support surface and then reacting with metallocenes [47]. Therefore, the support must be pre-treated before the interaction with metallocene in order to reduce the OH concentration and prepare an adequate surface for metallocene adsorption and reaction in a non-deactivating way [48]. Performance of polymerization using supported catalyst system depends on catalyst preparation method and polymerization conditions. There are 3 main methodologies to produce immobilization of metallocene complexes as follows [49].

Method 1 Indirect method: MAO is impregnated on support. For this method, the support is firstly pretreated by a little amount of MAO dissolved in a solvent, for example, toluene under mild condition. Then, the supported MAO will be filtrated and washed by toluene for exceeding MAO removal. This can store for a period of time. It depends on support type. Before using in reaction, the supported MAO will be mixed with metallocane catalyst and MAO goes on to activate metallocene. Indirect method is the most similar homogeneous system. The low molecular weight of polymer is obtains from this method. For propylene polymerization, Xu *et al.* [50] discovered the syndiotacticity form notices when the metallocene catalyst supported on cocatalyst pretreated silica. In addition, Harrison *et al.* [51] also studied effect of OH group of varied support (alumina and silica). These work found amount of MAO impregnation depended on concentration of OH group so metallocene content could be increased with increasing amount of OH group.

Method 2 Direct supporting of inserted materials: The key of this method is metallocene catalyst was impregnated on dry supports which may be pretreated or not before. This method is as like as first method but just few steps are different. Firstly, the metalocene catalyst is soluble in solvent such as toluene before reacts with support. When it finishes, the supported metallocene catalyst is filtrated and washed by hydrocarbon solvent. This method can be prepared under either mild condition or high temperature for a long contact time. For mixing step, both of temperature and contact time are an important influence. Immobilized metallocene complex is prepared by direct heterogeneous technique have generated higher molar mass than homogeneous catalyst [52]. This strategy single active sites out from each other. Thus, bimolecular deactivation process is inhibited. Amount of MAO using in this reaction is also less than homogenous system.

Method 3 Covalent bonding on the support: The steps in this method are different from previous method (method 1 and 2). A prominent point of this method, ligand of metalocene catalyst chemically bonded with support. First step, the ligands such as cyclopentadienyl is added into the support. The support and cyclopentadienyl will link each other. The next step, metal compound such as zirconium chloride is added into the system. Currently, titanium and neodymium halide is also used to produce the attached metallocene. This method uses low Al/Me ratios to produced high active catalytic centers. This method creates different active species [53].

The mechanism of each methodology which produces metallocene catalyst over support is shown in **Figure 2.12.**

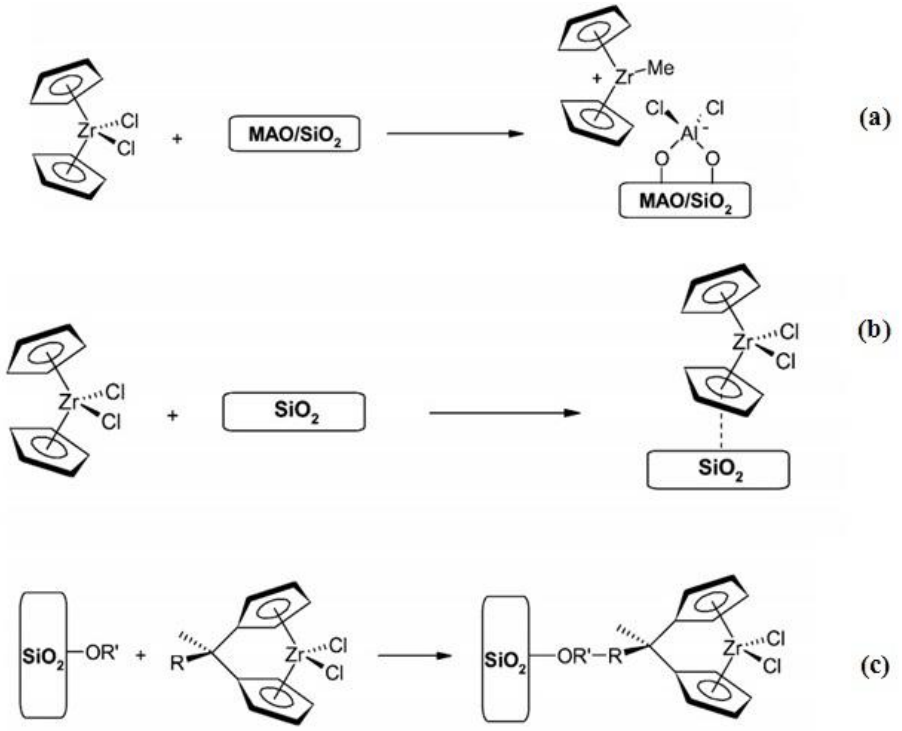


Figure 2.12 Mechanism of each method for producing supported metallocene catalyst: (a) indirect method, (b) direct method (c) Covalent bonding on the support [49]

2.4.3 Effect of Lewis acids modified supports

The disadvantage of heterogeneous system is lower activity than homogenous system because of the formation of inactive species between catalyst and support. Furthermore, formation of different active species, deactivation of catalyst during supporting procedure and mass transfer resistance may contribute to decreased catalyst activity [54]. Therefore, some modifications of supports, namely thermal and chemical treatments, are normally required to generate highly active heterogeneous.

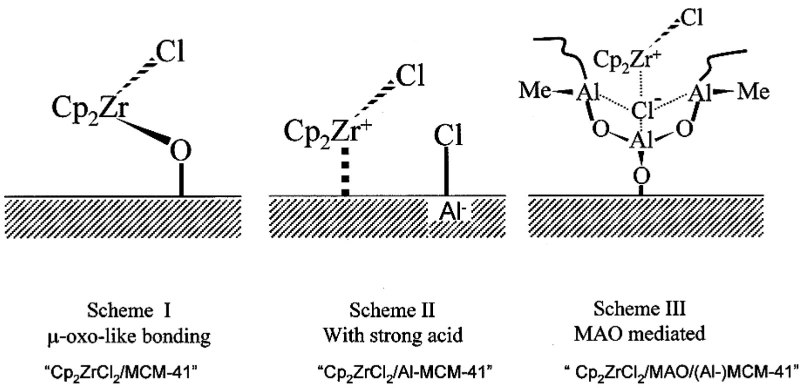
Mostly, the modifications are performed in order to reduce hydroxyl group on the surface, provide the surface with uniform species and change the electronic properties of the support.

Some workers have paid attention to role of surface acidity properties of supports influencing polymerization activity [55-56]. Mostly, in order to modify Lewis acid, Al and Ga have been added into the system. The nature of the element and its content (Si/element atomic ratio) will be considered the acid site distribution (i.e. the concentration and strength of Lewis and Bronsted sites).

Rahiala *et al.* [57] have pointed out the determinant an effect of the structure and surface properties of Al-modified MCM-41 (Si/Al=32) material on metallocene (zirconocene chloride) adsorption and catalyst activity in ethylene polymerization. This research has shown that the additional aluminium incorporated into the MCM-41 support (Si/Al=32) has a big effect on catalyst activity. Clearly higher activity was observed as compared to the purely siliceous MCM-41 supported catalyst.

Miyazaki *et al.* [58] had studied effect of Lewis acid sites to propylene polymerizations by adding various metals-containing MCM-41 (GaMCM-41, ZnMCM-41, AIMCM-41, and TiMCM-41) using rac-ethylene(bisindenyl)zirconium dichloride (rac-Et(Ind)2ZrCl2) and triisobutylaluminum as catalyst and cocatalyst, respectively. It found that order of polymerization activity was as follows: GaMCM-41>ZnMCM-41>AIMCM-41>> TiMCM-41. The relation between polymer yield and Lewis acid strength had been noticed. The only strong Lewis acid sites can activate the metallocene compound effectively.

K.-S. Lee *et al.* [59] investigated three different zirconocene compounds were immobilized on Al-MCM-41, and their catalytic characteristics in ethylene polymerization and compared with those of homogeneous zirconocene catalysts. The effect of Lewis acid site on the catalytic activity in ethylene polymerization was correlated with proper surface species models of metallocene on the Al-MCM-41. A study was encountered the activities of zirconocene catalysts directly supported on Al-MCM-41(Cp_2ZrCl_2/Al-MCM-41) were higher than those over the zirconocene catalysts supported on MAO-treated (Cp_2ZrCl_2/MAO/Al-MCM-41). Conversely, the zirconocene catalyst supported directly on pure silicate MCM-41(Cp_2ZrCl_2/MCM-41) did not show any activity in ethylene polymerization. The difference in catalytic activities between MCM-41 and Al-MCM-41 must be due to the presence of Lewis acid sites in Al-MCM-41. The activities of zirconocene catalysts supported on Al-MCM-41 an increase of the amount of Lewis acid sites (accordingly, with Si/Al ratio decreasing). The difference in activities was explained by surface species models on the interaction between the metallocene and supports. K.-S. Lee *et al.* suggested surface species models of various Cp_2ZrCl supported on silica as following **Figure 2.13.**



Scheme I
μ-oxo-like bonding
"Cp_2ZrCl_2/MCM-41"

Scheme II
With strong acid
"Cp_2ZrCl_2/Al-MCM-41"

Scheme III
MAO mediated
" Cp_2ZrCl_2/MAO/(Al-)MCM-41"

Figure 2.13 Surface species models of various Cp_2ZrCl_2 supported on silica [59].

Campos *et al.* [60] had investigated Ga pretreated silicates supported metallocene compound prepared by direct synthesis for ethylene polymerization. Ga-MCM-41 improves supported catalyst performance. Immobilize ability of support on metallocene catalyst strongly enhance when MCM-41 was pretreated by only small amounts of Ga. Furthermore, interaction between zirconocene and the Lewis acid centers significantly which affected from the adding Ga played an important role in formation of active species. Appropriate ratio of Si/Ga can be obvious from the result in polymerization activity levels.

In addition, Campos *et al.* [60] had researched effect of concentration/strength of acid sites of Ga-MCM-41 and the catalytic performance of zirconocene dichloride for ethylene polymerization. They suggested the model shown in **Figure 2.14.**

That model indicated interactions between metallocene compound and various acidic silicate surface species. According to model, weak Bronsted acid sites do not enough to create cationic active species. Thus, polymerization activity is still low level. However, Lewis acid or strong Bronsted acid sites can produce active species. Adding Ga influences to increase acid strength. Hence, it could be concluded that active sites of catalysts increased with increasing of acid strength.

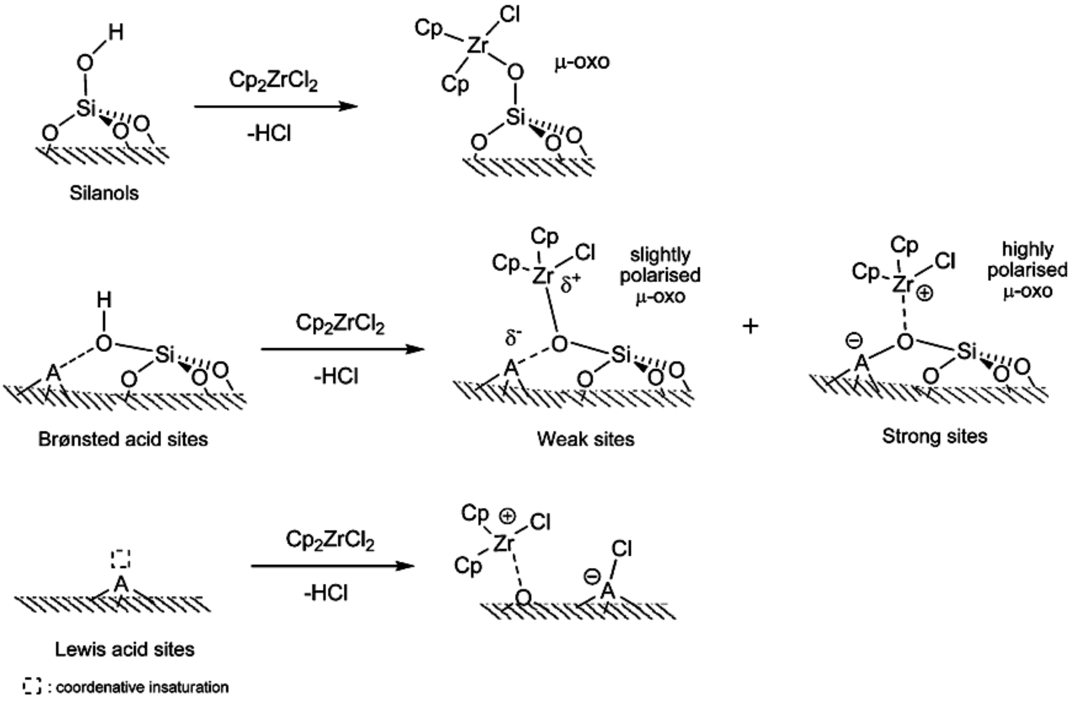


Figure 2.14 Models for the interactions of metallocene Cp_2ZrCl_2 with species present in acidic silicate surfaces (A: acidic element) [60]

Kaivalchatchawal *et al.* [11] studied the effects of B and Ga modifications of the silica support on the copolymerization behavior were investigated based on catalytic activity. It was found that the silica support modified with BCl_3 exhibited the highest activity. However, both B and Ga modifiers are capable of an enhancement the catalytic activity, probably attributed to stronger interaction between the MAO and support together with the acidic sites exerted by the modification which could assist MAO to activate the catalyst during polymerization. Besides, a role of B as a spacer to keep apart the catalyst on the silica surface was proposed as another probable reason for activity increased. This led to the more homogeneous-like behavior with less effect of support and also caused the higher comonomer incorporation content.

In Ziegler-Natta catalyst for polymerization, acid treatment influenced to increasing activity. Yenjitrattanawalee had confirmed the relation between Lewis acid and activity. Refer to adding the Lewis acid BCl_3 and TEA in chemical treatment of silica, the results shown that catalyst activity was improved by pre-chemical treated silica. Besides improved activity by Lewis acid, it also affect to physical properties.

2.4.4 Microcrystalline cellulose (Avicel PH 101)

A research had studied organic supported metallocene catalyst [61]. They were interested in organic as supported metallocene catalyst. Cellulose is organic so, it is obtained from wood, bacteria, and cotton. Moreover, cellulose was manufactured in many countries such as Finland, India, Ireland and Japan. Normally, cellulose (Avicel PH 101) consists of lignin, hemicelluloses sugars. The properties significantly are fine, white powder, porous, odorless, tasteless, and insoluble in water and organic solvent. Water-cellulose interaction affects to crystalline, and particle size correlated with flow properties.

In polymer industries, biopolymer (cellulose, fiber) is composite with polymers such as polyethylene, polypropylene, etc. because of its eco-friendly, decreasing waste plastics and renewable nature. Cellulose-polyethylene composite has developed to improve properties of cellulose composite such as tensile properties and compatibility between hydrophilic of cellulose and hydrophobic of thermoplastic materials [62-63]. Medicine fields widely employ avicel to merge the medicine content. In the research producing medicine pellet, avicel does not only increase the compression performance, but also remove humanity. Furthermore, avicel also reduces rate of medicine decomposition.

2.4.5 Coir dust

Coir is a lingo-cellulosic natural fiber. It is a seed-hair fiber obtained from the outer shell, or husk, of the coconut. It is not brittle as glass fiber, is amenable to chemical modification, is non-toxic and poses no waste disposal problems. It is resistant to abrasion and can be dyed. Total world coir dust production is 250,000 tonnes. Coir dust is derived from the fiber separation process from the fibrous mesocarp of the coconut. This process is carried out to separate the highest commercial value long fibers, from their counterparts, short and medium fibers, and the powder form (coir dust). The latter is the fraction of the lowest commercial value (80 US$/t) and it has been used basically as a growing medium for plants [64]. The coir fiber industry is particularly important in some areas of the developing world. Over 50% of the coir fiber produced annually throughout the world is consumed in the countries of origin, mainly India [65]. Because of its hard-wearing quality, durability and other advantages, it is used for making a wide variety of floor furnishing materials, yarn, rope etc. However, these traditional coir products consume only a small percentage of the potential total world production of coconut husk. Hence, research and development efforts have been underway to find new use areas for coir, including utilization of coir as reinforcement in polymer composites [66-68]. In addition, it shows an additional agro-industrial nonfood feedstock (agro-industrial and food industry waste) that should be considered as feedstock for the formulation of eco-compatible composite materials.

2.5 Copolymerization of ethylene/α-olefins

The copolymerization of ethylene with α-olefins has commercial significance in the polyolefin industry. It is used for the production of elastomers and linear low density polyethylenes (LLDPEs) materials. For the production of LLDPE, the polymer can be synthesized by the polymerization of ethylene and short chain 1-olefins, namely 1-hexene, 1-octene and 1-decene [69]. Beside Conventional Ziegler-Natta catalysts systems, metallocene and post-metallocene catalysts has also been widely used to produce LLDPEs. The comparison between Ziegler-Natta catalysts and metallocene catalysts produced LLDPEs, multi-sited Ziegler-Natta catalysts shows a broader molecular weight distribution (MWD) and a non-uniform comonomer distribution (the higher the molecular weight of polymer molecules and the lower the comonomer incorporation) [70-71]. Whereas, homogeneous metallocene catalysts possess mostly one type of active center, which is more accessible to higher α-olefins, and is able to produce polymer with narrower comonomer and MWDs, it is claimed that metallocene LLDPE presents better mechanical and worse processability performance when compared to Ziegler–Natta LLDPE [72].

Adding comonomer affects on the LLDPEs properties such as the average molecular weight of the macromolecules and its distribution, the degree of crystallization, the melting temperature and the amount and distribution of the monomeric units this can be called “comonomer effect” [73-74]. The “comonomer effect” has been widely studied using both conventional Ziegler-Natta and metallocene catalyst systems [14, 49]. Many reasons, both chemical and physical in nature, have been proposed to account for the ‘‘comonomer effect’’. This effect does not only influence to previous properties, it also factors to increase number of active centers and diffusion [75-76]. Previous studies present that an increase in the quantities of 1-olefin provides higher activity which relates to a physical phenomenon improving the monomer diffusion in the lower crystalline copolymer structure.

Besides the comonomer quantity, the length of the comonomer also affects the properties of LLDPE. Although short chain comonomers are commonly used in the process, making films formed from these materials more flexible and better processible, long chain comonomers can provide different LLDPE properties [61].

CHAPTER III

EXPERIMENTAL

In the current study, two types of support were investigated, composing of coir dust and cellulose as a support for zirconocene MAO catalyst in ethylene polymerization. The following topic was studied the copolymerization of ethylene/ 1-hexene with the acidic modification of cellulose supported zirconocene catalysts, the experiments were divided into five parts:

(i) Preparation of coir dust and cellulose
(ii) Preparation of the acidic modification of cellulose support
(iii) Preparation of catalyst
(iv) Ethylene polymerization
(v) Characterization of coir dust, cellulose, and obtained polymer

3.1 Material and chemicals

Table 3.1 Chemicals will be used in experiments

No.	Material and chemicals	Supplier	Purification
1	*rac*-ethylenebis (indenyl)zirconium dichloride (*rac*-Et[Ind]$_2$ZrCl$_2$)	Aldrich Chemical Company, Inc.	-
2	Methylaluminoxane (MAO)	Donated from PTT Public Co., Ltd., Thailand	-
3	1-Hexene (97% pure)	Aldrich Chemical Company, Inc.	Distillation
4	Toluene	EXXON Chemical Ltd., Thailand.	Distillation
5	Hydrochloric acid	Sigma	-

6	Methanol (Commercial grade)	SR lab	-
7	Sodium (99%)	Aldrich Chemical Company, Inc.	-
8	Benzophenone (99%)	Fluka Chemie A.G. Switzerland	-
9	Ultra high purity argon gas (99.999%)	Thai Industrial Gas Co., Ltd.	
10	Ethylene gas (99.9% pure)	*National Petrochemical Co., Ltd. Thailand.*	
11	Microcrystalline cellulose (Avicel PH 101)	-	-
12	Coir dust	Local area	
13	Ethanol 99.99%	*J.T. Baker*	-

3.2 Equipments

Generally, metallocene catalyst has to work without oxygen and moisture. Therefore, the glove box which is used equipment for producing inert atmosphere is applied in this work during preparation and polymerization process. Glove box is not only used, but Schlenk techniques (Vacuum and Purge with inert gas) are the other set of the equipment used to handle air-sensitive product.

3.2.1 Cooling system

The cooling system was in the solvent distillation for condense the newly evaporated solvent.

3.2.2 Inert gas supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3×10^{-10} m to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at 300 ^{o}C overnight before flowing the argon gas through all the above columns. The inert gas supply system is shown in **Figure 3.1**.

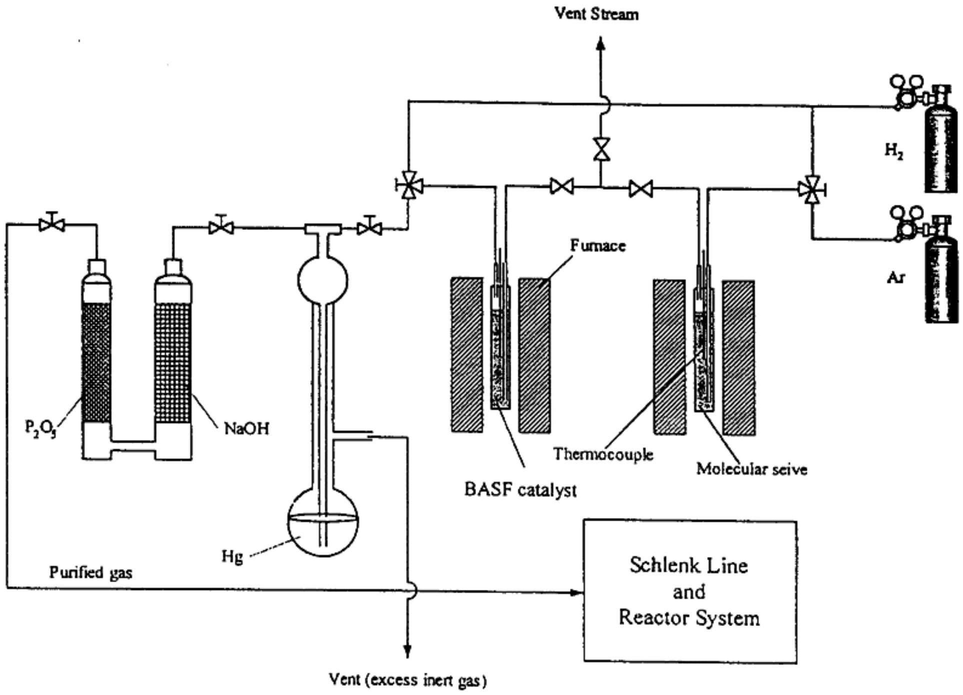


Figure 3.1 Inert gas supply system

3.2.3 Magnetic stirrer and heater

The magnetic stirrer and heater model RTC basis from IKA Labortechnik will be applied to mix the solution and control heat of reaction during polymerization.

3.3.4 Polymerization reactor

A 100 ml stainless steel autoclave will be employed as the copolymerization reactor.

3.2.5 Schlenk line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contains enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line is shown in **Figure 3.2.**

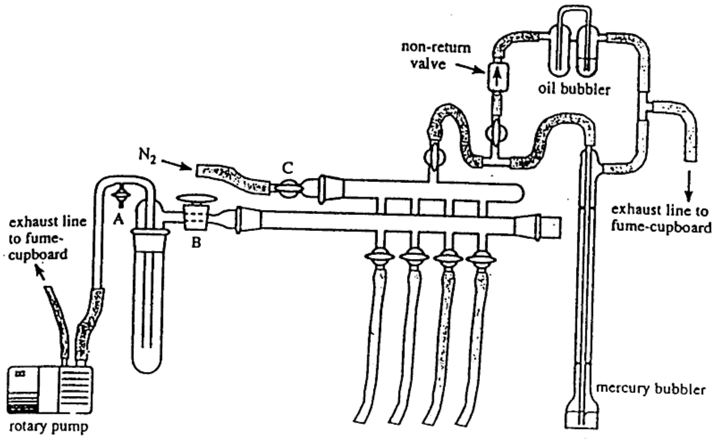


Figure 3.2 Schlenk line

3.2.6 Schlenk tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in **Figure 3.3**. Sizes of Schlenk tubes were 50, 100, and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture.

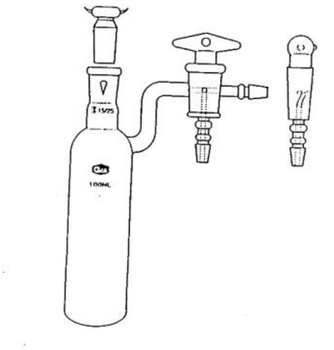


Figure 3.3 Schlenk tube

3.2.7. Vacuum pump

The vacuum pump model 195 from Labconco Corporation will be used to protect system from oxygen. A pressure of 10^{-1} to 10^{-3} mmHg will be enough for the vacuum supply to the vacuum line in the Schlenk line.

3.2.8 Polymerization line

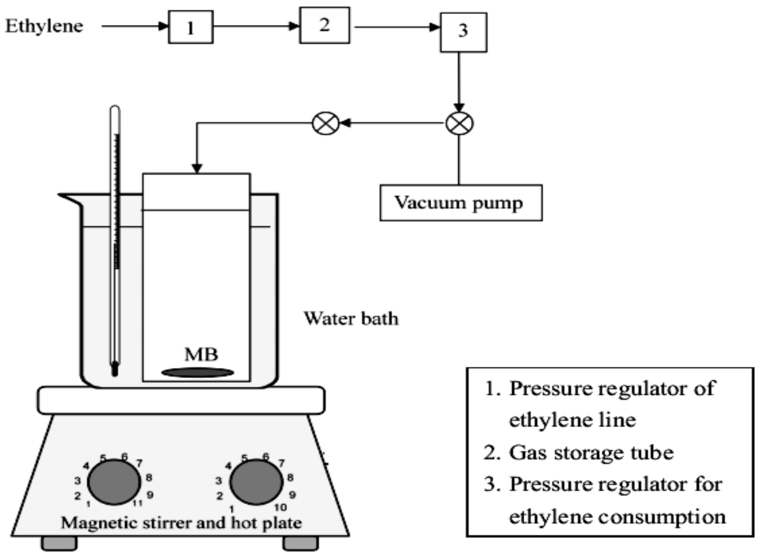


Figure 3.4 Diagram of system in slurry phase polymerization

3.2.9 Glove box

The MRBAUN LABstar Glove box, controlled atmosphere equipment, provided an inert surrounding for handling greatly moisture and oxygen sensitive materials. It consists of 2 parts for producing inert atmosphere; gas purification system, and closed loop gas recirculation to remove O_2 and H_2O. Additionally, oxygen and moisture analyzer, MB-OX-SE1 and MB-MO-SE1 respectively, are also applied for checking oxygen and moisture content in Glove box system.

3.3 Characterization

In this research, characterization can be divided into 2 main parts; firstly, supports were identified for knowing general properties**.** Secondary, polymers were characterized for checking polymer properties.

3.3.1 Characterization of supports and Modified supports

3.3.1.1 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

Morphology of supports and modified supports were investigated using Scanning Electron Microscope (SEM), JEOL model JSM-6510 LV. The samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen. EDX will be performed using Link Isis series 300 program.

3.3.1.2 Fourier transforms infrared spectroscopy (FTIR)

To observe structural characteristics (eg. functional group or molecular structure) of the chemical group, the samples will be collect by FTIR. The sample was weighed a small amount (2-5 mg) directly in pellet with KBr binder. The mearsurements were restricted in 4000-1300 cm^{-1} region. Absorbance FT-IR spectra were recorded by a Bomem MB-102 spectrometer with 32 scans at resolution of 4 cm^{-1}.

3.3.1.3 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phase of sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with CuKα ($\lambda = 1.54439x10^{-10}$ m). The spectra were scanned at a rate 2.4 degree/min in the range $2\theta = 20\text{-}80$ degrees.

3.3.2 Characterization method of polymer

3.3.2.1 X-ray diffraction (XRD)

In this part, it were operated as same as part of characterization of supports.

3.3.2.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC), DSC 204 *F1 Phoenix*®, was used to measure melting temperature (*Tm*) and crystallinity (*X*c) of polymer at 200 °C with ramp rate of 10°C/min. Approximately 10 mg of sample was used for each DSC measurement.

3.3.2.3 Scanning electron microscope (SEM)

To observe the morphology of polymer, JEOL JSM-35F scanning electron microscope (SEM) at Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University will be applied. The sample will be conductive to prevent charging by coating with gold particle by ion 45 sputtering device.

3.4 Supporting procedure

3.4.1 Preparation of coir dust

The coir dust was heated at 150 °C for 2 hours under argon atmosphere with a heating rate of 10 °C min^{-1}.

3.4.2 Preparation of cellulose

Cellulose support was calcined under argon at 150 °C for 4 hours prior to the modification step.

3.4.3 Preparation of gallium-modified cellulose supports

The gallium modification on the cellulose supports was prepared by the incipient-wetness impregnation of cellulose. The use of $Ga(NO_3)_3$ as a gallium source. Gallium nitrate [$Ga(NO_3)_3$] was dissolved in deionized water and impregnated into the cellulose support using incipient wetness to give a final modified cellulose support with 1, 2, and 5 wt % of Ga. The support was calcined under argon at 150 °C for 2 hours. The resulting mixture was referred to Ga-modified cellulose.

3.4.4 Preparation of boron-modified cellulose supports

The steps for producing B-modified cellulose; first of all, the varied amount of boron metal was added to 1 g of cellulose in 20 mL of hexane. Then, the mixture was stirred for 1 hour at room temperature. After solvent was evaporated under vacuum using Schlenk technique, it was washed 3 times with 20 mL of toluene and finally dried under vacuum.

3.5 Preparation of stock catalyst solution

$Et(Ind)_2ZrCl_2$ 0.0083 g ($1.98x10^{-5}$ moles) was added into 20 mL of toluene solution, stirred at room temperature giving yellow transparent solution.

3.6 Ethylene polymerization

Metallocene system is extremely sensitive to oxygen and moisture. For this reason, Schlenk techniques and/or glove box will be applied for operating all of work under argon atmosphere.

3.6.1 *In situ* ethylene polymerization

The ethylene polymerization reactions were operated in a 100 ml semi-batch stainless steel autoclave reactor with a magnetic stirrer.

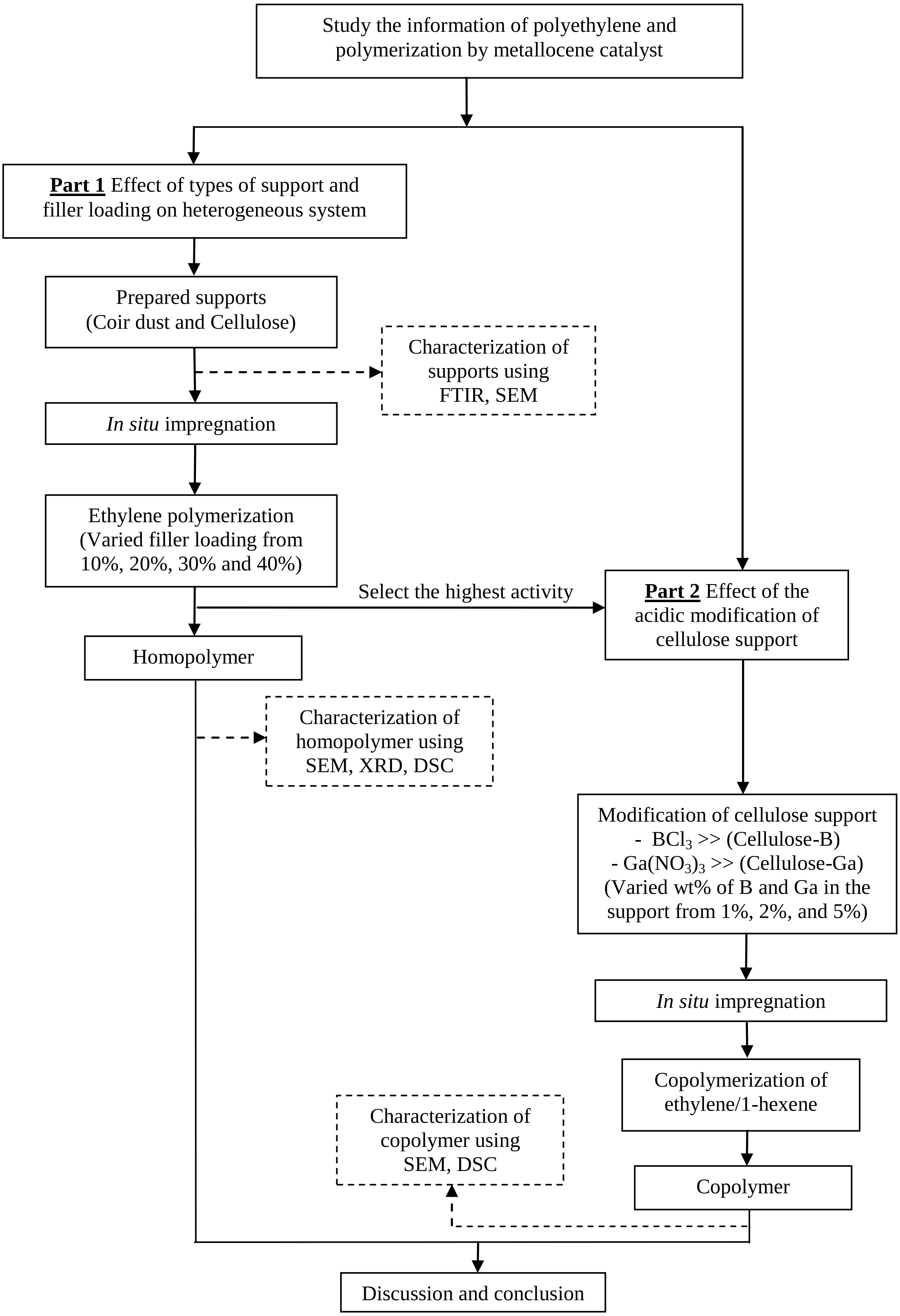
- From the beginning, the desired amount of the supports and methylaluminoxane (MAO) 1.1 mL ($[Al]_{MAO}/[Zr]=1135$) were mixed and stirred for 30 min aging at room temperature.
- $Et(Ind)_2ZrCl_2$ 1.5 mL ($5x10^{-5}$ M) mixing with toluene (to adjust total volume of 30 ml) was added into the autoclave reactor.
- To stop reaction, the reactor was frozen in liquid nitrogen for 10 min, and then the reactor was evacuated to remove argon.

- The reactor was heated up to polymerization temperature (70°C) and the mixture solution was stirred during heating up.
- When the reactor reached 70^{o}C, ethylene was fed into the reactor to start reaction and time was collected.
- After all ethylene was consumed (6 psi from pressure gauge), the ethylene valve was closed. The solution in reactor was added of acidic methanol (0.1% HCl in methanol) and stirred overnight.
- Finally, wet polymer was separated by filtered suspension from solution, and the polymer was washed using methanol and dried at room temperature to obtain dried polymer as white power. The polymer weight was collected and polymer powder was characterized to identify specific properties.

3.6.2 ***In situ*** **ethylene/1-hexene copolymerization**

In this part, it was operated as same as *in situ* ethylene polymerization, but some steps will be difference. In this part, 1-hexene (ethylene: 1-hexene = 1:0.25) was put into the reactor after the reactor was frozen in liquid nitrogen to stop reaction for 10 min. And others step were still operated in the previous part. The polymer as white power will be also getting in this section.

3.7 Research methodology



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of types of support and filler loading on supported zirconocene catalyst during ethylene polymerization (Part 1)

In this part, the study of the activities and characteristics of polymer composites with using coir dust and cellulose as a support were obtained. This part was divided into 3 portions. In the first portion, coir dust and cellulose are characterized for explaining. Then, effect of types of support and filler loading on the activity of metallocene catalyst is shown in second portion. The last portion was investigated to disclose the characterizatics of polymer, such as morphology, crystallization behavior and melting temperature.

4.1.1 Characterization of support

4.1.1.1 Characterization of supports with scanning electron microscope (SEM)

The morphologies of coir dust and cellulose were characterized by scanning electron microscopy (SEM) as shown in **Figure 4.1** and **Figure 4.2**. Based on the SEM results, the isolated particles of coir dust and cellulose showed a size ranging from 170-150 μm and 49-152 μm, respectively. The particle size of coir dust seemed to be larger when compared with cellulose. The coir dust displayed short fiber with flake surface, whereas, cellulose presented the mixture between rough and pellet shape surface. Both samples apparently exhibited non-uniform shape.

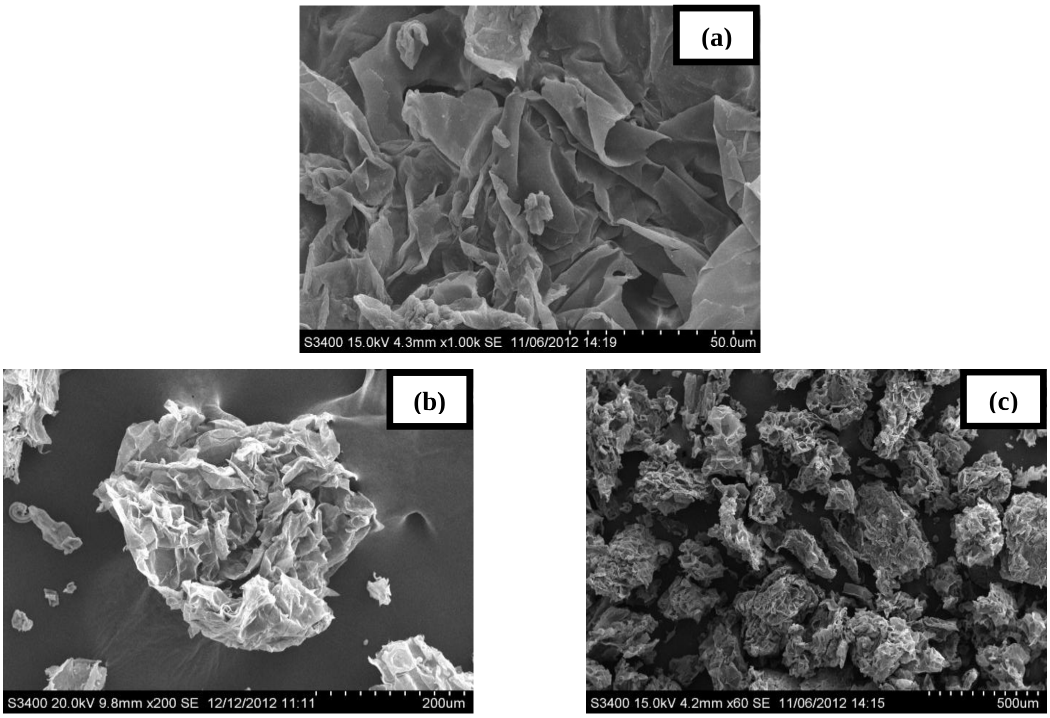


Figure 4.1 SEM micrographs of coir dust: (a) coir dust (scale 50 μm), (b) coir dust (scale 200 μm), (c) coir dust (scale 500 μm)

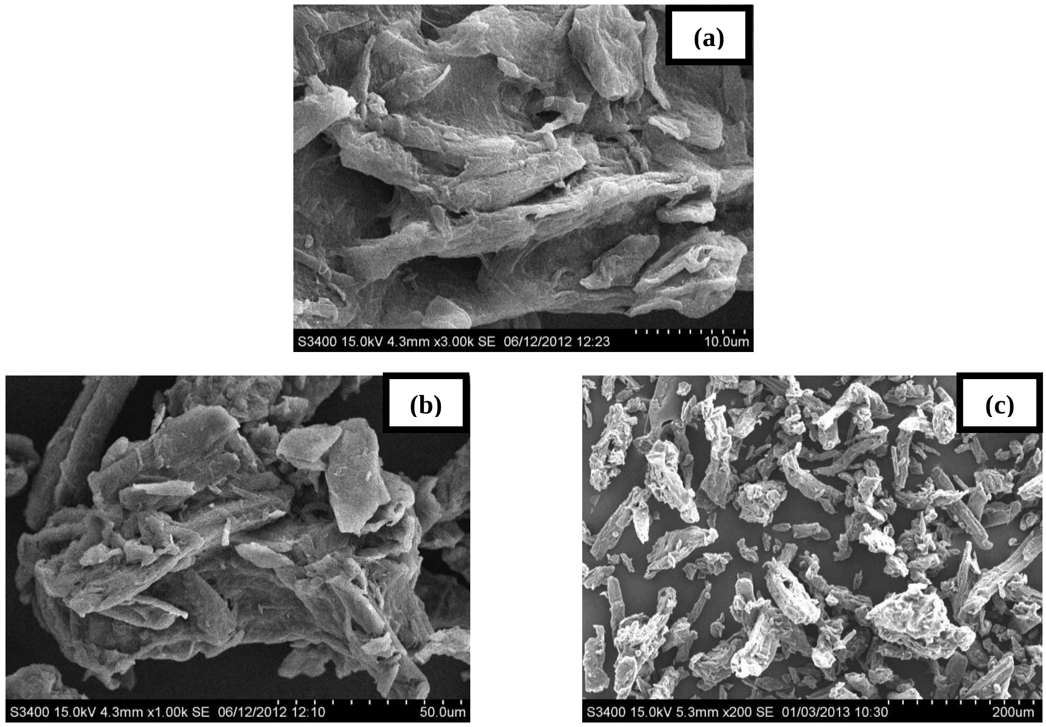
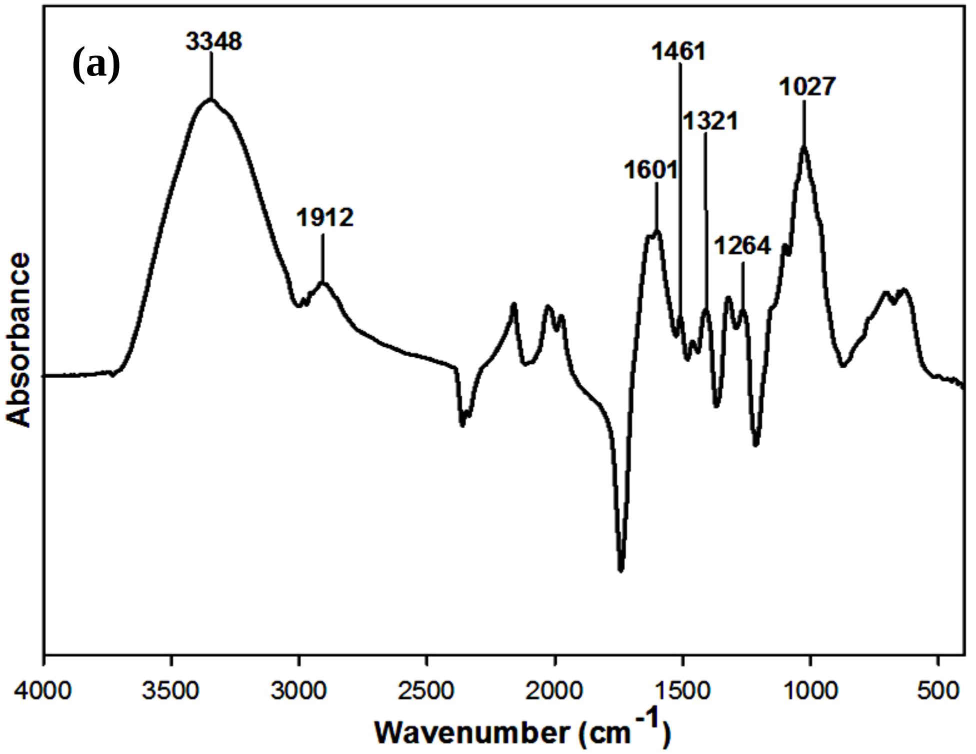


Figure 4.2 SEM micrographs of cellulose: (a) cellulose (scale 10 μm), (b) cellulose (scale 50 μm), (c) cellulose (scale 200 μm)

4.1.1.2 Characterization of supports with Fourier transform infrared spectroscopy (FTIR)

The FT-IR spectra of coir dust and cellulose are compared in **Figure 4.3.** It was observed that wavenumbers of obtained peaks are also different. The analysis of the spectra with reference to publish data showed several typical features of the coir dust. The exhibition of broad band at 3348 cm^{-1} is an indication of the presence of the stretch vibration of boned hydroxyl groups on the coir dust. The broad absorption peak at 1912 cm^{-1} assigned to C−H stretch from methyl and methylene groups [77]. The peak at 1601 cm^{-1} represents the C=O bonds on hemicelluloses from carboxylate groups and at 1461 cm^{-1} is assigned to CH_2 symmetric bending peaks [78]. The existence of C−O of carboxylic acid groups gave rise to the peak at 1264 cm^{-1}. The band at 1321 cm^{-1} is characteristic of weak vibration of aliphatic N−O group. The peak shown at 1027 cm^{-1} is associated with the strong and broad band of C−O of primary alcohol and medium vibration of primary amine ($-NH_2$) in the structure [79].

Compared with the cellulose, several of these characteristic bands changed in absorbance or wave number in the cellulose spectra. The IR spectrum of cellulose shows a broad band in the 3600-3100 cm^{-1} corresponding to the stretching of the surface hydroxyls, gives considerable information concerning the hydrogen bonds. The presence of cellulose sample can be further confirmed by the shift of the band from 2900 cm^{-1}, corresponding to the C−H stretching vibration, to higher wavenumber values and by the strong decreasing in the intensity of this band [80]. The peak at 1444 cm^{-1} was assigned to a symmetric CH_2 bending vibration. The wavenumbers at 1151 and 1101 cm^{-1} were referred to C−O−C stretch of the β-1,4-glycosidic linkage in cellulose. The C−O stretching of cellulose was observed at 1020 cm^{-1}. Peaks at 960 and 877 cm^{-1} are due to the C−OH out-of-plane bending. The last group of peaks at 800 cm^{-1} was presented of C−H deformation in cellulose [81].



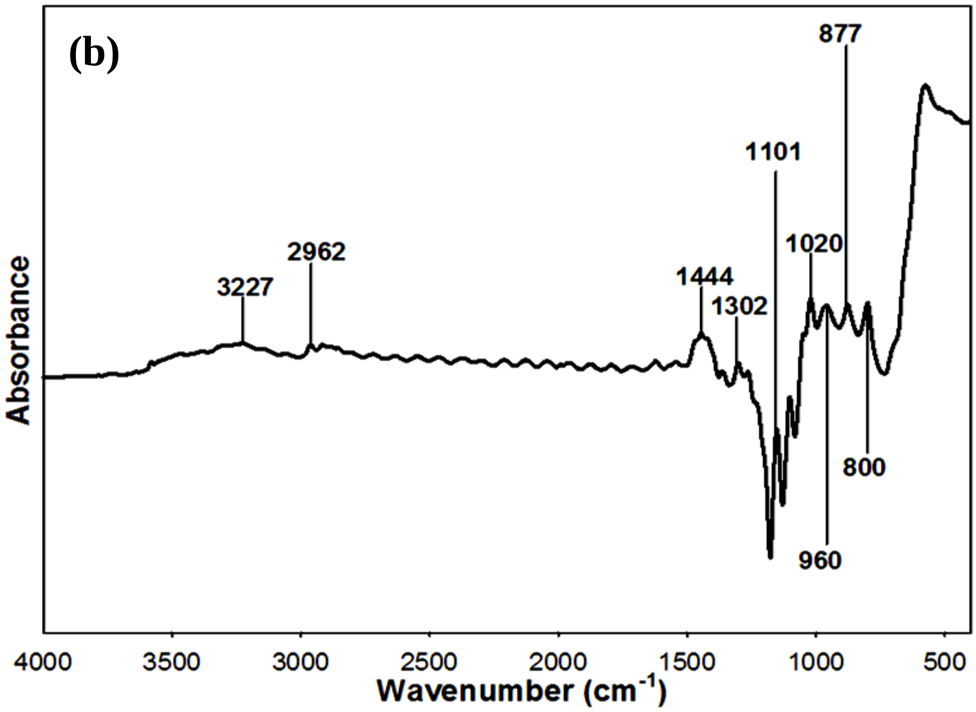


Figure 4.3 FT-IR spectra of (a) coir dust, (b) cellulose

4.1.2 Catalytic activity

In situ polymerization of ethylene with catalyst precursors prepared via *in situ* impregnation method was carried out. In this system, the coir dust and cellulose as support were reacted with the desired amount of MAO at room temperature for 30 min, which allowed the preparation of catalysts in form of suspensions. After the *in situ* polymerization was done, the polymerization time and yield were recorded. The polymerization activity results are also shown in **Table 4.1.**

Table 4.1 Catalytic activities of various supported MAO during ethylene polymerization (*In situ* impregnation)

Samples	**Filler**	**Amount of filler (%wt)**	**Yield[a] (g)**	**Time (s)**	**Activity[b] (kg PE/mol Zr.h)**
PE	-	-	0.7773	95	19,678
PE/coir dust10	Coir dust	10	0.5848	126	11,139
PE/coir dust20	Coir dust	20	0.6014	186	7,760
PE/coir dust30	Coir dust	30	0.5388	207	6,246
PE/cellulose10	Cellulose	10	0.5903	124	11,406
PE/cellulose20	Cellulose	20	0.6440	128	12,037
PE/cellulose30	Cellulose	30	0.8320	124	16,077
PE/cellulose40	Cellulose	40	0.6189	153	9,708

a The polymer yield was limited by the amount of ethylene fed (0.018 mol).
b Activities were measured at polymerization temperature of 70 ^{o}C, [ethylene] = 0.018 mol, $[Al]_{MAO}/[Zr]_{cat}$ = 1135 in toluene with total-volume = 30 mL and $[Zr]_{cat} = 5x10^{-5}$ Molar

According to **Table 4.1**, it was noticeable that the heterogeneous system exhibited lower activities compared to the homogeneous one. Many reasons for the decrease in activity are due to i.e. the presence of support interaction [82], deactivation of active sites during the supporting process and steric effect of the support surface, which acts the role of a vast ligand [83].

The influence of filler loading on ethylene polymerization was studied. **Table 4.1** is summarized the resulted catalytic activities obtained from both coir dust and cellulose with different amounts of filler. For coir dust system studies, catalytic activities were decreased with increasing coir dust loading. Many research obtained the trend result in the same way [85-86]. The result of this experimental can be attributed to the more steric hindrance arising from coir dust is that causes a decrease in activity due to this steric hindrance provides difficult accessibility to the catalyst sites [9].

Then, considering the results in cellulose system, the catalytic activity of loading of 30 %wt cellulose on the ethylene polymerization shows that the maximal activity. In that case, very high amount of cellulose (loading of 40 %wt cellulose in system) revealed negatively on polymerization activity. Increased activity with increasing at the amount of cellulose at the beginning can be attributed to increased bulk density in the heterogeneous system. Good bulk density can enhance distribution of active site [88]. Nevertheless, increased amount of cellulose to 40 %wt resulted in decreased activity. This was probably due to too much steric hindrance of cellulose particle preventing catalytic active sites from reaction with MAO in the providing less space for monomer attack to produce polyethylene chain [87].

For comparative studies, the resulted polymerization activities obtained from coir dust and cellulose were compared with the same filler loading. It was found that the polymerization activities obtained from the coir dust exhibited lower activity than the cellulose one. This may be suggested that the two main reasons for this decreased activity include (1) the larger particle size of coir dust may interact more with MAO resulting in reduced activities due to it is more difficult for zirconocene to react with the strongly interaction MAO on coir dust surface. It should be mentioned that the smaller particles have less support interaction [87] and (2) the amine functional group on coir dust surface leads to a zirconocene catalyst deactivation [89].

4.1.3 Characterization of polymer

4.1.3.1 Characterization of polymer with scanning electron microscopy (SEM)

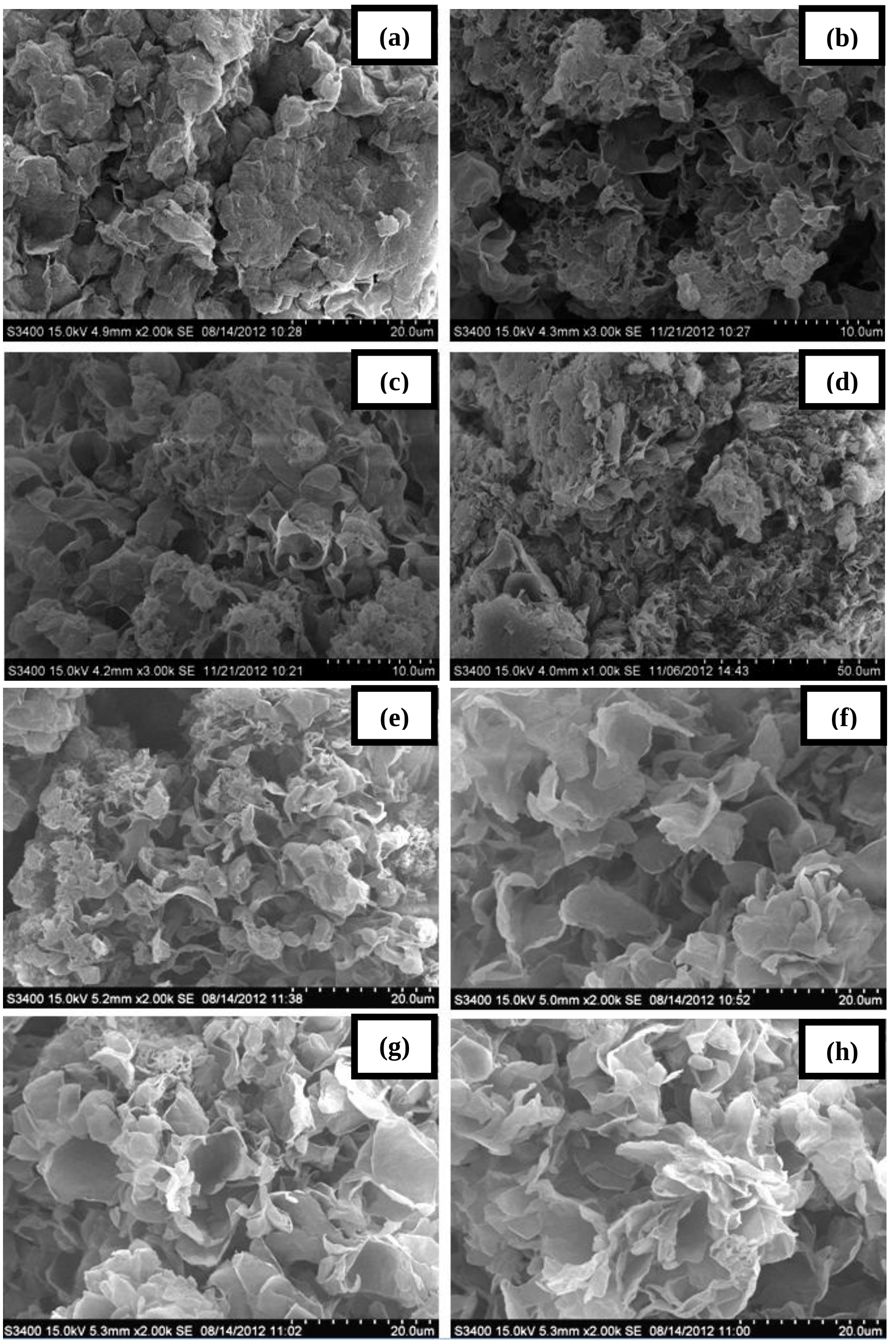


Figure 4.4 Morphologies of polymers obtained from the various filler loadings (a) PE, (b) PE/coir dust10, (c) PE/coir dust20, (d) PE/coir dust30, (e) PE/cellulose10, (f) PE/cellulose20, (g) PE/cellulose30, (h) PE/cellulose40

Figure 4.4 presents the scanning electron micrograph (SEM) of the polymers produced via the homogeneous and the heterogeneous catalytic system. Considering the effect of filler loading on morphology, the results indicated the similar morphologies for the supported system, but different from the homogenous system. The polyethylene from the homogeneous system has lower porosity particles than that from the supported system. Polyethylene obtained with cellulose displays larger pore size and more open structure. Therefore, filler loading and types of support apparently affected on the morphology of the resulting polymer.

4.1.3.2 The effect of various filler loading on melting temperature of polymers

PE, PE/coir dust and PE/cellulose were analyzed by differential scanning calorimeter (DSC). Melting temperature and melting enthalpy of synthesized polyethylene composites are listed in **Table 4.2**. The DSC curves of polymers are also shown in **Appendix C.**

Table 4.2 Melting and crystallization behavior

Samples	**T_m[a] (°C)**	**ΔH_{exp}[b](J/g)**	**X_c[c] (%)**
PE	133	163	57
PE/coir dust10	131	156	54
PE/coir dust20	134	154	54
PE/coir dust30	132	135	47
PE/cellulose10	131	168	58
PE/cellulose20	132	195	68
PE/cellulose30	137	194	68
PE/cellulose40	131	100	35

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

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

[c] Crystallinity (X_c) was calculated from equation in **Appendix B**

Considering the effect of coir dust loadings, it can be observed that there was no a significant change in the melting temperature for all coir dust systems. These high melting temperatures of the PE/coir dust composites (131-134 °C) indicate the branchless structure of the composites [90]. On the contrary, it is seen that PE/coir dust composites with adding of coir dust is different in the crystallinity. Decreasing of crystallinity was pronounced at high loading of coir dust. It implied that the content of coir dust influenced the crystallization of polymer, but did not affect on melting temperature.

For cellulose system studies, it was found that the highest melting temperature of PE adding 30 %wt of cellulose was observed although it had the highest crystallinity. It was worth noting that the cellulose particles in polymer matrix can act as nucleating agents [85]. The melting temperature for all cellulose systems had a value in the range of 131-137 °C. It has been known that the crystallization of polymer trended to increase with increasing the cellulose loading. However, the system of PE/cellulose40 exhibited the different result from the others. This can be suggested that the larger amounts of cellulose particle locate themselves in the interlamellar spaces, which leave little room for additional crystallization [85]. Consequently, the presence of large amounts of cellulose may inhibit the formation of crystalline phase of polyethylene and exhibits a decrease in crystallinity [91].

4.1.3.3 The effect of various filler loading on the polyethylene crystallinity

The obtained PE/coir dust composites were further characterized by using XRD technique. Figure 4.5 shows the XRD patterns of PE/coir dust composites synthesized with different coir dust loadings. The XRD patterns for all coir dust systems were similar, exhibiting the characteristic two peaks at 2θ for the orthorhombic crystalline form of polyethylene of all samples at 21.4° and 24.1° [92]. Besides, the intensity of PE/coir dust composite with the presence of 30 %wt of coir dust was lower than all samples indicating a reduction in crystallinity of PE/coir dust composite produced, which were consistent with results obtained from DSC analysis.

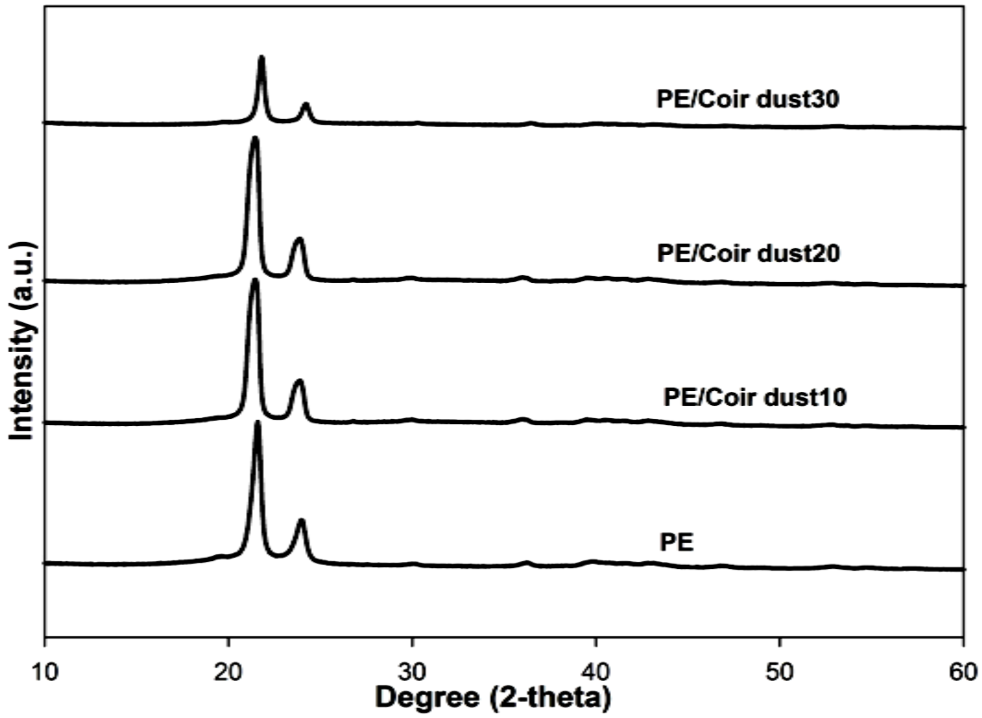


Figure 4.5 XRD patterns of polyethylene (various coir dust loading)

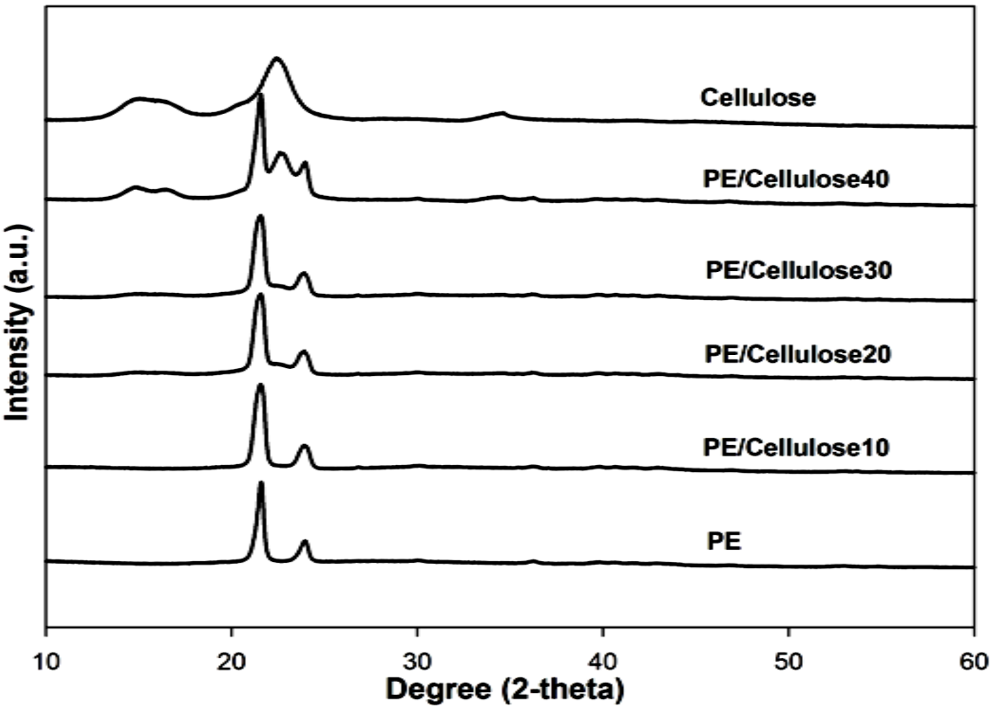


Figure 4.6 XRD patterns of polyethylene (various cellulose loading)

The evaluation of the crystallinity of the pure PE, pure cellulose and its composites with cellulose were performed by XRD. Changing of crystallinity can be observed as seen in **Figure 4.6**. It can be seen that the intensity of XRD characteristic peaks for all samples were changed based on the presence of %wt of cellulose in composites. However, the diffractograms for all the different tested PE compositions showed the characteristic peaks of the crystalline structure of PE, which according to Kuo *et al.* that are assigned to the (110) and (200) planes [92]. Moreover, no change in peak positions were observed, indicating that there were no crystalline structures formed due to the presence of cellulose in the polymer composites, but different from the PE/cellulose40 system. XRD patterns also confirm the reduction of crystallinity in PE/cellulose40 compared with all samples. In **Figure 4.6**, it can be seen that small amorphous peak was observed around 13.3°-17.8° and showing a peak corresponding to $2\theta=22.5°$,which may be assigned to cellulose (002) plane [93]. This result corresponds with the DSC data.

Regarding to XRD patterns taken of cellulose sample, it was observed that the pure cellulose presents the peaks at approximately 14.8, 16.2, 34.5 and 22.5 degrees (2θ), corresponding to planes in the sample with Miller indices ($\bar{1}10$), (110), (004), and (002) planes [93]. Cellulose contains crystalline and amorphous regions, and crystallinity, a measure of weight fraction of the crystalline region, is one of the most important measurable properties of cellulose. Following Garvey [94] we used the (002) spacing to evaluate the size of the crystals because it is the most obviously resolved of the four X-ray reflections. It can be seen that the width of the crystalline peak (002) has been directly related to crystallite size and estimated to be about 4 to 7 nm in most references [92]. Average crystallite size has been estimated by using the Scherrer formula. The degree of crystallinity of commercial cellulose is 83 % and of the prepared is 81 % [95].

4.2 The effect of the acidic modification of cellulose support on metallocene heterogeneous system (Part 2)

With regard to the obtained result in 4.1 (Part 1), it was found that the addition of 30 %wt of cellulose in the polymerization system revealed the highest activity. As a consequence, this condition was selected to use in this part in order to be further developed for the heterogeneous system and to generate the more efficient supported metallocene catalyst. Besides, relating to supports, B and Ga were employed to modify cellulose acidic properties for investigating how they would impact on the ethylene/1-hexene copolymerization in terms of catalytic activity and polymer properties. **Figure 4.7** illustrates the heterogeneous system in this part.

In this study, three kinds of supports composing of non-modified cellulose, B-modified cellulose (Cellulose-B), and Ga-modified cellulose (Cellulose-Ga) were used for supporting the zirconocene/MAO catalyst. After modification with B and Ga, the non-modified cellulose, and the modified cellulose supports were characterized by FTIR, XRD, SEM/EDX, and ICP-OES.

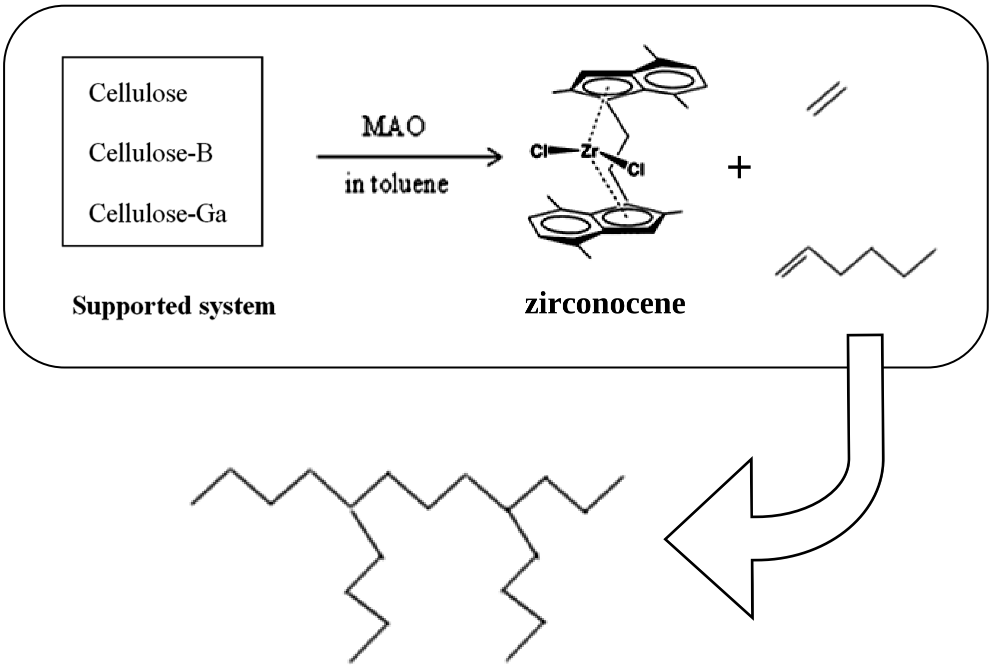


Figure 4.7 Heterogeneous system in **Part 2**

4.2.1 Characteristics of support

4.2.1.1 Characterization of supports with Fourier transform infrared spectroscopy (FTIR)

The IR spectra of non-modified cellulose support and acidic cellulose support modification by employing B and Ga, having different loading of acidic (B and Ga) on each supports of 1, 2, and 5%wt are represented in **Appendix E**. **Figure 4.8** shows the FTIR spectra of non-modified cellulose and modified cellulose with the B content of 5 %wt. Compared with the non-modified cellulose, it was found that the modified cellulose did not lead to the obvious change in the peak of the characteristic bands of cellulose, indicating that the B content did not have significant effect on these structural parameters. However, the intensities of characteristic peaks for cellulose changed after treatment with B. The intensity of the band at 1151 and 1101 cm^{-1} (C−O−C stretch of the β-1,4-glycosidic linkage in cellulose) results in an obvious increase after treatment B of cellulose. Also, the peaks at 960 and 877 cm^{-1} in the BCl_3 modified cellulose have lower intensities than those of corresponding non-modified cellulose. This could be due to a reduction of C−OH out-of-plane bending with respect to non-modified cellulose. Some shifts of the absorption bands to lower wavenumbers (1020 cm^{-1} band are attributed to the C−O stretching of cellulose) are evidenced. Moreover, the intensities at 1444 and 800 cm^{-1} also increased, resulting in much shaper peaks in those spectral regions.

With regard to the IR spectra of modified cellulose with the Ga content of 5 %wt, it is represented in **Figure 4.9**. These results are no significant difference between spectra for B modified cellulose and Ga modified cellulose samples. However, the peak at 800 cm^{-1} was absence. On the other hand, modification of cellulose with B results in the appearance of peak at 800 cm^{-1}.

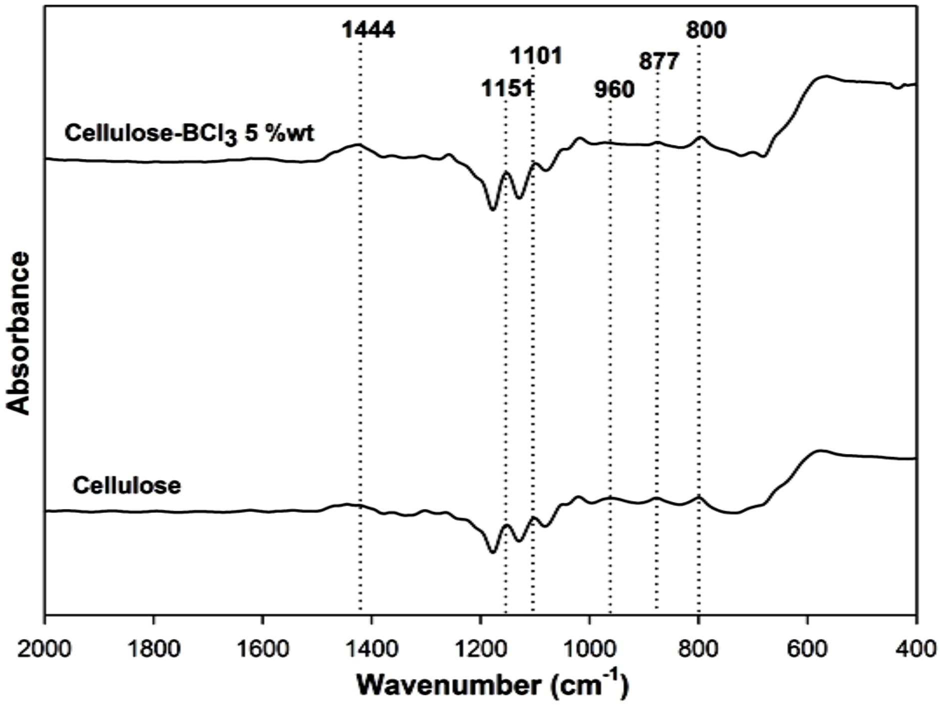


Figure 4.8 FT-IR spectra of modified cellulose with the B content of 5 %wt

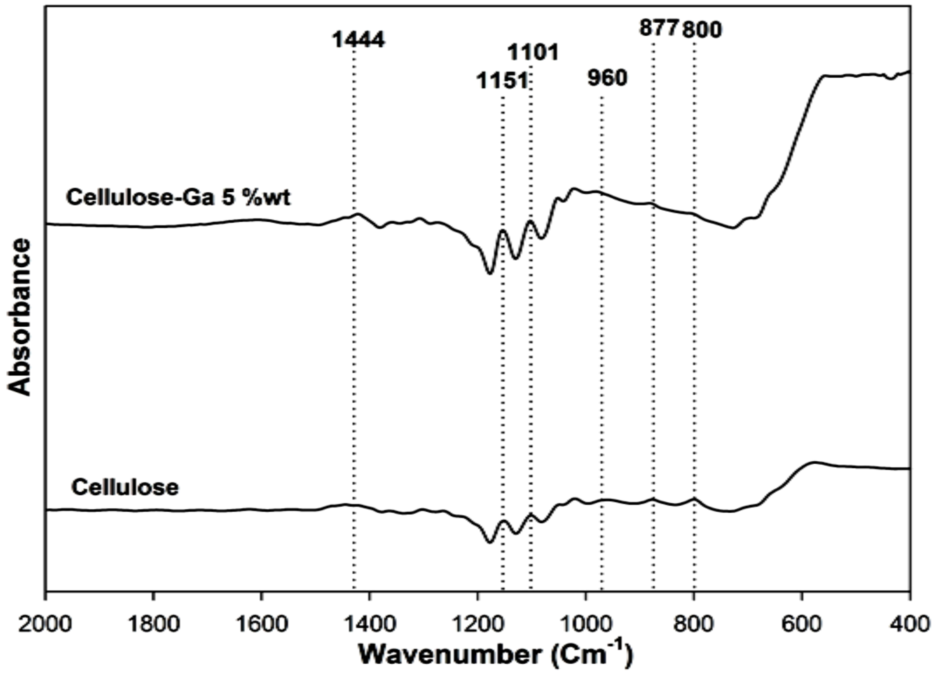


Figure 4.9 FT-IR spectra of modified cellulose with the Ga content of 5 %wt

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

The modified supported containing various weight percent of acidic (B and Ga) loading on cellulose were characterized using XRD measurement. The XRD patterns of the non-modified cellulose, B modified cellulose (Cellulose-B) and Ga modified cellulose (Cellulose-Ga) supports are shown in **Figure 4.10.** It was observed that the non-modified cellulose exhibited XRD peaks at 14.8, 16.2, 34.5, and 22.5 degrees (2θ) which are typical cellulose crystalline form, in good agreement with **Part 1.** After modification with 1%, 2% and 5%wt of acidic (B and Ga), all supports still exhibited the similar XRD patterns as seen for the non-modified cellulose one. This indicated that B and Ga were highly dispersed form, which was almost invisible by XRD. The XRD data were in accordance with the FTIR results, which revealed that the modification of acidic (B and Ga) did not change the main structural peculiarity of cellulose.

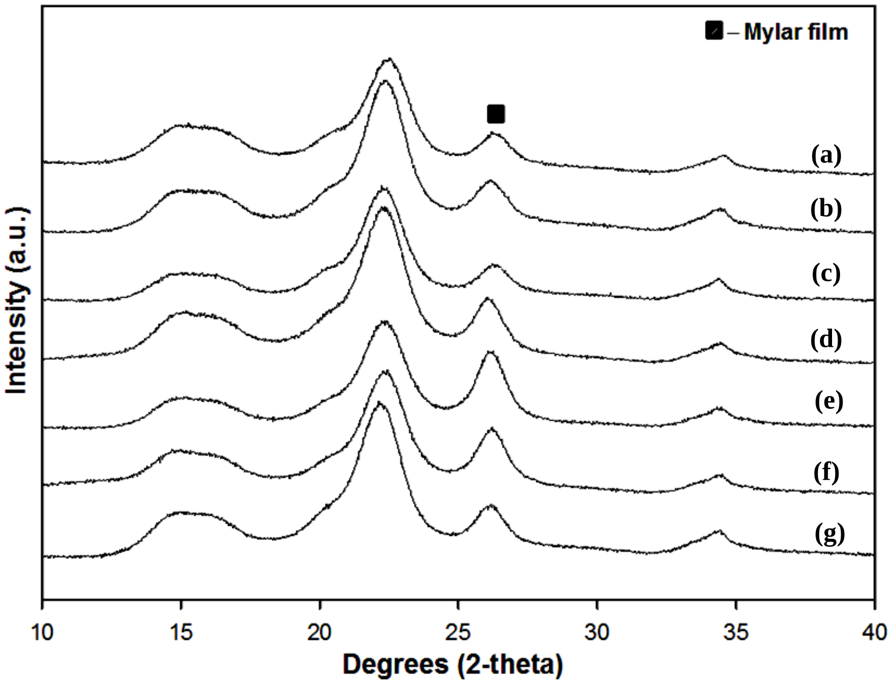


Figure 4.10 XRD patterns of different acidic-modified cellulose support with different acidic loading; (a) non-modified cellulose (b) cellulose-B-1% (c) cellulose B-2% (d) cellulose-B-5% (e) cellulose-Ga-1% (f) cellulose-Ga-2% (g) cellulose-Ga-5%

4.2.1.3 Characterization of supports with scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX)

The morphology of different acidic-modified cellulose support with different acidic loading was observed by a scanning electron microscope (SEM). The SEM micrographs of non-modified cellulose and those modified with 1%, 2% and 5% wt of acidic (B and Ga) are shown in **Figure 4.11**. It can be seen that the cellulose modified with B shows rather different from those of all samples. The original form of cellulose changed into a gel-like substance, while the morphology of cellulose modified with Ga are similar to that of non-modified cellulose.

Based on the EDX measurement, the element composition and elemental distributions present on the various cellulose samples can be determined. After modified with 1%, 2%, and 5%wt of acidic (B and Ga), the amount of main elements in all samples as shown in **Table 4.3** and the EDX mapping of all samples are also shown in **Appendix D.** The distribution of Ga element was similar in all samples of the cellulose modified with Ga, while the cellulose modified with Lewis acid BCl_3 (boron content) shows the distribution of Cl element as well. However, SEM/EDX cannot be used to determine the content of B due to boron cannot be detected by SEM/EDX. Therefore, it is necessary to find other techniques to measure the value of B content. One technique for obtaining a bulk composition of cellulose modified with Lewis acid BCl_3 (boron content) that determine the content of B is inductively coupled plasma optical emission spectrometry (ICP-OES). We report on these results using ICP-OES to determine B content of samples, the content of boron are listed in **Table 4.3**. These results demonstrated that for cellulose modified with B, B can reach into its pore leading to lower B present on the cellulose surface. On the other hand, according to the EDX examination on Ga modified cellulose, it was worth noting that Ga modifiers were mostly deposited at the cellulose surface. This is due to size of Ga larger than B, by looking at the atomic mass of Ga more than B. In order to provide a better understanding of the effect of acidic modification on the cellulose as mentioned earlier, the conceptual model is shown in **Figure 4.12**.

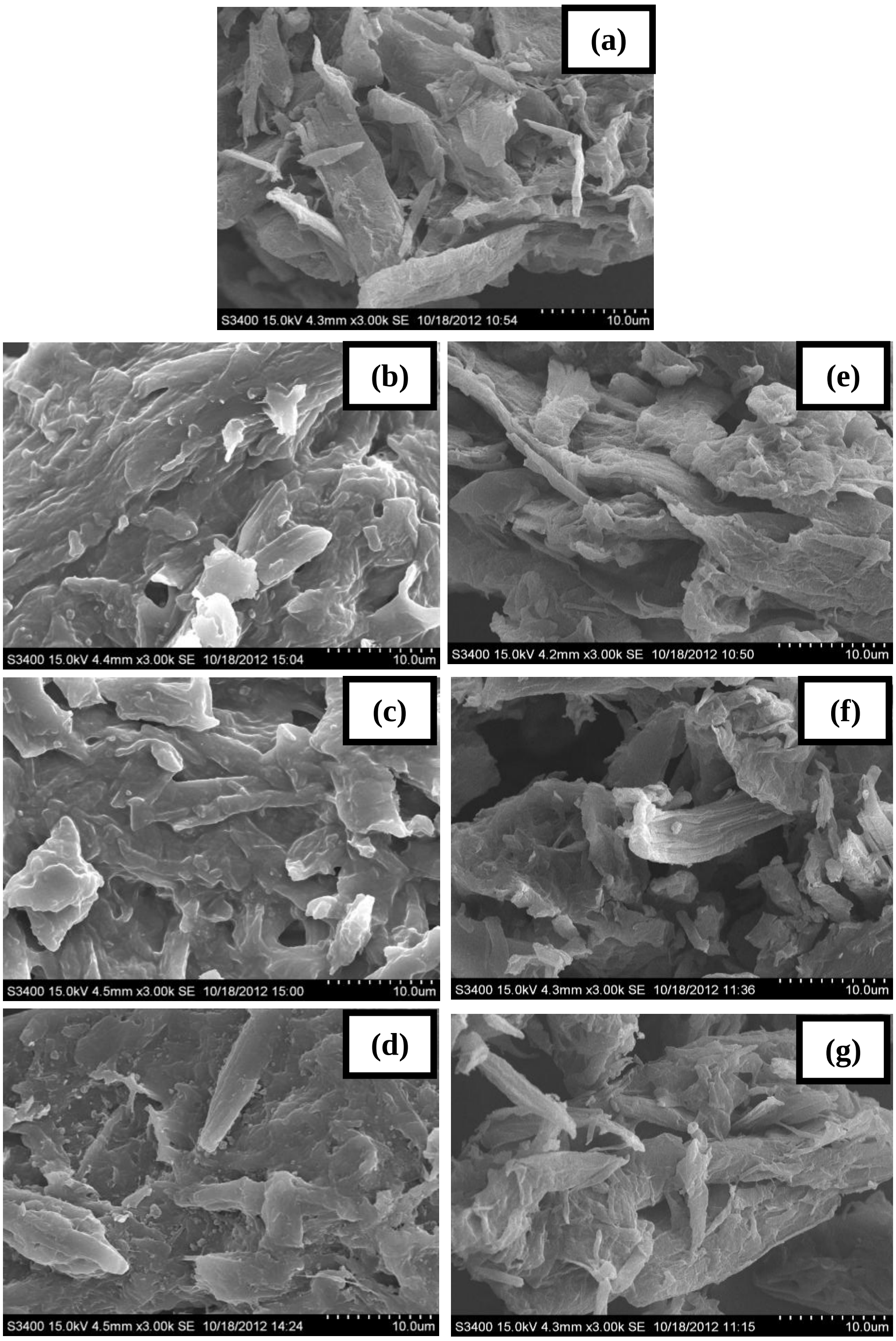


Figure 4.11 SEM micrograph of different acidic-modified cellulose support with different acidic loading; (a) non-modified cellulose (b) cellulose-B -1% (c) cellulose-B-2% (d) cellulose-B-5% (e) cellulose-Ga-1% (f) cellulose-Ga-2% (g) cellulose -Ga-5%

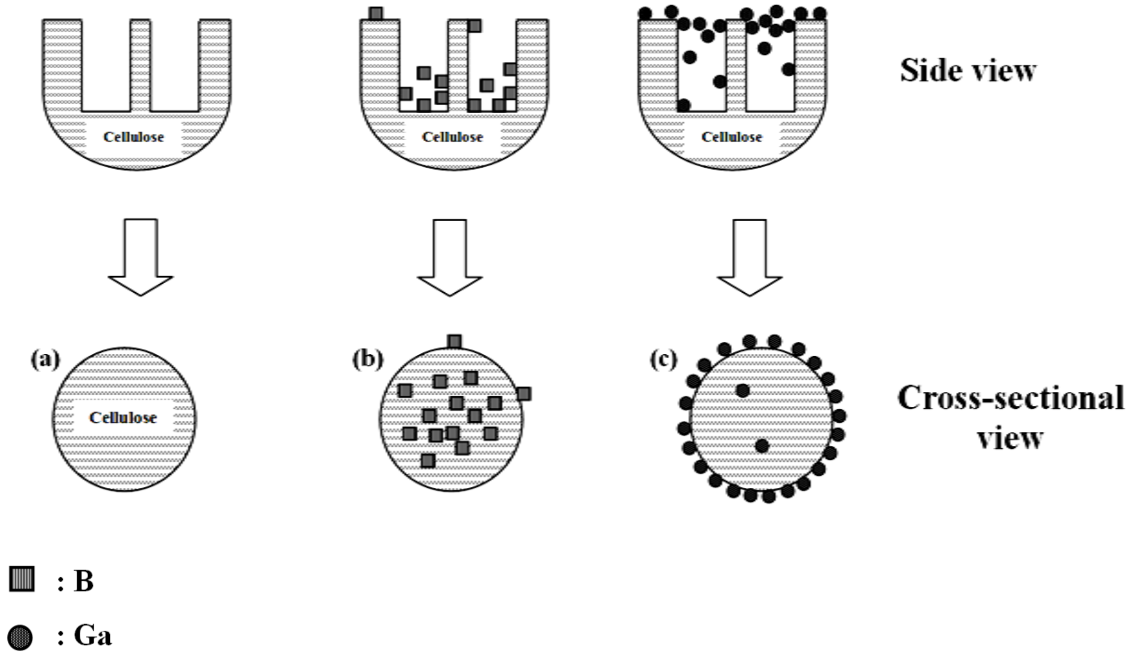


Figure 4.12 conceptual models in effect of acidic-modification on the cellulose support; (a) non-modified cellulose (b) B modified cellulose (c) Ga modified cellulose

Table 4.3 modified cellulose component characterized by EDX and ICP technique

sample	[C] (%wt) EDX	[O] (%wt) EDX	[Cl] (%wt) EDX	[Ga] (%wt) EDX	[B] (%wt) ICP-OES
cellulose-B-1%	55.21	44.62	0.17	-	0.15
cellulose-B-2%	56.99	42.66	0.35	-	0.28
cellulose-B-5%	55.78	43.79	0.43	-	0.68
cellulose-Ga -1%	56.74	41.84	-	1.42	-
cellulose-Ga -2%	53.73	43.75	-	2.52	-
cellulose-Ga -5%	55.55	40.11	-	4.34	-

4.2.2 Catalytic activity

Table 4.4 Summary of ethylene/1-hexene copolymerization catalytic activities (*In situ* impregnation)

System	Types of modifier	Wt% of Lewis acid in support	Time (s)	Yield[a] (g)	Activity[b] (kg PE/mol Zr.h)
Homogenous	-	-	90	0.9293	24,781
Cellulose	-	-	87	0.7998	22,063
Cellulose-B(1)	B	1	198	0.7904	9,580
Cellulose-B(2)	B	2	147	0.6925	11,306
Cellulose-B(5)	B	5	123	0.6870	13,404
Cellulose-Ga(1)	Ga	1	89	0.8703	23,521
Cellulose-Ga(2)	Ga	2	71	0.7736	26,223
Cellulose-Ga(5)	Ga	5	84	0.7765	22,185

a The polymer yield was limited by the amount of ethylene fed (0.018 mol).
b Activities were measured at polymerization temperature of 70 ^{o}C, [ethylene] = 0.018 mol, [ethylene] = 0.00045 mol, $[Al]_{MAO}/[Zr]_{cat}$ = 1135 in toluene with total volume = 30 mL and $[Zr]_{cat}$ = $5x10^{-5}$ Molar

The effect of modification of Lewis acid on ethylene/1-hexene copolymerization was investigated. Both B and Ga modifier were observed to exhibit opposite effects in activity as shown in **Table 4.3**. Comparing the homogenous system with non-modified cellulose, it was found that the non-modified cellulose system exhibited lower activities compared to the homogeneous one. This is due to the more steric hindrance in the heterogeneous system that causes a decrease in activity because this steric hindrance renders difficult accessibility to the catalyst sites [85]. This is known as the supporting effect [89]. Considering the effect of cellulose modification with B and Ga, it can be seen that cellulose modification with Ga exhibited positive effect on polymerization activity, whereas the activities of the B modified cellulose were lower than non-modified cellulose one. This was presumably due to cellulose can be broken down chemically into its glucose units by treating it with Lewis acid BCl_3, thereby leading to change in physical structure of cellulose.

As shown in **Figure 4.11**, the structure of B modified cellulose was changed into a gelatinous form. The change of physical structure indicates that the main factor causing the disruption of hydrogen bonding. This is known as the hydrolysis reaction [96].

With regard to the result of Ga-modified cellulose system, it can be observed that the Ga modified cellulose exhibited higher activity than the non-modified cellulose for the entire different Ga loading. The reason is that the acidity obtained from the introduction of Ga on the cellulose surface would play an important role on the higher formation of the active centers resulting in high activity compared with non-modified cellulose [97]. In the case mentioned above, an increase in the amount of Ga loading (5 %wt) apparently resulted in a slight decrease in the catalytic activity. It was noticed that the activity went to a maximum with the certain amount of Ga loading (2 %wt). Besides, for cellulose-Ga-2 wt% gives better activity than the homogenous one. This may be suggested that the cellulose can improve distribution of active site and prohibit the formation of $ZrCH_2CH_2Zr$ species, which is formed via bimolecular process. Hence, ethylene/1-hexene can adsorb on active site easier. This suggests that the existence of an optimum surface acidity level beyond which zirconocene becomes unable to drive efficiently the polymerization of ethylene. These results are consistent with the observations by Miyazaki *et al.* [98] and Sano *et al.* [99]. With all results mentioned above, it can be concluded that Ga is more appropriate to use as acidic modifier on the cellulose support.

4.2.3 Characterization of polymer

4.2.3.1 The effect of cellulose modified support on the morphologies of copolymers

The morphology of the synthesized LLDPE/cellulose composites has been observed by a scanning electron microscope (SEM). SEM micrographs for the copolymers produced via the homogenous and the heterogeneous catalytic system are shown in **Figure 4.13**. It can be observed that the morphologies of LLDPE produced via the heterogeneous system are different from pure LLDPE. All the LLDPE/cellulose composites show a mixed type of morphology consisting of a growth of polymer chains on the cellulose surface and cellulose particles, as the cellulose particle coexist with LLDPE matrix. Considering the effect of acidic-modification on morphology, the results indicated that LLDPE/modified cellulose composites and LLDPE/non-modified cellulose composites exhibited the similar morphology. It can be concluded that there was no significant change in polymer morphologies upon various modified cellulose supports used.

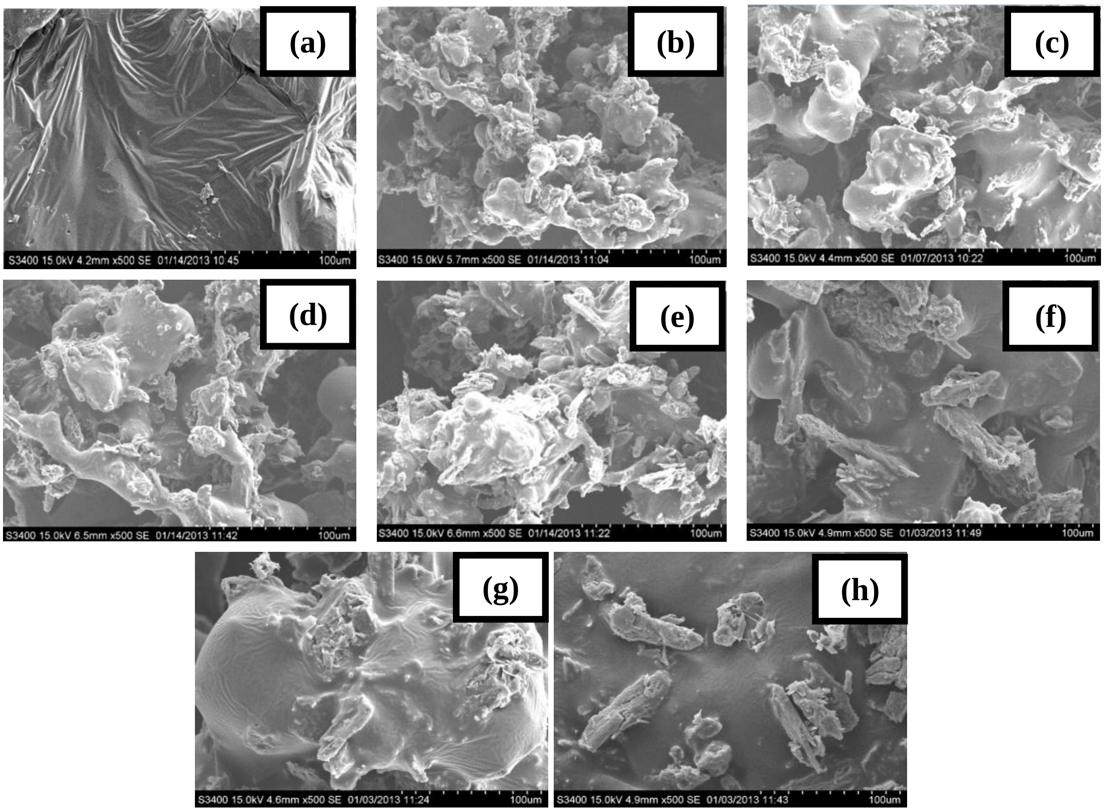


Figure 4.13 Morphologies of polymers obtained from the various modified cellulose (a) LLDPE (b) LLDPE/non-modified cellulose (c) LLDPE/cellulose-B-1% (e) LLDPE/cellulose-B-2% (e) LLDPE/cellulose-B-5% (f) LLDPE/cellulose-Ga-1% (g) cellulose-Ga-2% (h) LLDPE/cellulose-Ga-5%

4.2.3.2 The effect of cellulose modified support on melting temperature of polymers

Table 4.5 Melting and crystallization behavior

Polymer Samples	**T_m[a] (°C)**	**ΔH_{exp}[b](J/g)**	**X_c[c] (%)**
Homogenous	112	3	1
Non-modified cellulose	114	53	19
Cellulose -BCl_3 -1%	114	97	34
Cellulose -BCl_3 -2%	105	46	16
Cellulose -BCl_3 -5%	116	84	29
Cellulose -Ga -1%	115	98	34
Cellulose -Ga -2%	n.o.	n.o.	n.o.
Cellulose -Ga -5%	102	52	18

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

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

[c] Crystallinity (X_c) was calculated from equation in **Appendix B**

n.o. refers to not observe

Appendix C. shows the DSC curves that correspond to heating on the scan analysis of pure LLDPE, LLDPE/non-modified cellulose composites and LLDPE/ modified cellulose composites. Table 4.5 summarizes the thermal properties obtained from this scan. From DSC analysis, it can be observed that there was no significant change in T_m. The melting temperature for all samples had a value in the range of 102-116 ^{o}C. By adding cellulose (non-modified cellulose and modified cellulose) to the LLDPE, an increase in crystallization enthalpy (ΔH_{exp}) was observed when compared with unfilled LLDPE. The absence of T_m of the copolymer obtained from the cellulose-Ga-2% indicating that noncrystalline polymer was produced upon high degree of 1-hexene incorporates [63]. All results mentioned above, it can be concluded that the content of cellulose (non-modified cellulose and modified cellulose) influenced the crystallization of polymer, but did not affect on melting temperature.

CHAPTER V

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

In the first part, coir dust and cellulose were used as filler for polyethylene composite obtained via *in situ* polymerization with zirconocene/MAO catalyst. It was found that the cellulose exhibited higher activity due to the larger particle size of coir dust may interact more with MAO resulting in reduced activities. The enhanced catalytic activity can be achieved via increasing at the amount of cellulose; the catalytic activity of loading of 30 %wt cellulose shows the highest activity. On the other hand, the catalytic activities were decreased with increasing coir dust loading. The melting temperature of ethylene polymerization ranged between 131-137 °C. The 30 %wt cellulose supported system gave the highest crystallinity of polymer.

In the second part, the LLDPE/cellulose composites were produced via *in situ* polymerization of ethylene/1-hexene with zirconocene/MAO catalyst using cellulose supports having different acidic modification. The Ga modified cellulose gave the higher activity than that of the non-modified one. This was suggested that the acidity obtained from the introduction of Ga on the cellulose surface would play an important role on the higher formation of the active centers. The polymerization activities obtained from cellulose-Ga-2% exhibited the highest activity among the cellulose having Ga modification. Conversely, the B modified cellulose gave lower activity than that of the non-modified one. Considering the morphologies of copolymers, it can be observed that the morphologies of LLDPE produced via the heterogeneous system are different from pure LLDPE. However, there was no significant change in the melting temperature upon all systems. By adding cellulose to the LLDPE, an increase in crystallization enthalpy (ΔH_{exp}) was observed when compared with unfilled LLDPE. It can be concluded that the content of cellulose influenced the crystallization of polymer, but did not affect on melting temperature.

5.2 Recommendations

- Polymers and copolymers should be further determined other main properties for any application such as molecular weight, molecular weight distribution, and mechanical properties.
- Investigation of other modifier should be studied.
- Investigation of other organic supports should be studied.
- Effect of Lewis acids on the polymerization reaction without cocatalyst should be investigated.

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APPENDICES

APPENDIX A

(CALCULATION OF SUPPORT PREPARATION))

A.1 Calculation of support composition (Cellulose-Ga)

A.1.1 Preparation of 1.0% Ga-modified cellulose by the incipient wetness impregnation method are shown as follows:

Reagent: - Gallium(III) nitrate hydrate $Ga(NO_3)_3$
Molecular weight = 255.74 g/mol
- Support: - Cellulose

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:
Gallium = 1.0 g
Cellulose = 100 – 1.0 = 99.0 g

For 1 g of cellulose support
Gallium required = 1x(1.0/99.0) = 0.0101 g

Gallium 0.0101 g was prepared from $Ga(NO_3)_3$ and molecular weight of Ga is 69.72

$$Ga(NO_3)_3 \text{ required} = \frac{\text{MW of Ga (NO 3)3 X Gallium Required}}{\text{MW of Ga}}$$

$$= (255.74/69.72)\text{x}0.0101 = 0.0370 \text{ g}$$

A.1.2 Preparation of 2.0% Ga-modified cellulose by the incipient wetness impregnation method are shown as follows:

Reagent: - Gallium(III) nitrate hydrate $Ga(NO_3)_3$
Molecular weight = 255.74 g/mol
- Support: - Cellulose

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:
Gallium = 2.0 g
Cellulose = 100 – 2.0 = 98.0 g

For 1 g of cellulose support
Gallium required = 1x(2.0/98.0) = 0.0204 g

Gallium 0.0204 g was prepared from $Ga(NO_3)_3$ and molecular weight of Ga is 69.72

$$Ga(NO_3)_3 \text{ required} = \frac{\text{MW of Ga (NO 3)3 X Gallium Required}}{\text{MW of Ga}}$$

$$= (255.74/69.72)\text{x}0.0204 = 0.0748 \text{ g}$$

A.1.3 Preparation of 5.0% Ga-modified cellulose by the incipient wetness impregnation method are shown as follows:

Reagent: - Gallium(III) nitrate hydrate $Ga(NO_3)_3$
Molecular weight = 255.74 g/mol
- Support: - Cellulose

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Gallium = 5.0 g
Cellulose = 100 – 5.0 = 95.0 g

For 1 g of cellulose support
Gallium required = 1x(5.0/95.0) = 0.0526 g

Gallium 0.0526 g was prepared from $Ga(NO_3)_3$ and molecular weight of Ga is 69.72

$$Ga(NO_3)_3 \text{ required} = \frac{\text{MW of Ga (NO 3)3 X Gallium Required}}{\text{MW of Ga}}$$

$$= (255.74/69.72)\text{x}0.0526 = 0.1929 \text{ g}$$

A.2 Calculation of support composition (Cellulose-B)

A.2.1 Preparation of 1.0% B-modified cellulose by the incipient wetness impregnation method are shown as follows:

Reagent: - Boron(III)Chloride BCl_3, 1 M in hexanes
Molecular weight = 117.16 g/mol
- Support: - Cellulose

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:
Boron = 1.0 g
Cellulose = 100 – 1.0 = 99.0 g

For 1 g of cellulose support
Boron required = 1x(1.0/99.0) = 0.0101 g

Boron 0.0101 g was prepared from BCl_3 and molecular weight of B is 10.81

$$BCl_3 \text{ required} = \frac{\text{MW of BCl 3 X Boron Required}}{\text{MW of Boron}}$$

$$= (117.16/10.81)\text{x}0.0101 = 0.1095 \text{ g.}$$

$$\frac{0.1095 \text{ g.}BCl_{3\text{required}}}{} \left| \frac{1000 \text{ ml}}{117.16 \text{ g.}BCl_3} \right. = 0.9346 \text{ ml } BCl_{3\text{required}}$$

A.2.2 Preparation of 2.0% B-modified cellulose by the incipient wetness impregnation method are shown as follows:

Reagent: - Boron(III)Chloride BCl_3, 1 M in hexanes
Molecular weight = 117.16 g/mol
- Support: - Cellulose

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:
Boron = 1.0 g
Cellulose = 100 – 2.0 = 98.0 g

For 1 g of cellulose support
Boron required = 1x(2.0/98.0) = 0.0204 g

Boron 0.0204 g was prepared from BCl_3 and molecular weight of B is 10.81

$$BCl_3\ \text{required} = \frac{\text{MW of BCl 3 X Boron Required}}{\text{MW of Boron}}$$

$$= (117.16/10.81)\text{x}0.0204 = 0.2211\ \text{g.}$$

$$\begin{array}{l|l} 0.2211\ \text{g.}BCl_{3\text{required}} & 1000\ \text{ml} \\ \hline & 117.16\ \text{g.}BCl_3 \end{array} = 1.8872\ \text{ml}\ BCl_{3\text{required}}$$

A.2.3 Preparation of 5.0% B-modified cellulose by the incipient wetness impregnation method are shown as follows:

Reagent: - Boron(III)Chloride BCl_3, 1 M in hexanes
Molecular weight = 117.16 g/mol
- Support: - Cellulose

Based on 100 g of catalyst used, the composition of the catalyst will be as follows:

Boron = 5.0 g
Cellulose = 100 – 5.0 = 95.0 g

For 1 g of cellulose support
Boron required = 1x(5.0/95.0) = 0.0526 g

Boron 0.0526 g was prepared from BCl_3 and molecular weight of B is 10.81

$$BCl_3\ \text{required} = \frac{\text{MW of BCl 3 X Boron Required}}{\text{MW of Boron}}$$

$$= (117.16/10.81)\text{x}0.0526 = 0.5701\ \text{g.}$$

$$\begin{array}{l|l} 0.5701\ \text{g.}BCl_{3\text{required}} & 1000\ \text{ml} \\ \hline & 117.16\ \text{g.}BCl_3 \end{array} = 4.8660\ \text{ml}\ BCl_{3\text{required}}$$

APPENDIX B

(CALCULATION OF POLYMER PROPERTIES)

B.1 Calculation of crystallinity of polymer

The crystallinities of polymers were determined by differential scanning calorimeter (DSC). The % crystallinity of polymers is calculated from the following equation.

$$\%\ \text{crystallinity} = (\Delta H_{\text{sample}} / \Delta H_{100\ \%\ \text{crystalline}}) \times 100$$

Where ΔH_{sample} = the heat fusion of sample (J/g)

$\Delta H_{100\%\ \text{crystalline}}$ = the heat fusion of perfectly crystalline polyethylene (286 J/g)

APPENDIX C

(DIFFERENTIAL SCANNING CALORIMETER)

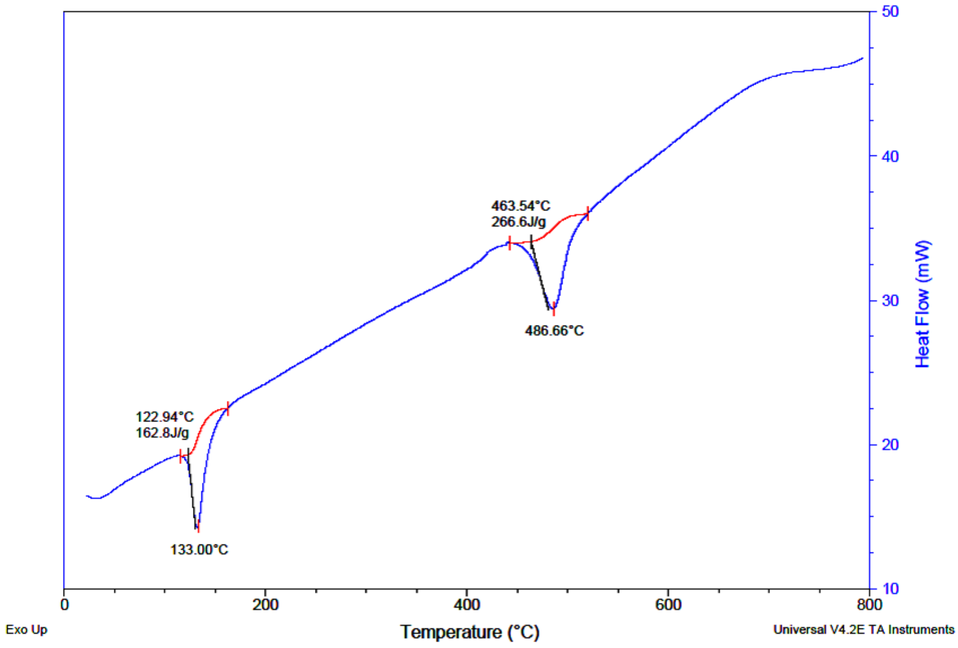

Figure C-1. DSC curve of polyethylene obtained from the homogeneous catalytic system

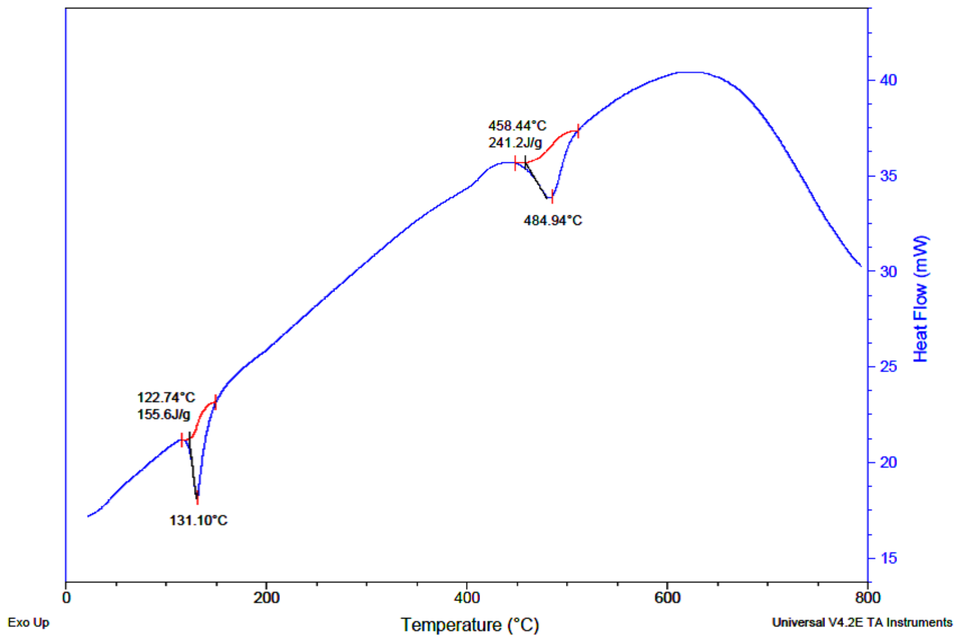

Figure C-2. DSC curve of polyethylene produce with 10 %wt of coir dust

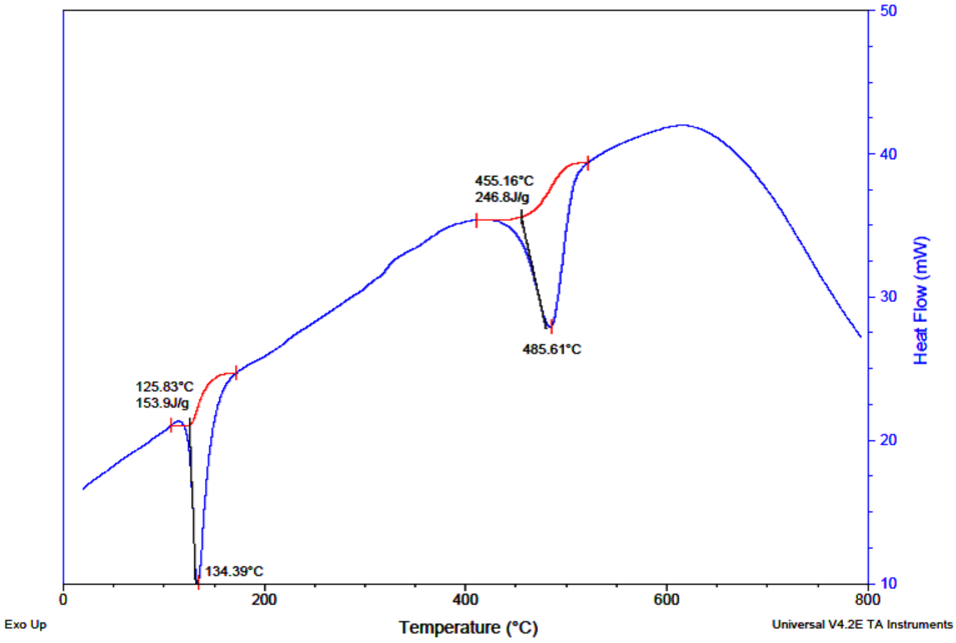

Figure C-3. DSC curve of polyethylene produce with 20 %wt of coir dust

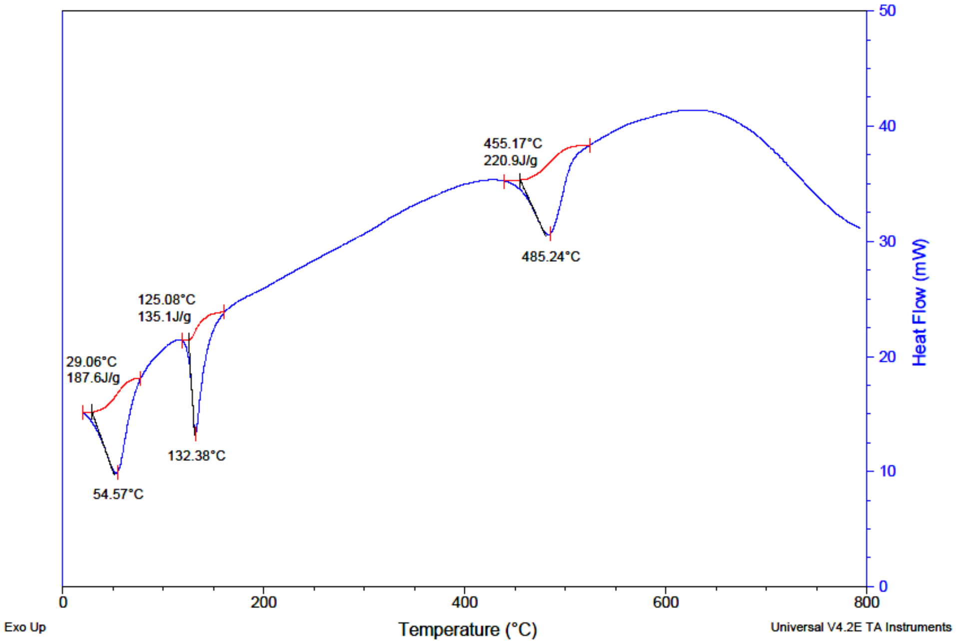

Figure C-4. DSC curve of polyethylene produce with 30 %wt of coir dust

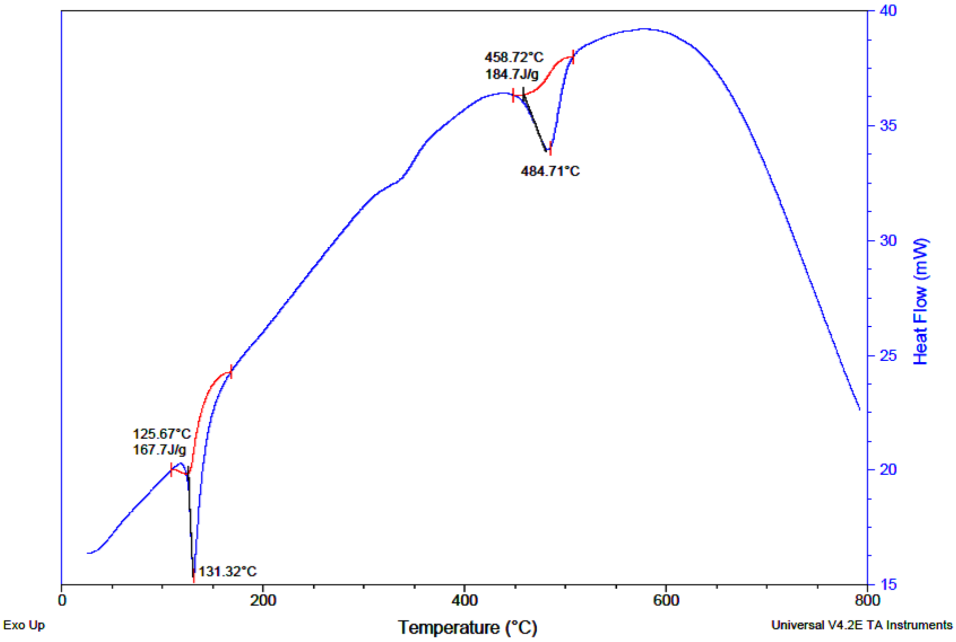

Figure C-5. DSC curve of polyethylene produce with 10 %wt of cellulose

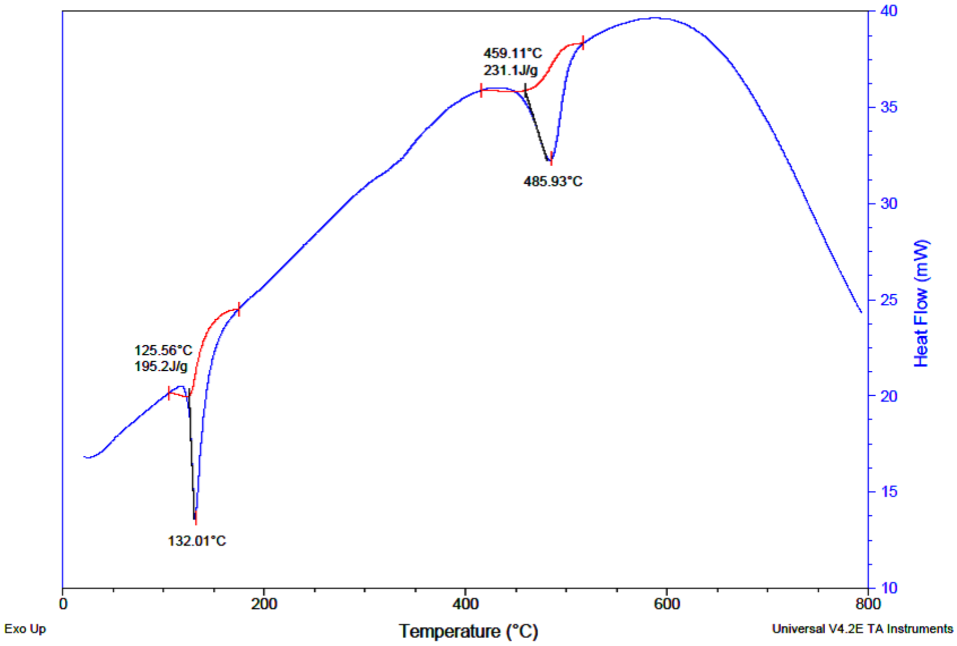

Figure C-6. DSC curve of polyethylene produce with 20 %wt of cellulose

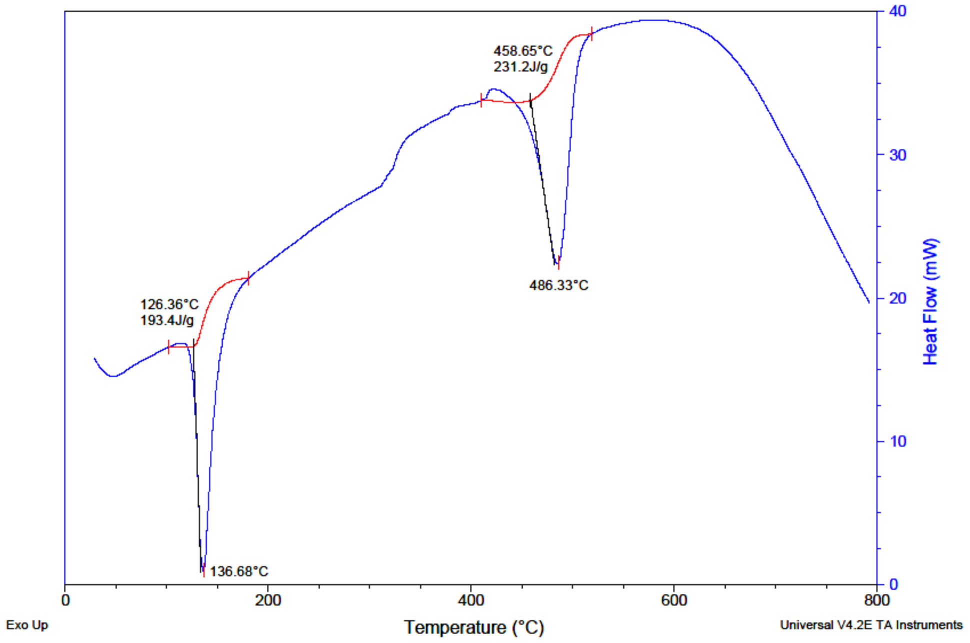

Figure C-7. DSC curve of polyethylene produce with 30 %wt of cellulose

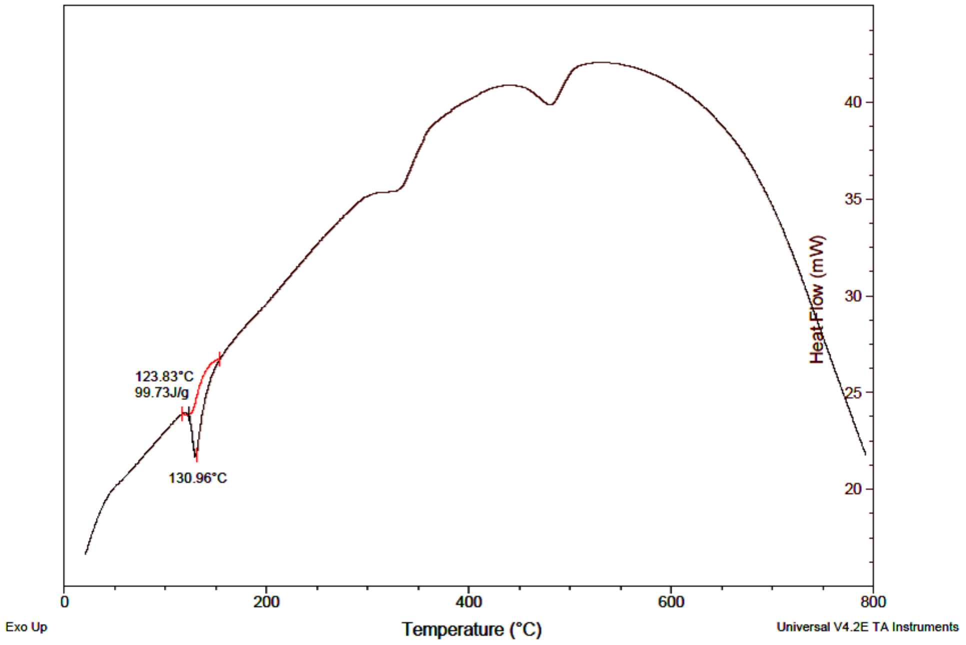

Figure C-8. DSC curve of polyethylene produce with 40 %wt of cellulose

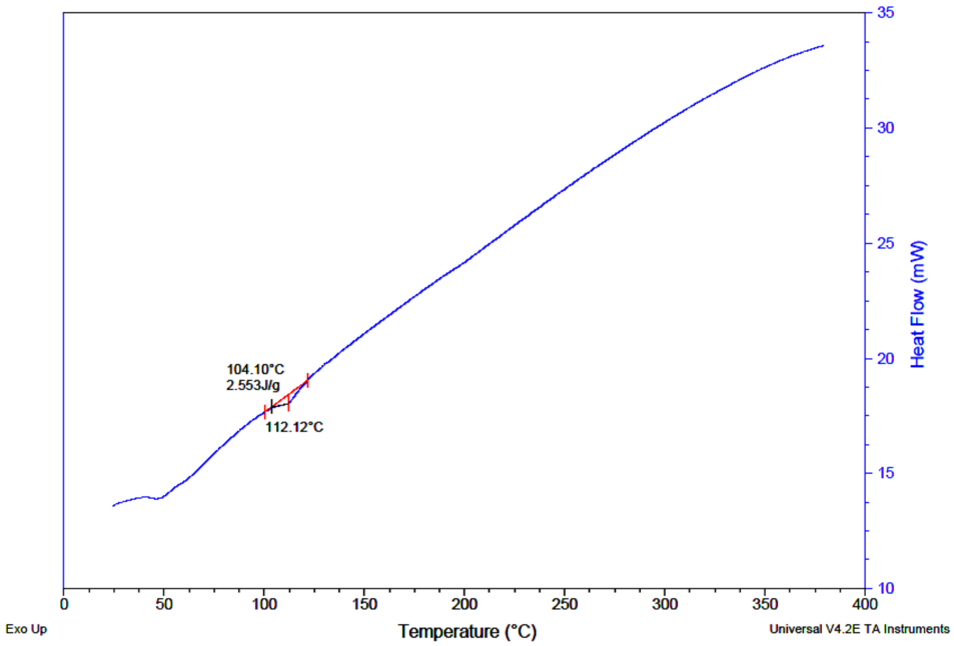

Figure C-9. DSC curve of ethylene/1-hexene copolymer obtained from the homogeneous catalytic system

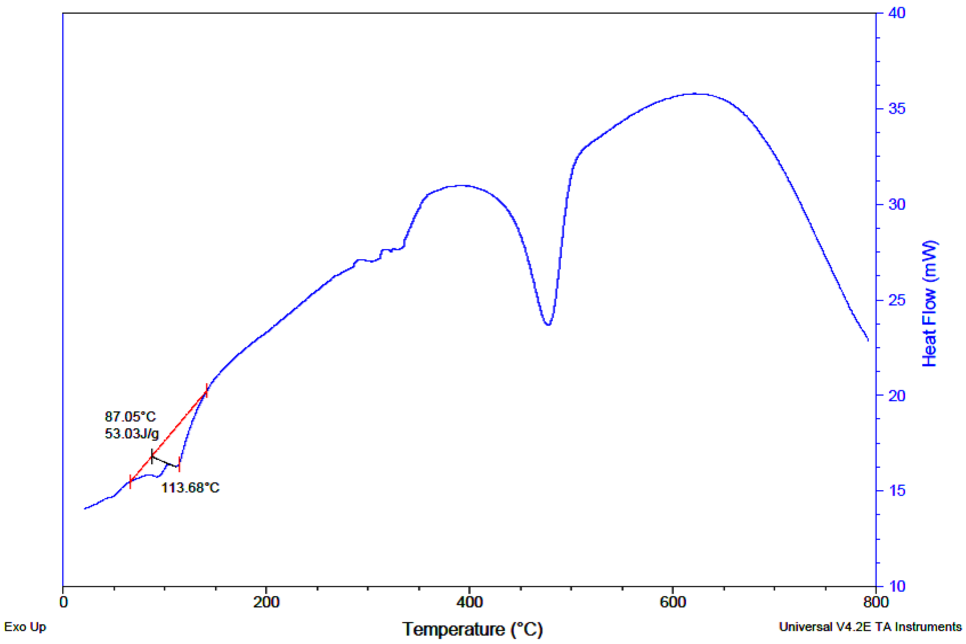

Figure C-10. DSC curve of ethylene/1-hexene copolymer produce with non-modified cellulose

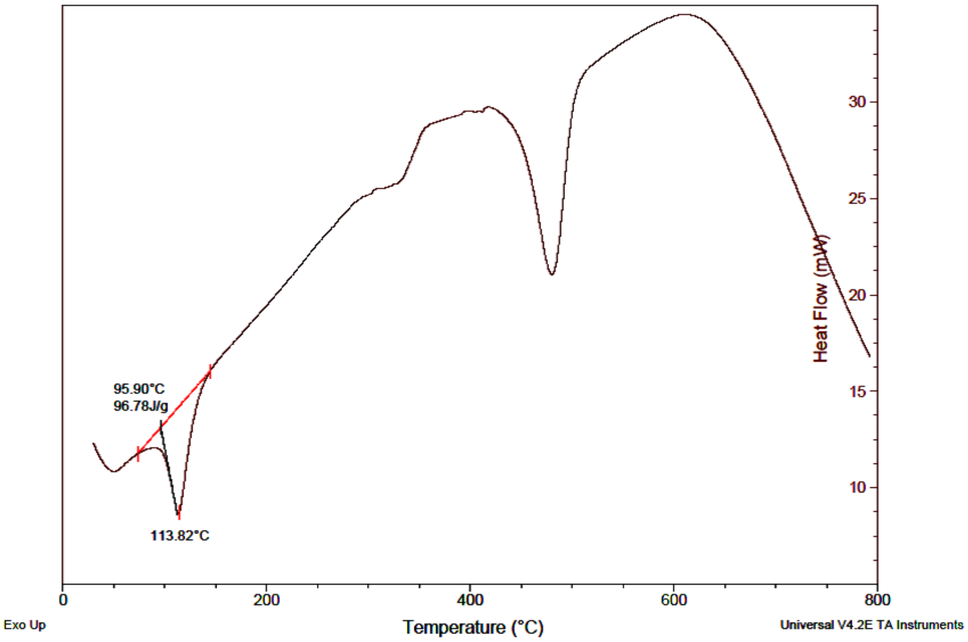

Figure C-11. DSC curve of ethylene/1-hexene copolymer produce with cellulose-B-1%

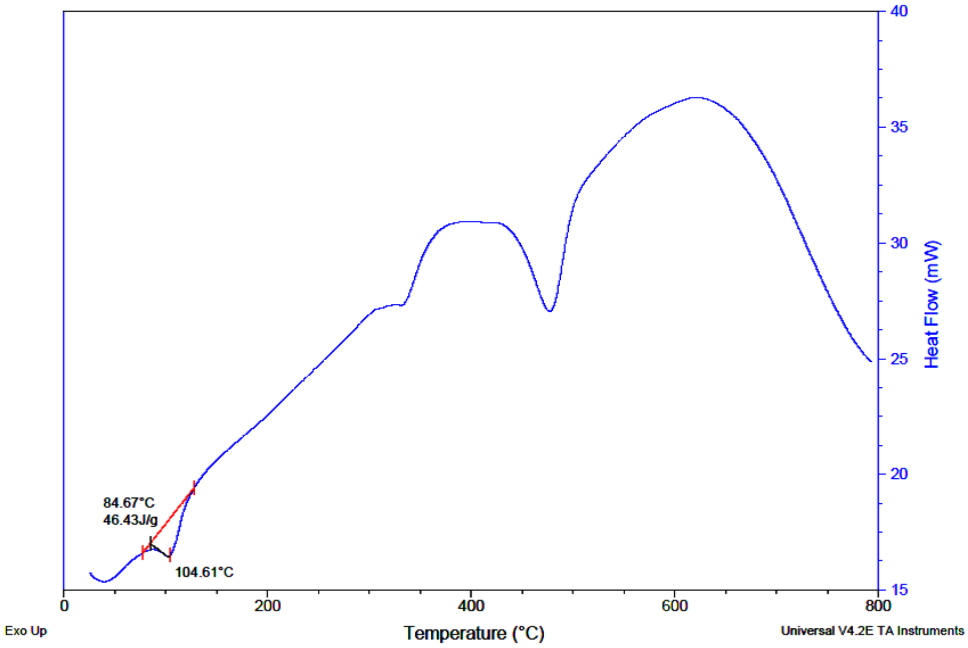

Figure C-12. DSC curve of ethylene/1-hexene copolymer produce with cellulose-B-2%

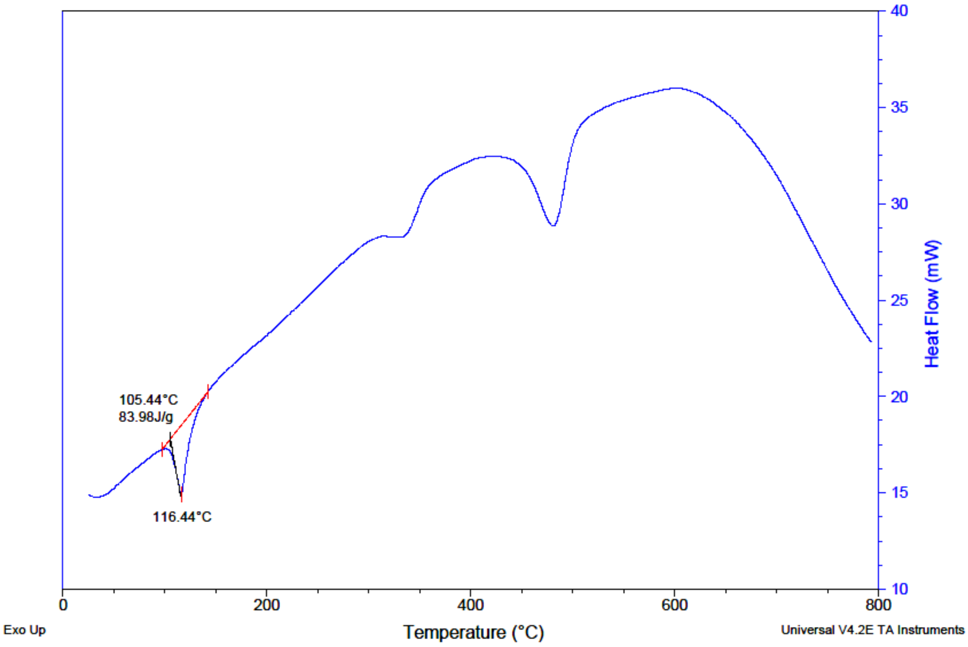

Figure C-13. DSC curve of ethylene/1-hexene copolymer produce with cellulose-B-5%

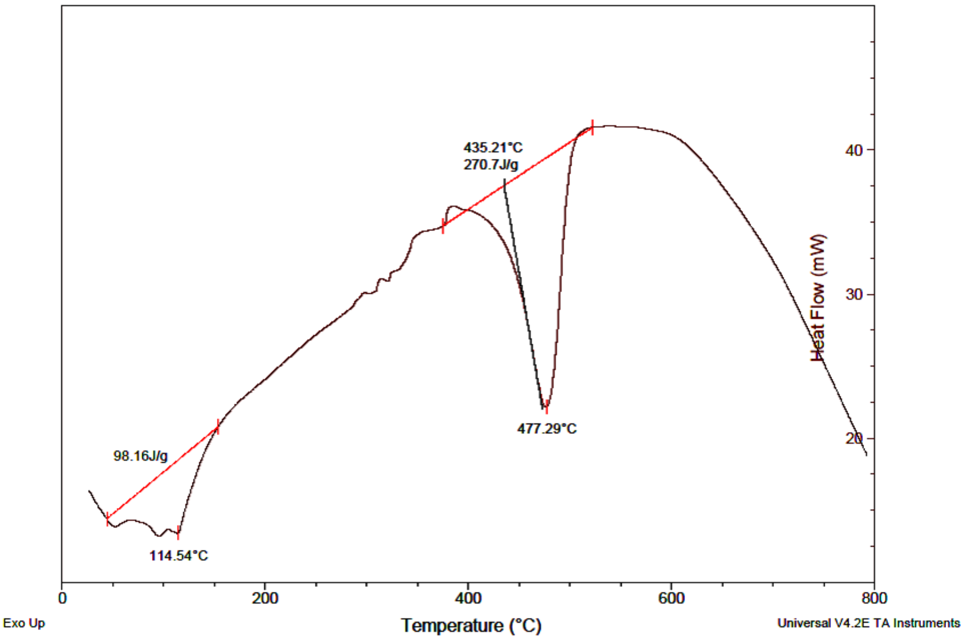

Figure C-14. DSC curve of ethylene/1-hexene copolymer produce with cellulose-Ga-1%

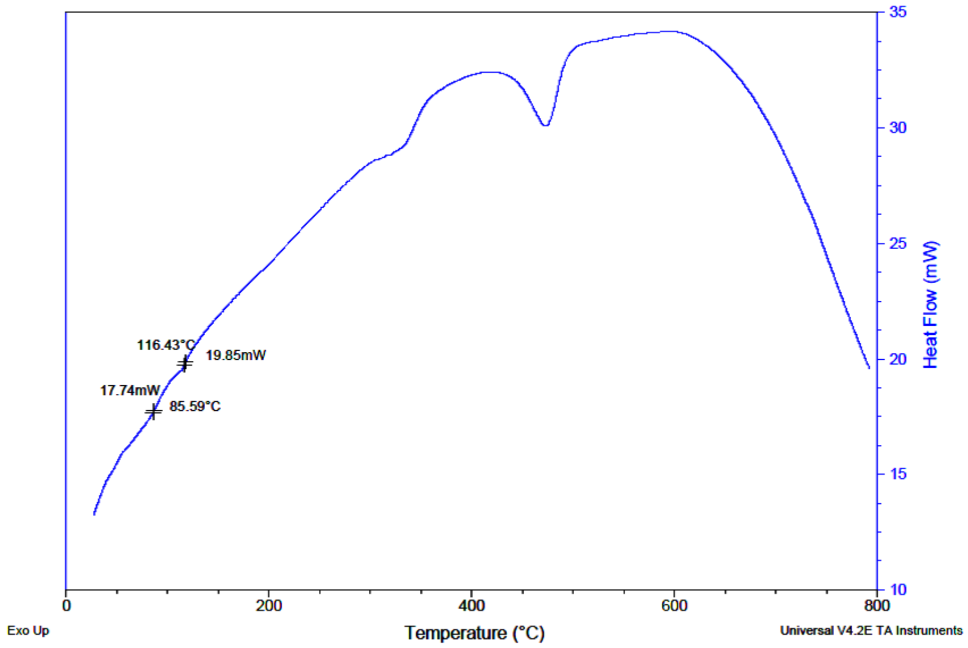

Figure C-15. DSC curve of ethylene/1-hexene copolymer produce with cellulose-Ga-2%

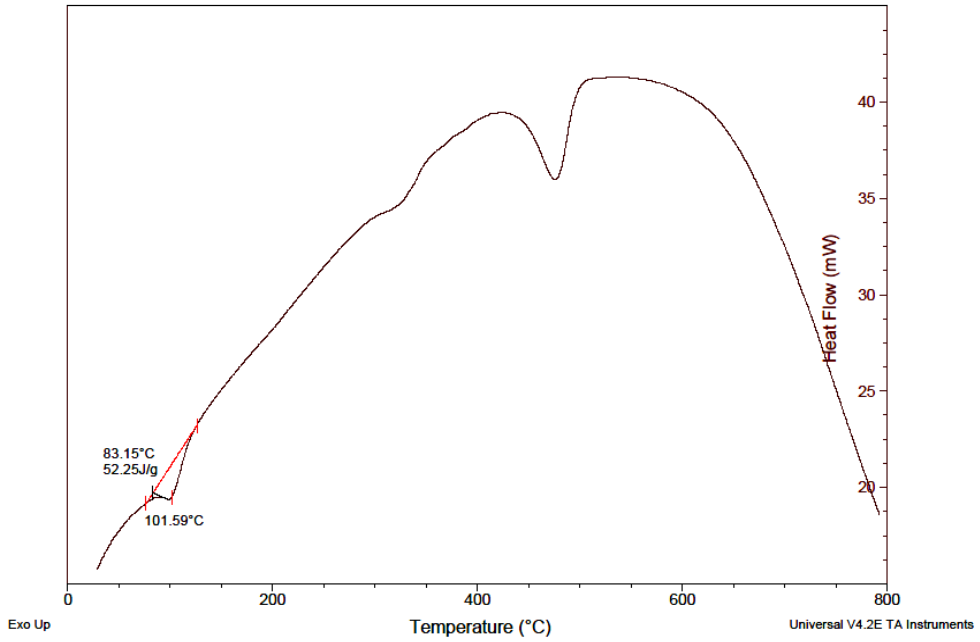

Figure C-16. DSC curve of ethylene/1-hexene copolymer produce with cellulose-Ga-5%

APPENDIX D

(ENERGY DISPERSIVE X-RAY SPECTTROSCOPY)

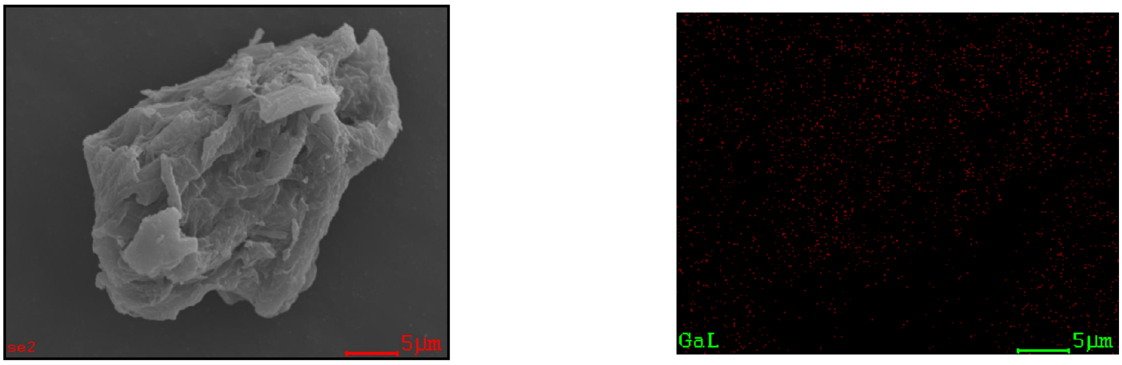

Figure D-1 SEM/EDX mapping for Ga distribution of modified cellulose with the gallium content of 1 %wt

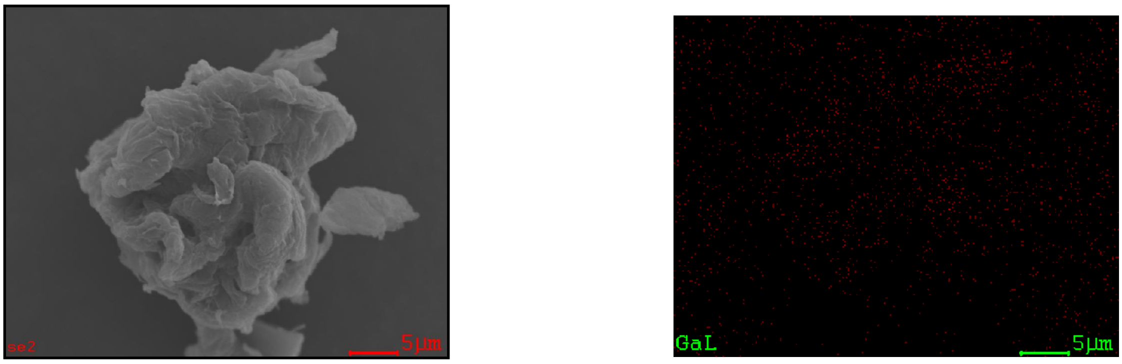

Figure D-2 SEM/EDX mapping for Ga distribution of modified cellulose with the gallium content of 2 %wt

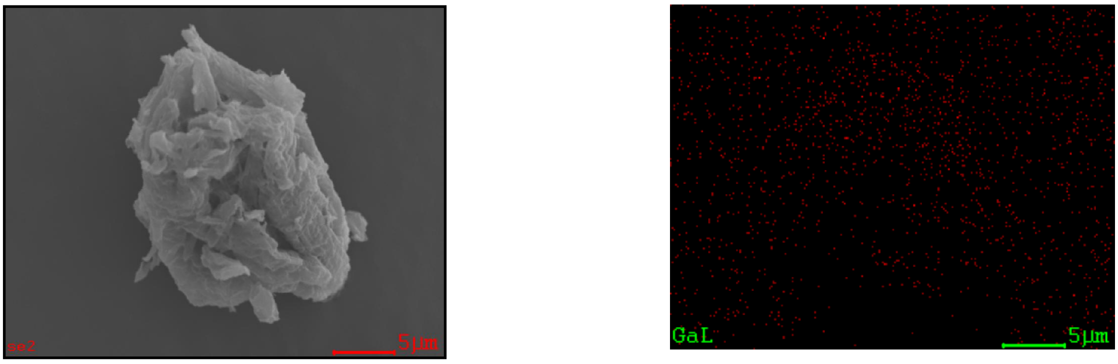

Figure D-3 SEM/EDX mapping for Ga distribution of modified cellulose with the gallium content of 5 %wt

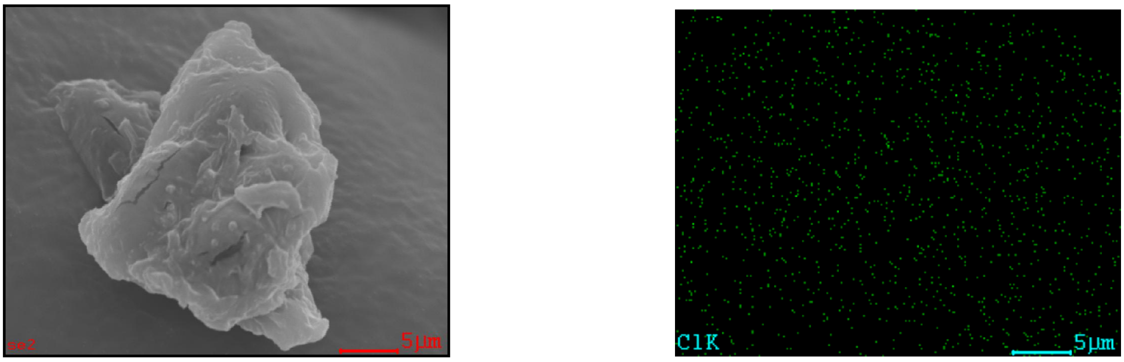

Figure D-4 SEM/EDX mapping for Cl distribution of modified cellulose with the boron content of 1 %wt

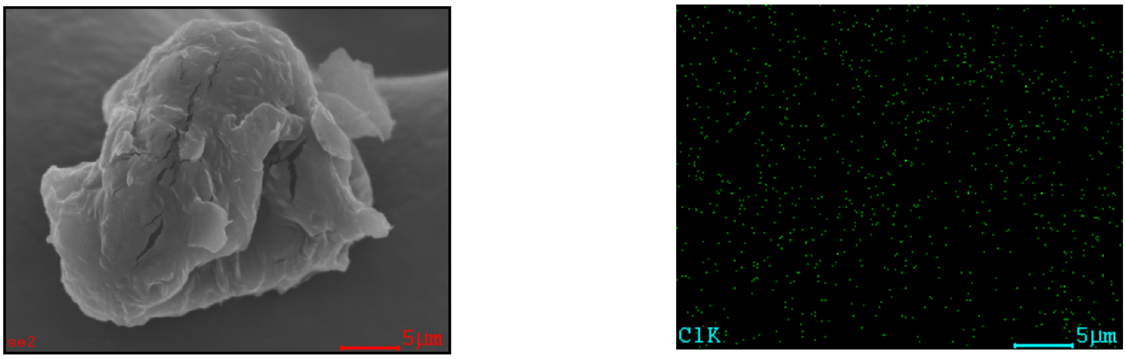

Figure D-5 SEM/EDX mapping for Cl distribution of modified cellulose with the boron content of 2 %wt

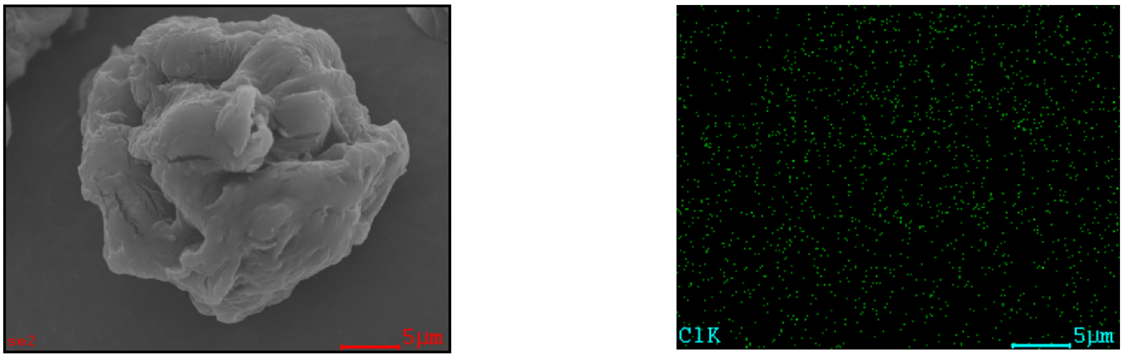

Figure D-6 SEM/EDX mapping for Cl distribution of modified cellulose with the boron content of 5 %wt

APPENDIX E

(FOURIER TRANSFORMS INFRARED SPECTROSCOPY)

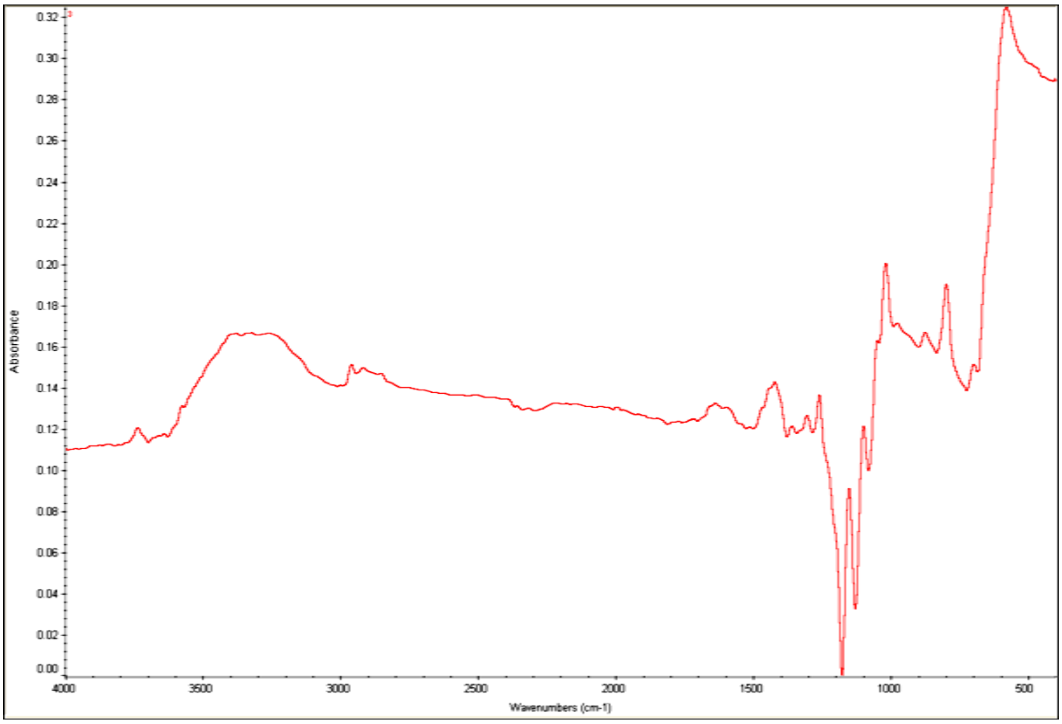

Figure E-1 FT-IR spectra of modified cellulose with the boron content of 1 %wt

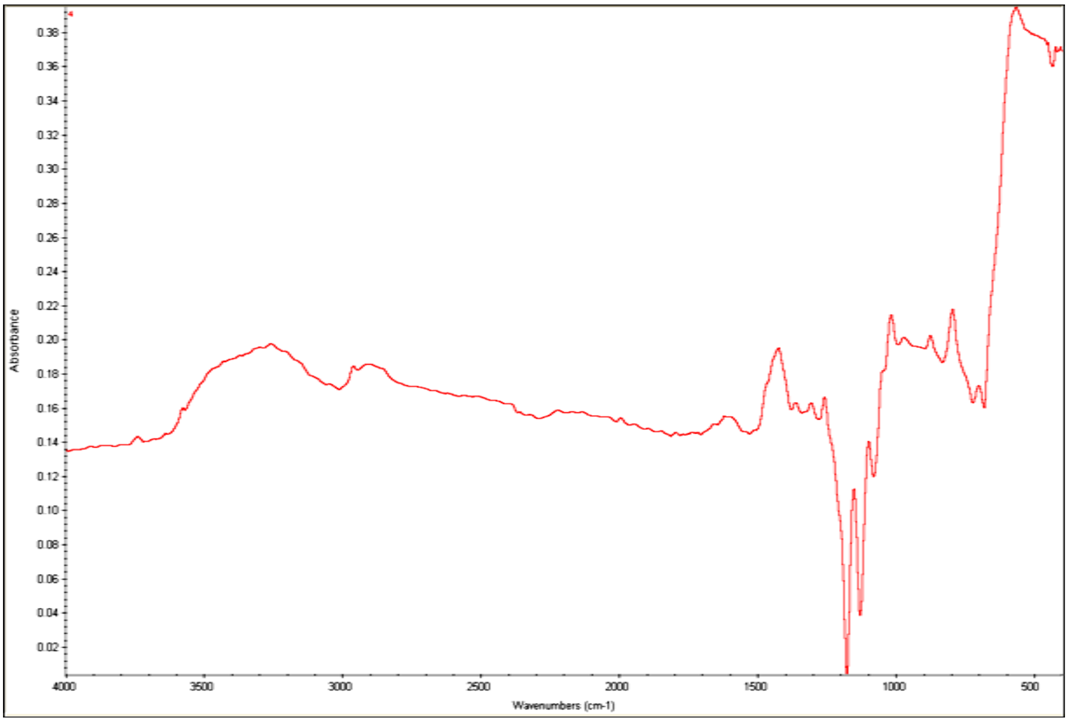

Figure E-2 FT-IR spectra of modified cellulose with the boron content of 2 %wt

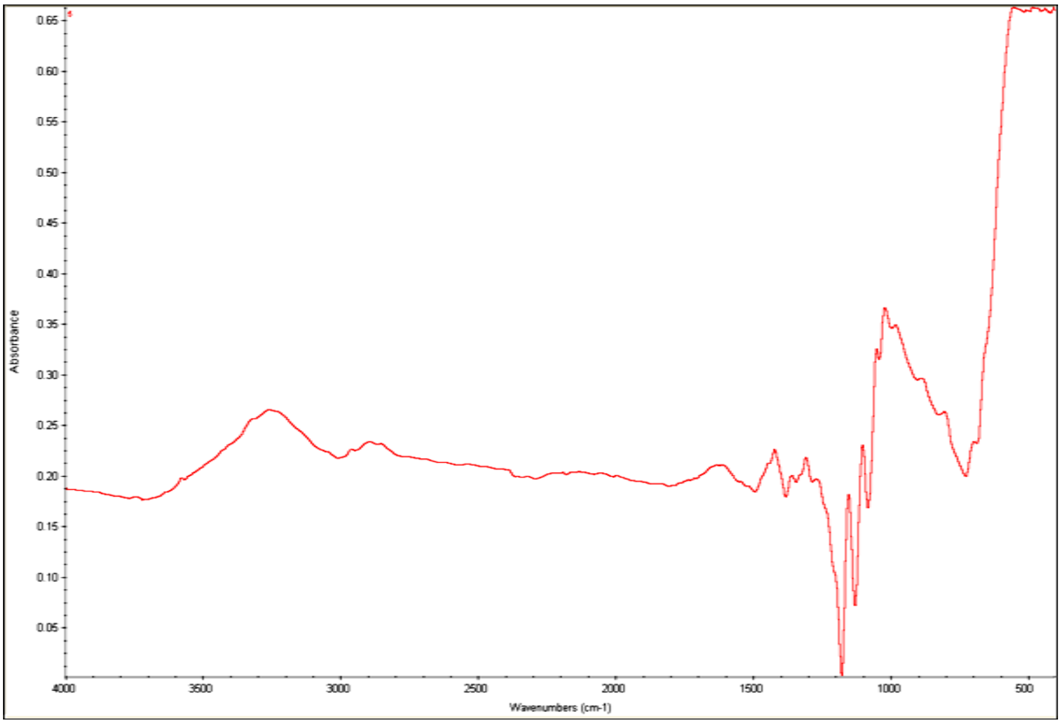

Figure E-3 FT-IR spectra of modified cellulose with the boron content of 5 %wt

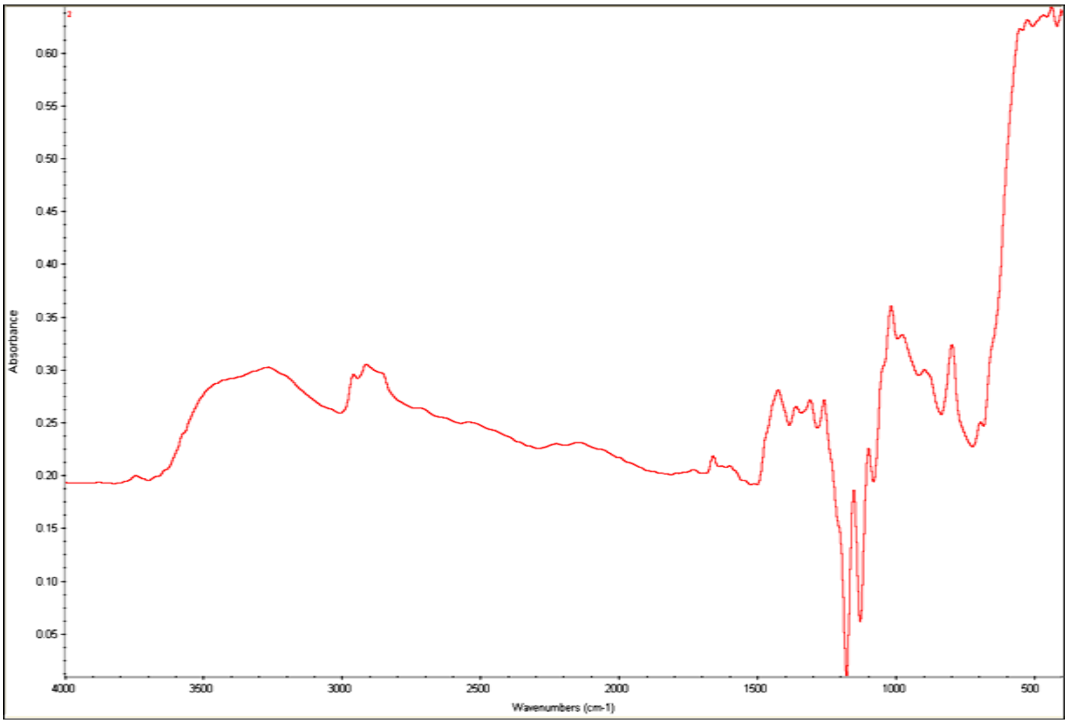

Figure E-4 FT-IR spectra of modified cellulose with the gallium content of 1 %wt

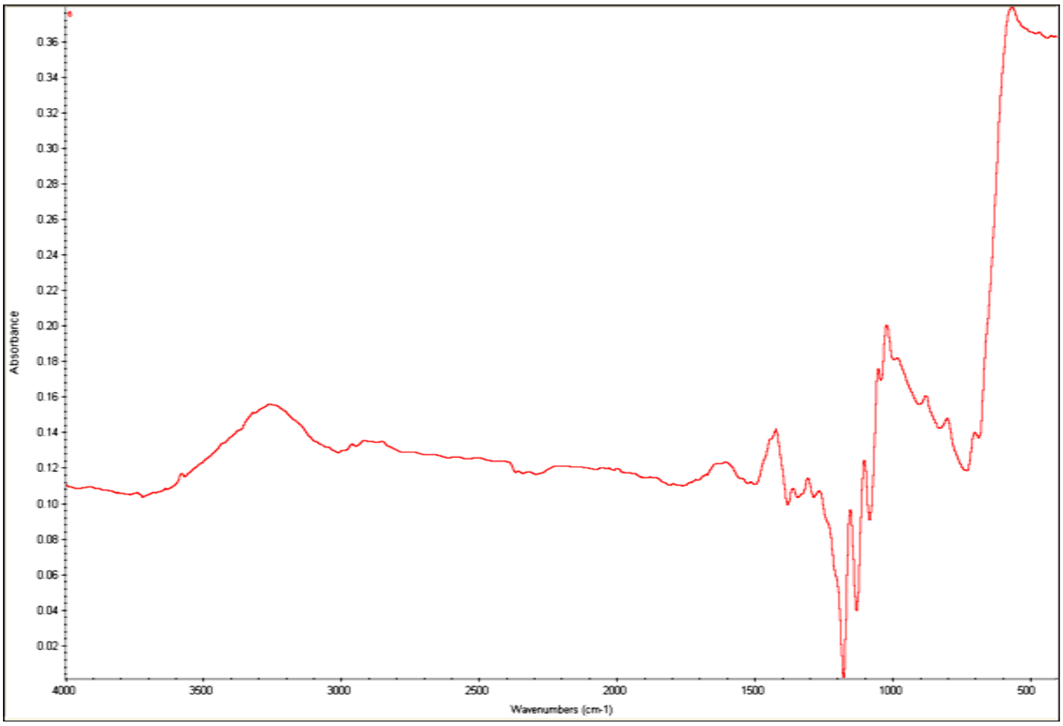

Figure E-5 FT-IR spectra of modified cellulose with the gallium content of 2 %wt

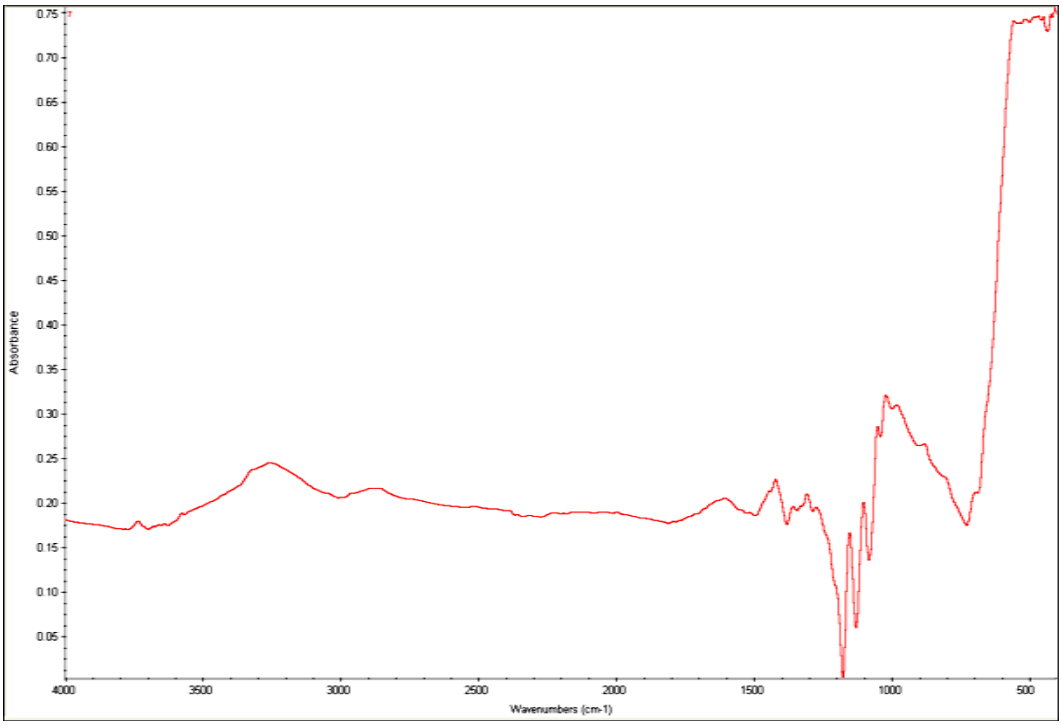

Figure E-6 FT-IR spectra of modified cellulose with the gallium content of 5 %wt

APPENDIX F

(LIST OF PUBLICATION)

- Suttivutnarubet, C., Yokkloy, T., Chaichana, E., Jongsomjit, B. “Synthesis of coir-dust/PE composites via in situ polymerization with metallocene/MAO catalyst” Proceedings of Pure and Applied Chemistry International Conference (PACCON 2013) 23 - 25 January 2013; The Tide Resort, Chonburi, Thailand.

VITA

Miss Chatuma Suttivutnarubet was born on April 28, 1989 in Bangkok, Thailand. She received the Bachelor's Degree of Chemical Engineering from the Department of Chemical Engineering, Faculty of Engineering, Srinakharinwirot University in April 2011. She continued her Master's degree in Chemical Engineering, Chulalongkorn University under the Catalysis and Catalytic Reaction Engineering group in June, 2011.