ผลิตภัณฑ์เชื้อเพลิงและวัสดุเชิงประกอบจากการแปรสภาพทางเคมีความร้อนของเศษพลาสติกประเภทเทอร์มอเซตเสริมแรงด้วยเส้นใยแก้ว

นางสาวแก้ว แซ่เตียว

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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ปีการศึกษา 2554

FUEL AND COMPOSITE PRODUCTS FROM THERMOCHEMICAL CONVERSION OF GLASS FIBER REINFORCED THERMOSET PLASTIC WASTE

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Materials Science
Department of Materials Science
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Thesis Title	FUEL AND COMPOSITE PRODUCTS FROM THERMOCHEMICAL CONVERSION OF GLASS FIBER REINFORCED THERMOSET PLASTIC WASTE
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Field of Study	Materials Science
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แก้ว แซ่เตียว : ผลิตภัณฑ์เชื้อเพลิงและวัสดุเชิงประกอบจากการแปรสภาพทางเคมีความร้อนของเศษพลาสติกประเภทเทอร์มอเซตเสริมแรงด้วยเส้นใยแก้ว. (FUEL AND COMPOSITE PRODUCTS FROM THERMOCHEMICAL CONVERSION OF GLASS FIBER REINFORCED THERMOSET PLASTIC WASTE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ดวงดาว อาจองค์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ. ดร. วิบูลย์ ศรีเจริญชัยกุล, ดร. ดวงเดือน อาจองค์, 125 หน้า

งานวิจัยนี้ศึกษาการแปรสภาพทางเคมีความร้อนของเศษวัสดุเชิงประกอบพอลิเอสเทอร์ชนิดไม่อิ่มตัวและอิพอกซีเสริมแรงด้วยเส้นใยแก้วร้อยละ 30 และ 60 โดยน้ำหนัก โดยชนิดของเรซินที่แตกต่างกันประกอบด้วยออร์โทพทาลิก ไอโซพทาลิก และไวนิลเอสเทอร์ และอิพอกซีเรซินทีบ่มด้วยแอมีน (MDA) และแอนไฮไดรด์ (MTHPA) โดยศึกษาพฤติกรรมทางความร้อนและจลนพลศาสตร์ด้วยเครื่องเทอร์โมกราวิเมตริกแอนาไลเซอร์ ผลการทดลองพบว่าพฤติกรรมทางความร้อนของเศษวัสดุเชิงประกอบขึ้นอยู่กับโครงสร้างทางเคมีของเรซินและปริมาณเส้นใยแก้ว โดยพบว่าค่าพลังงานกระตุ้น (E_a) ของเศษวัสดุเชิงประกอบพอลิเอสเทอร์ชนิดไม่อิ่มตัวและอิพอกซีอยู่ในช่วง 177-204 และ 179-195 กิโลจูลต่อโมล ตามลำดับ โดยไวนิลเอสเทอร์มีค่าพลังงานกระตุ้นสูงที่สุดเนื่องจากในโครงสร้างเป็นเส้นตรงที่ประกอบด้วยบิสฟีนอลเอในสายโซ่หลักซึ่งมีเสถียรภาพต่อความร้อนดี การเพิ่มขึ้นของปริมาณเส้นใยแก้วมีผลทำให้ค่าพลังงานกระตุ้นของการสลายตัวของเศษวัสดุเชิงประกอบลดลง จากการไพโรไลซิสเศษวัสดุเชิงประกอบที่อุณหภูมิสุดท้าย 600 700 และ 800 องศาเซลเซียสในเตาปฏิกรณ์แบบเบดนิ่งภายใต้บรรยากาศไนโตรเจน พบว่าที่อุณหภูมิ 600 และ 800 องศาเซลเซียส เกิดผลิตภัณฑ์ของเหลวและแก๊สมากที่สุดตามลำดับ ส่วนผลิตภัณฑ์ของแข็งมีสัดส่วนมากที่สุดที่อุณหภูมิ 600 องศาเซลเซียสและประกอบด้วยเส้นใยแก้วเป็นส่วนใหญ่ซึ่งสามารถนำไปผลิตวัสดุเชิงประกอบใหม่ได้ ผลิตภัณฑ์ของเหลวประกอบด้วยสารประกอบของออกซิเจนที่มีสัดส่วนของแกโซลีนสูงซึ่งสามารถนำไปประยุกต์ใช้แทนน้ำมันดิบได้ ส่วนผลิตภัณฑ์แก๊สประกอบด้วยแก๊สคาร์บอนไดออกไซด์ (CO_2) และคาร์บอนมอนอกไซด์ (CO) เป็นส่วนใหญ่ แก๊สมีเทน (CH_4) และไฮโดรเจน (H_2) ในปริมาณเล็กน้อย สมบัติเชิงกลของเศษวัสดุเชิงประกอบที่เตรียมจากเส้นใยแก้วรีไซเคิลที่อุณหภูมิ 600 องศาเซลเซียสสามารถนำเส้นใยดังกล่าวไปใช้เป็นวัสดุเสริมแรงในการเตรียมวัสดุเชิงประกอบใหม่ได้โดยไม่มีผลอย่างมีนัยสำคัญต่อค่าความทนแรงกระแทกและความทนแรงดัดโค้งจนถึงอัตราส่วนของเส้นใยร้อยละ 5 และ 10 โดยน้ำหนัก ตามลำดับ

ภาควิชา ....วัสดุศาสตร์....... ลายมือชื่อนิสิต..

สาขาวิชา.......วัสดุศาสตร์....... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก................................

ปีการศึกษา ....2554....... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม................................

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม................................

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KEYWORDS: Thermochemical conversion/ Pyrolysis/ Unsaturated Polyester/ Epoxy composite waste/ Recycled glass fiber.

KAEW SAETIAW: FUEL AND COMPOSITE PRODUCTS FROM THERMO CHEMICAL CONVERSION OF GLASS FIBER REINFORCED THERMOSET PLASTIC WASTE. ADVISOR : ASSOC. PROF. DUANGDAO AHT-ONG, Ph.D, CO-ADVISOR : ASST. PROF. VIBOON SRICHAROENCHAIKUL, Ph.D, DUANGDUEN ATONG, Ph.D, 125 pp.

Study on thermochemical conversion of unsaturated polyester and epoxy composite wastes reinforced with 30 and 60 wt% glass fiber by pyrolysis process was carried out in this research. Different types of resin matrix consisted of orthophthalic, isophthalic unsaturated polyester, vinyl ester and epoxy cured with amine (MDA) and anhydride (MTHPA). Thermal behavior and kinetic parameters of the composite wastes were first investigated by Thermo gravimetric Analyzer (TGA). Results showed that thermal behavior of composite wastes significantly depended on their chemical structure and glass fiber content. The activation energy (E_a) for decomposition of unsaturated polyester and epoxy composite wastes were in the range of 177-204 and 179-195 KJ/mol, respectively. Vinyl ester showed highest E_a and good thermal stability structure due to the presence of bisphenol A in main chain and methacrylate at the end of vinyl ester backbone. Higher glass fiber content resulted in the decrease in activation energy for decomposition of composite wastes. The composite wastes were then pyrolyzed in a fixed bed reactor at final temperature of 600, 700 and 800ºC under nitrogen atmosphere. Pyrolysis temperature of 600ºC and 800ºC resulted in the highest fraction of liquid and gaseous products, respectively. The maximum solid fraction was obtained from pyrolysis temperature of 600ºC and mainly composed of glass fiber which was used to recycle by new composite preparation. The liquid products were comprised of oxygenated compounds with high fraction of gasoline which can be further applied as crude oil. The gaseous products largely consisted of carbon dioxide (CO_2) and carbon monoxide (CO), and some amount of methane (CH_4) and hydrogen (H_2). The mechanical properties of composites prepared from recycled glass fiber at temperature of 600ºC indicated that it can be used as reinforcement to prepare new composite with no significant effect on impact and flexural strength up to 5 and 10 wt%, respectively.

Department : Material Science Student' Signature
Field of Study : Material Science Advisor's Signature
Academic Year : 2011 Co-advisor's Signature
. Co-advisor's Signature

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CHARPTER I

INTRODUCTION

Currently, composite wastes have been increasing with the growing of composite industries such as automobile, chemical, and electrical industries with regard to their excellent properties, particularly in terms of high strength to weight ratio, high chemical and corrosion resistance, good thermal and electrical insulation, and high temperature performance. Glass fiber reinforced thermoset plastics such as epoxy and unsaturated polyester composites are popularly used for various applications such as insulation, chemical or electronic applications.

However, both epoxy and unsaturated polyester are thermoset plastics which hardly be recycled or remolded to other shapes by thermal process like thermoplastics because they are crosslinked with curing agent to form three dimensional network structure which neither fusible nor soluble. Furthermore, they are non biodegradable and not a combustible material because they are consisted of large amounts of inorganic fiber components and filler that are not suitable for dealing with by incineration. Currently, glass fiber reinforced plastic composite wastes generated from manufacturing process and unusable products in Thailand have been increased to 2,500 tons per year and sent to landfill for disposal, leading to environmental problems and being impacted to nearby local residents. This problem is urgently required an appropriate method to manage these wastes in order to avoid or reduce landfill disposal.

Variety methods for recycling composite wastes have been studied, including mechanical recycling, chemical recycling, incineration or combustion recycling, and thermal recycling. Mechanical recycling is the size reduction of composite wastes and then the recyclate composites were used as a filler to produce new composite, but the mechanical properties of composite consisted of recyclate particle show lower strength than that of composite with original fiber . For chemical recycling, it is the separation of resin matrix away from fiber by using organic solvent. This method recovers both fiber and resin in form of monomer or dimmer and further used to prepare new composite. Comparing to mechanical recycling, this method is not popular since it requires strong concentration of solvent and is considered as a dangerous method. The Incineration or combustion process is the burning of composite waste under oxygen atmosphere to mainly produce energy. However, the energy obtained from the combustion process has low heating value due to high content of inorganic fiber in composite. The latest technology developed to recycle composite wastes is thermal recycling or by pyrolysis process which is one of the thermochemical conversion process. Pyrolysis process of composite waste is referred to thermal degradation of polymer resin matrix by thermal energy in the absence of oxygen into small molecule as gases or fuel oil and solid residue contained with glass fiber. Pyrolysis process is considerably attractive method as it directly converts all compositions in unusable wastes into valuable products such as solid, liquid, and gaseous products.

From the literature, many researches have been studied on the effects of pyrolysis temperature on the product distributions of the glass fiber reinforced thermoset plastics. However, there are no studies on the effects of different types of resin matrix on pyrolysis products, yield, and distribution. In fact, there are three types of unsaturated polyester matrix, including orthophthalic, isophthalic, and vinyl ester, which have been widely used in composite industries and possibly affected on the pyrolysis products and distribution. Similarly, several researches have been focused on the pyrolysis of epoxy matrix reinforced with glass fiber, but they did not report on the influences of epoxy curing agent, although the properties of cured epoxy such as thermal, mechanical, and electrical properties are strongly depend on the characteristic of each curing agent.

Therefore, this research was designed to investigate the thermochemical conversion of 30 wt% and 60 wt% glass fiber reinforced unsaturated polyester and epoxy composite wastes by pyrolysis process in order to convert their compositions into fuel products such as liquid oil and to recycle glass fiber. The composite wastes containing 30 wt% glass fiber were generated from hand lay up process of pipe connector or fitting composite product, while the ones with 60 wt% glass fiber were generated from generated from filament winding process of conduit and pipe composite product. Both composites wastes were first studied their thermal behavior by using Arrhenius equations and then were pyrolyzed in a horizontal fixed bed reactor.

The objectives of this research were to investigate the effects of glass fiber content (i.e., 30 wt% and 60 wt%), types of curing agent for epoxy matrix (i.e., amine and anhydride), types of unsaturated polyester resin (i.e., orthophthalic, isophthalic, and vinyl ester) on the pyrolysis products, yields, and distribution carried out at different pyrolysis temperatures (i.e., 600ºC, 700ºC, and 800ºC). The obtained solid product was characterized its physical appearance by Scanning electron microscope (SEM), functional group by Fourier transform infrared spectrophotometer (FTIR), and then used to prepare new composite. For condensable liquid product, its fuel oil properties such as flash point, pour point, acidity, gross calorific value (GCV), and specific density were compared with those of conventional fuel oil. In addition, its boiling point ranges and distillated product fraction was identified by using Gas chromatography simulated distillation (GC-Simdist). Finally, the collected gaseous products were verified gas composition by using Gas chromatography and evaluated their gross calorific value by calculation method.

Additionally, the other objective was to recycle glass fiber obtained from the pyrolysis process of unsaturated polyester and epoxy composite waste by using as reinforcement to prepare new unsaturated polyester and epoxy composite by bulk molding compound (BMC) method at the ratios of 5, 10, 15, and 20 wt%. Their mechanical properties such as flexural strength, flexural modulus, and impact strength were compared with those of BMC composites prepared from original glass fiber. Furthermore, the fractured surface of three-point bending tested specimens was observed by SEM to investigate the relationship between morphologies and their mechanical strength.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Composite Material

Composite material is a macroscopic material composed of two or more constituents which are not soluble in each other. One of the constituent is a discontinuous phase called reinforcement phase embedded in continuous phase, known as matrix phase.

The reinforcement materials are usually stiffer and stronger than matrix phase. They used to enhance the properties of the composite are better than that of each individual component, normally in term of mechanical properties such as strength and modulus with suitability application. The reinforcement phase material may be in the form of fibers, particles, or flakes.

The matrix phase materials are generally continuous which are weaker or lower strength than reinforcement material. The primary functions of matrix are not only to bind the reinforcement materials together and also to distribute the stresses from local area to among the constituent reinforcement materials. Moreover matrix phase also protects the reinforcement material from mechanical and environmental damage.

The performance and properties of composites are designed to be superior to either constituent material alone. Furthermore, they are low cost and easy to process to provide desired properties. Therefore, they have been widely used for many applications, such as automobile, aerospace or structural material to replace metallic material. They have unique advantages over monolithic or other plastic materials in relation shift to high strength to weight ratio, long life term, corrosion resistance, thermal insulation and conductivity. However, the characteristics or properties of composites are significantly depend on their constituents.

2.2 Classification of Composites

Composite materials can be classified according to their major constituent According to the major class of matrix series are divided in to three types consisting of metal matrix composites (MMCs), ceramic matrix composites (CMCs),and polymer matrix composites (PMCs) (Figure 2.1.). For the consituent of reinforcement refers to the form or geometry of reinforcement separated into two series, fiber reinforced composites (fibrous composites) and particle reinforced composites (particulate composite). In this research focused on fibrous composite due to raw material used in study.

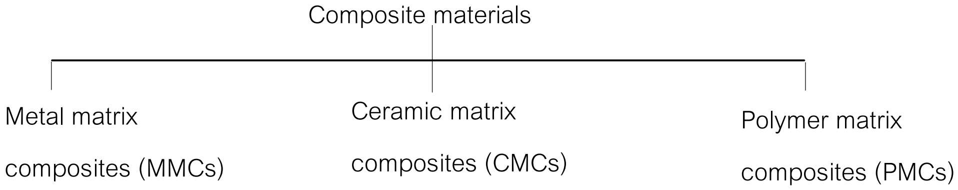


Figure 2.1 Classification of matrix composites [1].

2.2.1 Metal Matrix Composites (MMCs)

Metal matrix composites are consisted of metallic materials such as Titanium, Aluminum and magnesium wildly reinforced with boron or carbon fiber. They have high strength, fracture toughness and stiffness better than that of polymer matrix composite. However, their maximum service temperature is limited by softening temperature of the metal matrix. Furthermore, they are easily corroded under corrosion conditions or oxidizing environments. Therefore, they are wildly interested in research and used for specific applications such as structural components on space shuttle orbiters [2].

2.2.2 Ceramic Matrix Composites (CMCs)

Ceramic materials are used for matrix composites such as silicon carbide, aluminum oxide, silicon nitride reinforced with ceramic fiber. Ceramic matrix composites show good chemical thermal and mechanical properties in terms of good corrosion resistance, stability at elevated temperatures and high compressive strength, respectively. They are used for high-temperature applications in the aerospace industry, automobile parts, sub-marine equipments and tools.

2.2.3 Polymer Matrix Composites (PMCs)

The polymers are alternative materials for composite matrix. They are extensively selected due to easy to process providing good mechanical, electrical and thermal insulation properties. Fiber reinforced plastic composite materials (FRP) are one type of polymer matrix composite. They are popular used for many applications, including chemical industry electrical industry. The polymer matrix can be classified into two categories consisting of thermoplastics, and thermosets, Thermoplastics can be fabricated under stress at elevated temperature and cooled into composite. Typically thermoplastics include acrylic, nylon, polyethylene, and polystyrene. These plastics might be reinforced with natural and synthetic fibers, including cotton, silk, cellulose or self reinforcement. However, they have low thermal stability because it may be flow at high temperature suited for remolded or fabricated. Thermoset plastics are the most predominant types of matrix systems. They undergo polymerization and cross-linking with curing agent to form three dimensions network structure with covalent bonds. These strong bonds have the effect of pulling polymer chains together. This restricts the movement of polymer chains when they are heated above glass transition temperature. Consequently, thermoset resin are brittle at room temperature and high strength to weight ratio. Thermoset resin cannot be reshaped by heating, they just degrade or burn if they are heated at elevated temperature. The most common thermosetting plastics are unsaturated polyester and epoxy resin, which can be detailed as following section.

2.2.3.1 Unsaturated Polyester

Unsaturated polyester resins, commonly referred to polyester resins, are polymer chain containing alternating ester bonds prepared by a condensation polymerization of difunctional achohol (diols) and difuntional acid (diacid) to form polymer. Generally, the polymer resins are dissolved in styrene monomer, cross-linking monomer, to provide usable viscosity. The resins have reactive double carbon-carbon bonds in which of acid component that can be crosslinked to form thermosetting materials. Polyester resins are primarily used in a wide range of glass fiber reinforcement for quick curing systems in variety of commercial products (automobile, boats, ships, structural components, storage tanks). The unsaturated polyesters are very popular for composite applications because of their low cost, easy to process, low densities, good corrosion resistance, and high strength to weight ratios. On the other hand, their mechanical properties are limited at elevated temperature.

A wide variety of unsaturated polyester resins used for composite applications with differing structures of glycol and isomeric of aromatic diacid, which have impart on final cured product properties. There are three types of unsaturated polyester resin extensively known as orthophthalic polyester, isophthalic polyester, and vinyl ester as for composite industries as following detailed:

- **Orthophthalic** polyester resin (ortho) is original family chemistry of polyester resins utilized in general purpose (GP). It is prepared by a condensation polymerization of orthophthalic acid and maleic anhydride with propylene glycol (1-2 propanediol) shown in Figure 2.2 It is wildly used in many applications such as water and pipe line or storage tank, although it has a limitation of thermal stability, and chemical resistance.

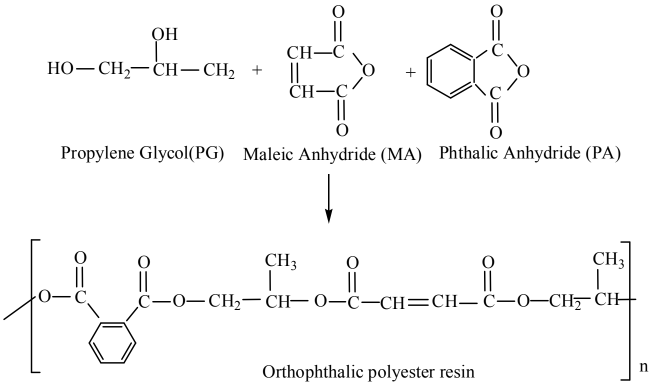


Figure 2.2 Synthesis of orthophthalic polyester resin [3].

- **Isophthalic** polyester resin (Iso) is prepared by a blending of isophthalic acid and maleic anhydride or fumaric acid and propylene epoxide

(Figure 2.3) resulting to higher molecular weight ($\overline{M}_n$ of 1500-2000. [3]) than orthophthalic polyester resins ($\overline{M}_n$ of 800-1000). Furthermore, this resin exhibits a higher heat distortion temperature, higher strength, greater flexibility and superior water resistance than orthophthalic resin. It is used in corrosion environment applications.

- **Vinyl ester** is the common name for an unsaturated resin prepared by the reaction of a bisphenol A glycidyl ether with methacrylic acid displayed in Figure 2.4. The main chain's resin consists of bisphenol diepoxide and terminal reactive double bonds of methacrylate derived from the carboxylic acid. These reactive groups can form a crosslinked network with styrene monomer. The properties of vinyl ester resins combine the best properties of epoxies and unsaturated polyesters resin, especially excellent chemical resistance due to the termination of mathacrylate sterically shield pendant group. Vinyl ester matrix composite are mostly preferred in corrosive industrial and marine applications.

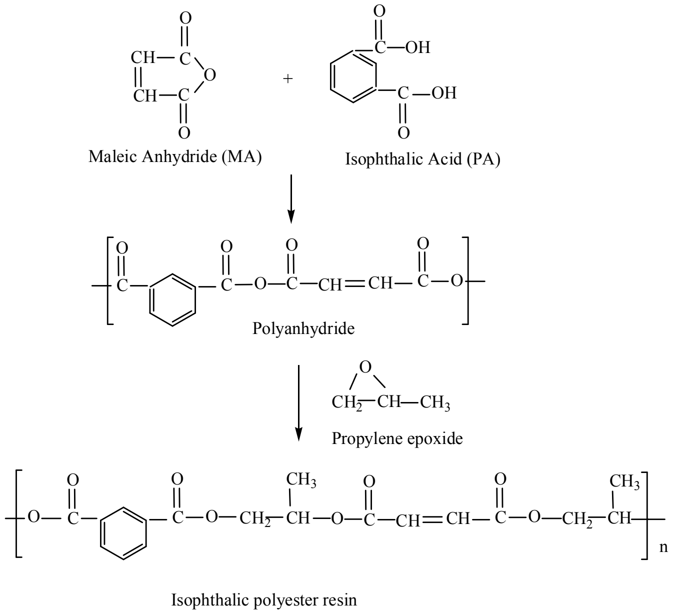


Figure 2.3 Synthesis of isophthalic polyester resin [3].

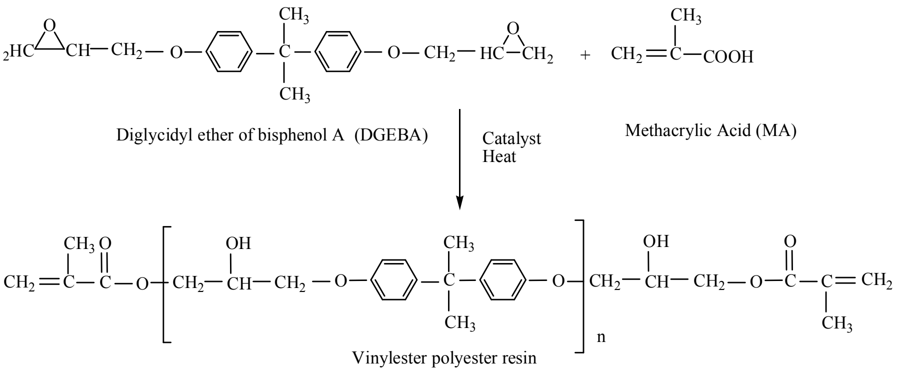


Figure 2.4 Synthesis of vinyl ester resin [3, 4]

The chemical crosslinked reaction of unsaturated polyester resin is free radical copolymerization by reacted with styrene diluents in presence of peroxide free radical as initiator/catalyst and small amount of cobalt naphthenate as activator at room temperature shown in Figure 2.5. During curing process, the viscosity of the resin increases and become to gels and subsequently forms a hard thermoset solid.

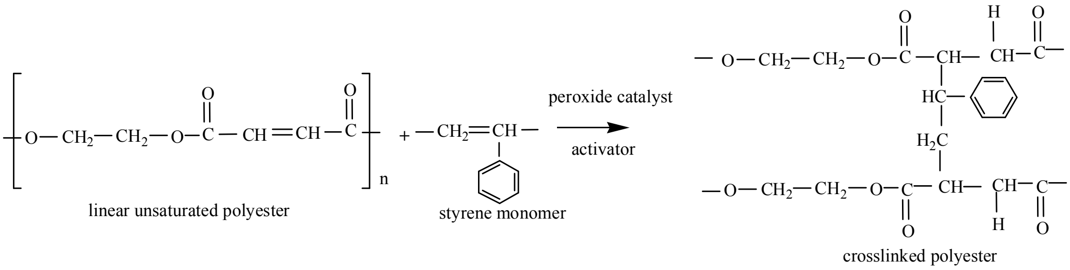
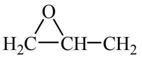


Figure 2.5 Chemical crosslinked reaction of unsaturated polyester resin [5].

2.2.3.2 Epoxy Resins

Epoxy resins are one of the most important thermosetting polymer applied for composite applications, They are polyether resins containing more than one epoxy group (oxirane) can be converted into resins into three-dimensional thermoset network structure. Figure 2.6 displays the condensation polymerization reaction of bisphenol A and epichlorohydrin with in the presence of alkali and catalyst to form epoxy resin refered to digiycidyl ether of bisphenil A (DGEBA) and commonly used as polymer matrix for composite applications

All epoxy resins contain the epoxide groups, which is a three member ring of two carbon and one oxygen atoms formed oxirane structure at the end chain, usually is  ,called the glycidyl group. This groups are attached for ring opening to formed network structure.

Epoxy resin has been used in a wide range of in high performance composites, such as structural material, coating, and microelectronics. This is because epoxy resins have variously excellent properties in terms of strength and stiffness, dimensional stability, chemical resistance and electrical insulation. In addition, epoxy resins can be easy processed for curing with various curing agents in order to achieve satisfied properties.

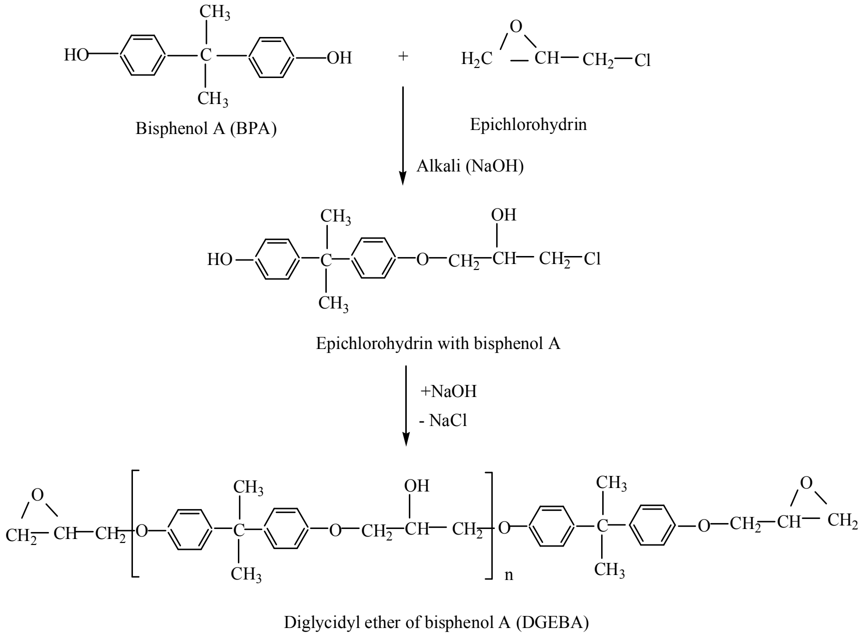


Figure 2.6 Synthesis of epoxy resin (diglycidyl ether bisphenol A;DGEPA) [6].

The properties of cured epoxy resins are related to their curing agent depending on the chemical structure and cured conditions . There are two main categories of curing agents for epoxy resins currently used on the market, such as amine , acid anhydride groups.

- **Amine curing.** In amine curing agents, each hydrogen on an amine nitrogen is reactive and can open one epoxide ring to form a covalent bond at room temperature Amine compounds are often used for epoxy curing classified into three categories; aliphatic, cycloaliphtic and aromatic [3]. The chemical structure of them are presented in Figure 2.7.

Aliphatic amines are the largest group of epoxy curing agents. The characteristics of these curing are low cost and low viscosity resulting to easy to process, but they have short pot life due to high exothermic reaction resulting to low thermal stability of cured resin (<80°C). The most common aliphatic amines used as epoxy curing are Ethylene diamine (ETA), Diethylene triamine (DETA).

Cycloaliphtic amines are referred to N-Aminoethylpiperazine (AEP), 1,8 Menthanediamine (MDA), These groups have longer pot life, better toughness and higher thermal stability than that of aliphatic amines, in spite of poorer chemical resistance.

Aromatic amines, generally provide the best properties of amine cured epoxy, including Diamino diphenyl methane (DDM), Meta phenylene diamine (MPD.). Aromatic amines contribute excellent in electrical insulation, good heat resistance (150 – 160°C), good mechanical and chemical resistance properties but they always require heat for cure to form solid network.

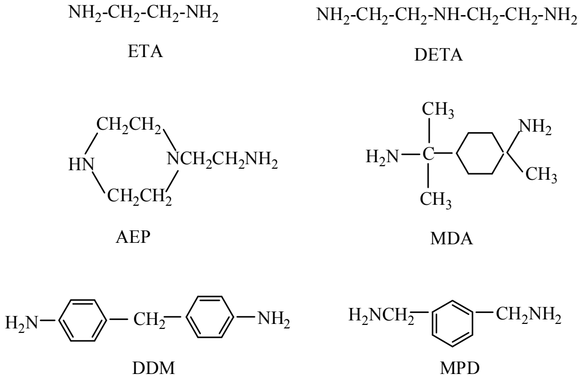


Figure 2.7 Chemical structure of amine curing agent [7].

The conversion of epoxy resins to three dimension thermoset network solid with amine curing agent can be occurred at room temperature by ring opening of epoxide groups by active hydrogen compounds such as water or other impurity and attached by nitrogen atom of curing agent to form network structure .Figure 2.8 shows network structure of epoxy cured with cycloalipatic amine;1,8 methanediamine (MDA).

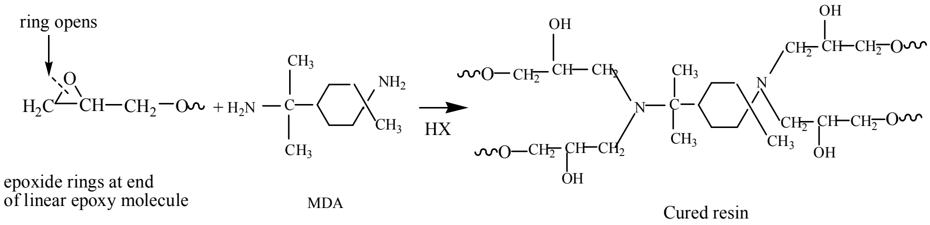


Figure 2.8 Chemical reaction of epoxy cure with MDA [7].

The chemical reaction of epoxy cured with amine is exothermic reaction and will proceed faster as an increasing of temperature. This reason may causes the crosslink reaction not complete consisting of unreacted amine molecule in the system. This leads to properties of cured resin having lower thermal and chemical resistance. Furthermore, these curing are toxic and cause severe irritation.

- **Acid anhydrides curing agent.** Anhydrides are the next commonest for epoxy curing agents and suited for electrical insulation applications. There are many types of acid anhydride for epoxy curing, for example, Phthalic anhydride (PA), Hexahydrophthalic anhydride (HHPA), Nadic methyl anhydride (NMA), Methyl tetrahydrophthalic anhydride (MTHPA). They have low viscosity, long pot life, and low exotherm They have higher temperature resistance than the aliphatic amines. Their chemical structure of these curing agents are displayed in Figure 2.9.

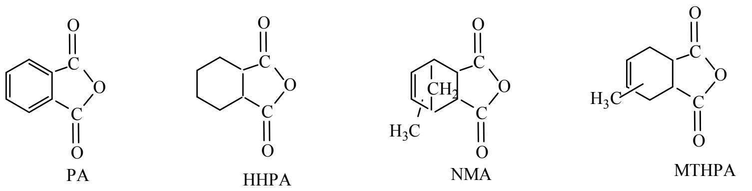


Figure 2.9 Chemical structure of anhydride curing agent [8].

The curing reactions of acid anhydride with epoxy resins occur at about 300°C and rather slow. Usually these systems are promoted by accelerator which should be shorter cure time. Manny types of accelerators include tertiary amine, boric-acid ester, Lewis acid, organic metal compounds, organic metal salts. The presence a small amount of accelerator results in the curing reactions of epoxy and anhydride are faster. The Typical chemical curing reaction of epoxy and acid anhydride are (phthalic anhydride with the presence of teritiary amine accelerator are revealed in Figure 2.10. The reaction was initiated from ring opening of cyclic anhydride by attaching of accelerator and then further reacts anhydride to form cured resin network.

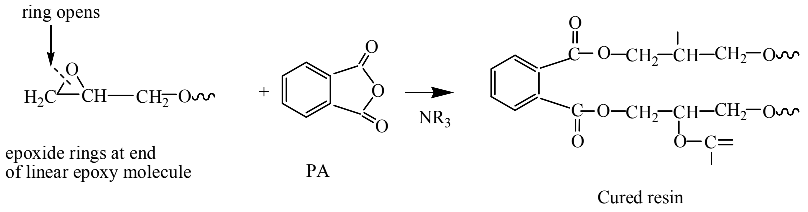


Figure 2.10 Chemical reaction of epoxy cured with PA [9].

The epoxy resins cured with anhydride have excellent electrical properties suited fore electronic application. Moreover epoxy anhydride composite are used for structural material in the part of aircraft.

2.3 Fiber Reinforced Composites (Fibrous Composites)

Fibrous composites consist of fiber embedded into matrix in order to enhance mechanical properties such as high strength to weight ratio, and high modulus with regard to fiber orientation because of anisotropic material. They are usually known as fiber reinforce plastic (FRP) There are many types of fiber used as reinforcement material for composite application.

2.3.1 Type of Fiber Reinforcements

Reinforcement fibers can be grouped into two classes; natural and synthetic fiber. The most commonly known of natural fiber are cotton, silk, wool, jute, and hemp.

These fibers are essentially micro composite consisting of cellulose fiber in lignin and hemi cellulose matrix. The strength and stiffness of these fibers are low compared with synthetic fibers. Currently, the synthetic fibers are used as reinforcement for composite industries include, glass ,boron, carbon, and Aramid fiber.

- **Glass fibers** are based on an alumina-lime-borosilicate composition the most extensively used in low- to medium-performance composite applications such as water pipe, storage water tank, panel in aircraft, rocket motor, pressure vessels. This is because they are low cost and easy to process to achieve final desired properties. On the contrary they are limited in high-performance composite applications due to low stiffness, low fatigue endurance, and rapid property degradation with exposure to severe hygrothermal conditions. Glass fibers are produced by the extrusion of molten mixture of silica (SiO_2) and other oxides (MgO) through small holes of a platinum and drawn at high speed, formed individual filaments. These filaments are gathered into groups (strands) and applied coupling agent (sizing) to the fibers surface in order to ensure interfacial bonding to the resin matrix.

- **Boron fiber** is a continuous monofilament prepared by chemical vapor deposition (CVD) of boron tricloride (vapor phase) deposited onto metal filament substrate (normally tungsten). Boron deposited on the tungsten wire in forms of fine crystalline structure with high density which contribute to high strength and stiffness of the filament. On the contrary, when the temperature up to 1000°C, boron can be molten and react with metal substrate. Currently, boron fiber is reinforced epoxy matrix composite used as aerospace and sporting applications.

- **Aramid fiber** is an aromatic polyimide which mostly known as Kevlar by Du Pong in 1972. Aramid fibers contribute good high temperature due to high glass transition temperature (T_g) of about 360°C, good dimensional stability and low thermal expansion. They are high tensile strength, medium modulus, and vary low density compared to glass and carbon fiber. These fibers have high strength in the longitudinal direction and weak strength in cross direction. This results from the rigidity of the arrangement of repeating aromatic polyamide in main chain polymer as rodlike planar sheet with strong covalent bonds. Generally, Aramid fibers are used as rope, cable, and reinforcement to produce high performance composite applications, including aerospace, marine, space shuttle

- **Carbon fibers** are manufactured from three precursors; polyacrylonitrile (PAN), pitch, and rayon. PAN, original precursor, are still popularly used as reinforcement for epoxy resins composite. They are the best reinforcement for advanced composite and engineering applications due to excellent properties in terms of high modulus and high temperature performance (1500ºC) because of graphitic structure. However carbon fibers are restricted in high cost due to the complexity of manufacturing process of oxidation, carbonization, graphitization step and sensitivity to moisture.

Fibers used as reinforcement material are prepared in different geometry characterized by the ratio of length to cross section diameter called aspect ratio. The long fibers have high aspect ration named as continuous fiber. Meanwhile, short fiber or discontinuous fibers are low of aspect ratio. The geometry of fiber usually used as reinforcement for composite material can be shortly detailed as

2.3.2 Geometry and Form of Fiber Reinforcement

The reinforcement materials for composite may be classified by its shape, in a number of different formats, including continuous or roving fiber, discontinuous fiber, and woven or mats.

- **Continuous fibers** or unidirectional roving consist of many individual strands or bundles of filaments, these fibers are characterized by the ratio of cross-sectional dimension known as aspect ratio. They have a high aspect ratio and provide the best mechanical properties in the longitudinal orientation fibers (Figure 2.11a) suited for filament and pulltrusion process. Furthermore, these fiber may be further woven in forms of bidirectional used to prepare laminated composite.
- **Discontinuous fibers** which known as short fibers (Figure 2.11b).They have low aspect ratio which may be embedded in matrix phase in random or preferred orientation .They are wildly used in forms of mats known as chopped strand mats for laminar composite preparation.
- **Multilayered fibers** are prepared by the stacking of many unidirectional (Figure 2.11c) or angle plies (Figure 2.11d) into sheet layers. Fibers can be aligned to preferred direction in order to achieve desired properties. This fiber are used to prepare laminar composite as structural material.

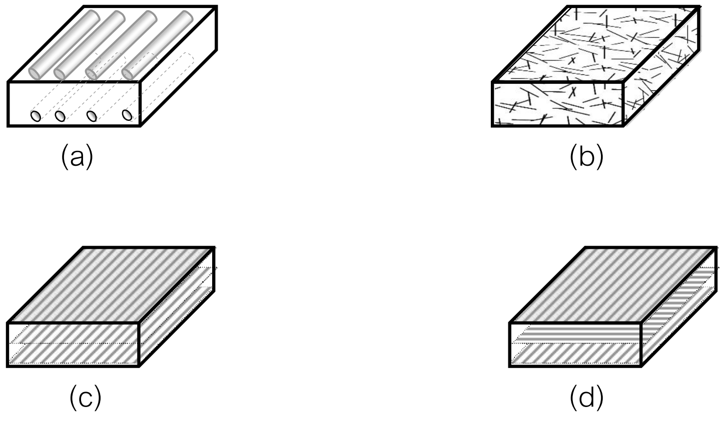


Figure 2.11 Example of fiber geometry in composites: (a) continuous unidirectional fiber, (b) discontinuous, unidirectional fiber, (c) laminar, and (d) hybrid composite.

2.4 Characteristic and Applications of Fibrous Composite Materials

The basis properties of fibrous composite materials are related with those constituents combined of both matrix and reinforcement phase. The physical and mechanical properties are strongly depended on reinforcement materials related to geometry, volume fraction of reinforcement and their arrangement, and interfacial bonding of fiber and matrix.

The geometry and their arrangement within the matrix have impacted on composite's the performance. If the fibers of a composite are aligned along the loading direction, the stiffness and the strength, especially tensile properties, are better transverse loading direction Similarly, the strength and stiffness of composite structure are increased with an increasing of volume fraction of reinforcements. However the difference in type of reinforcement and matrix are important factor on composite properties resulting to different properties.

2.5 Fibrous Composite Wastes Management

According to Fiber-reinforced composites consist of two main parts of resin matrix which crosslinked into three dimensional network structure and high content of inorganic fiber reinforcement. These constituents are not easily recycled or remoulded like thermoplastic material. These reasons have causing to an increasing of composite wastes. Currently, there are two ways for dealing with composite wastes including disposal by landfill and recycling method such as mechanical, chemical, and thermal method by thermochemical conversion process such as combustion, gasification, and pyrolysis process.

2.5.1 Disposal by Landfill

Landfilling is the primary and the popular common method to deal with composites wastes. Because composites are non biodegradable materials which can cause to environmental problems in terms of chemical leaching, loss of utility area, emission of toxic gases or undesirable odor Consequently, many researches have studied on recycling methods in order to find a good promising solutions revealed to mechanical, chemical, and thermal method by converting their compositions into usable material for further used.

2.5.2 Mechanical Recycling

The mechanical recycling is the size reduction of composite waste by shredding or grinding into suitable size for used as filler for a new composite preparation [8] . The applications of this filler depend on the compatibility with type of matrix composite. This method is currently used to recycle sheet molding compound

Derosa, et al. [8] recycled glass fiber reinforced polyester composite by size reduction into 6.30 millimeter called as recyclate fiber (RF) and used as reinforcement material at 5 wt.% to substitute virgin fiber (VF) as long as particle of recyclate fiber size for bulk molding compound (BMC) composite. The BMC consisted of 33.3 wt.% unsaturated polyester resin,11.7 wt.% of virgin fiber, 5 wt.% of recyclate fiber, and 50 wt.% of calcium carbonate ($CaCO_3$) filler. The results showed that the addition of recyclate fiber into BMC resulted in a 34 % reduction in flexural properties. They attributed that the interfacial bonding between recyclate fibers and polymer matrix were poorer than that of virgin fiber resulting in lower strength [9].

2.5.3 Chemical Recycling

The chemical recycling is the decomposition of resins matrix into organic solvent in order to separate polymer matrix away from the fiber into small molecule as dimer or monomer containing in the solution. Both of resin and recovered fiber can be used to substitute of original resin or fiber for new composite preparation after neutralized or cleaned.

Liu, Y., et al. [10] investigated the chemical recycling of epoxy reinforced with carbon fiber composite by using nitric acid solution. The bisphenol A epoxy resin was crosslinked with Isophorone Diamine (IPDA) curing agent and reinforced with 67 wt.% carbon fiber. The prepared composite was immersed in a 100 ml nitric acid solution concentration of 8M under control temperature of 90ºC for 20-100h. The decomposed solution was analyzed with gas chromatography/mass spectrometry (GC/MS). They found that the epoxy matrix was decomposed into low molecular weight compound. Meanwhile, insoluble carbon fiber was recovered and might be recycled.

Later, Dang, et al. [11] studied the chemical recycling of glass fiber reinforced epoxy cured with diamino diphenyl methane (DDA) composite by using nitric acid. The epoxy composites were immersed in nitric acid solution concentration of 4M under temperature controlled at 70ºC. The epoxy resin matrix was decomposed into low molecular weight compound. The decomposed products of epoxy resin were first neutralized (referred to NE) and then mixed with an virgin epoxy resin at the ratio from 5 to 30 wt%. of total weight of NE and epoxy resin named as recycled resin. The result from flexural strength of cured epoxy consisting of recycled resin was much higher than that of virgin resin when the content of NE not more than 30 wt% . They concluded that the cured epoxy consisting of recycled resin presented tertiary amine which acts as promoter leading to higher crosslinked density of epoxy cured network than that of virgin epoxy network. For glass fiber reinforcement could be separated and reused after cleaning.

2.5.4 Thermal Recycling (Thermochemical Conversions Process)

Thermochemical conversion processes is the converting process of organic material feedstock wastes such as biomass, municipal, industrial waste into renewable energy. The chemical compositions in material are either degraded, or craked by heat and formed a small molecule of solid char, liquid fuel, and fuel gas. There are three fundamental processes of thermochemical conversion including combustion, pyrolysis, and gasification process. The differences among them base on the condition to process in order to achieve desired main product.

2.5.4.1 Combustion Process

Combustion or Incineration process is the burning of organic material under excess oxygen atmosphere referred to a complex oxidation reaction which converts chemical energy into heat, carbon dioxide, and water. The energy recovery can be used for continuous process, such as to produce steam pressure for gas turbine, to rotate the blade for electric generator . However the efficiency of generated energy is limited by the time because it must be used as real time. Additionally, it may causes to global warming due to the emission of toxic gases such as hydrogen chloride, carbon monoxide, and sulfur dioxide gases. Incinerations of composite waste, the resin matrix is burned but inorganic fibers retained as ash or residue and may used as filler to produce Portland cement. However this method is not popular for recycling composite material due to high content of inorganic fiber resulting to low heating value of recovery.

Skrifvars, and Nystrom [12] studied the combustion of epoxy reinforced carbon fiber sandwich generated from manufacturing process in fluidized bed reactor at 480ºC for 1hour. They found that the epoxy matrix was easily combusted at 480ºC .The remaining fiber was cleaned and investigated diameter by using SEM. The results indicated that temperature used to fluidized bed process results in the reduction in size diameter of recycled fiber which related to an decreasing of tensile properties to 50% compared to virgin carbon fiber. Furthermore, the tensile properties of recycled fiber were decreased from virgin fiber which resulted from thermal defect on carbon fiber.

2.5.4.2 Pyrolysis Process

Pyrolysis process is defined as thermal degradation of the macromolecule organic material into small molecules in forms gas, liquid oil, and solid residues by thermal energy in the absence of oxygen. The degradation of materials are caused by free radical resulting from the dissociation and fragmentation of chemical bonds. During pyrolysis, the chemical compositions in material are first cracked into volatile matters and continuously formed light gases which may be either passed through as gaseous products or trapped to condense as liquid oil. For solid residues which not degrade mainly consist inorganic material. There are some researches studied the recycle composite by pyrolysis process such as

Torres, et al. [13,14] studied the effect of temperature on pyrolysis process of 25 wt.% glass fiber reinforced Orthophthalic polyester sheet molding compound waste .The composites waste was resized into 5x 5 cm^2 and used 200 g for each run . The pyrolysis process was carried out in autoclave stainless steel reactor at final temperature of 300, 400, 500, 600°C, and 700 °C with nitrogen passed thought rate of 1dm^3/min and held at that temperature for 30 min. After finished run, the pyrolysis products were kept and characterized. The residual solid were analyzed in terms of elemental compositions and the amount of organic matter consisted in such residues by using TGA under O_2 atmosphere at 500°C. The condensable liquids were centrifuged at 2500 rpm for 15 min to separate oil and water phase. For oil phase was determined the elemental compositions and gross calorific value. The gaseous products were analyzed by using gas chromatography. They concluded that at 300 °C pyrolysis was incomplete because solid yield (82.6 wt.%) was higher than theoretical (72.6 wt.%) expected. These results corresponded with the results of TGA which presented that the solid residue from 300 °C composed of more unpyrolysed organic matter than that of residue obtained at other temperatures. The characterization of pyrolysis liquids were a complex mixture of C_5-C_{20} organic compounds mainly contained of aromatic and oxygenated compounds. They are non polluting liquid oil having high gross calorific values (34-37 MJ/kg). For gaseous products showed rather low in gross calorific (13.9-16.4MJ/m^{3}N) but it can be used as sustainable process.

Cunliffe, et al. [15,16] Studied properties of products obtained from pyrolysis of commercial orthophthalic polyester reinforced with 30 wt.% glass fiber and 7 wt.% $CaCO_3$ filler. In a typical batch composite waste 1.5 kg was loaded into fixed bed reactor at final temperature of 450 °C under nitrogen gas purged at 3L/min and held at that temperature for 90 min. The main solid residues were glass fiber which used to substitute of virgin fiber for the preparation of dought moulding compound (DMC) up to 20 wt.% . The calorific value of condensable product was rather low (33.6 MJ/kg) due to its high oxygen content, but sufficiently used as fuel. On the other hand, flash point of condensable product was below the standard of flammable liquid specified by UK as 55°C. The generated gases mainly consisted of carbon monoxide (CO) and carbon dioxide (CO_2) (more than 75 vol.%) which derived from ester bonds

Currently, Pyrolysis is a mostly an appropriate method to covert various wastes such as biomass [17,18,19], tyres [20] into fuel products.

2.5.4.3 Gasification Process

Gasification is the process used to convert carbon based materials at elevated temperature under limited oxygen into combustible gas as called producer gas which is a mixture of carbon monoxide (CO), methane (CH_4), and hydrogen (H_2), and negligible of carbon dioxide (CO_2). These gases can be further purified into syngas mainly consisted of hydrogen and carbon monoxide and used as feedstock to produce chemical.

Gasification process is a complex thermal degradation continued of pyrolysis, after the temperature in the reactor is slightly increased. The fundamental gasification reactions of carbonaceous or hydrocarbon material take place in the reactor during gasification process as following equations [21]:

$$C + O_2 \rightarrow CO_2$$

$$C + \tfrac{1}{2}O_2 \rightarrow CO$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$$CO_2 + C \leftrightarrow 2CO$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

2.6 Thermochemical Products and Applications

The typical products obtained from thermochemical conversion by pyrolysis are gases, condensable liquids or oil, and solid residue (char). The percentage of each fraction strongly depends on conversion process, material and process temperature.

2.6.1 Gases

The Gaseous products are uncondensed gases which occurred by thermal decomposition of organic or volatile matter in raw material. The main components of generated gas are CO_2, CO, H_2, CH_4. The amount of individual gas depends on temperature and type of process either pyrolysis or gasification. Normally, conversion by gasification process provides higher gaseous fraction than pyrolysis process producing liquid oil as main product because of elevated temperature of gasification process. The increasing in temperature results in an decreasing in CO_2 and increasing of CO and H_2 due to secondary thermal cracking of hydrocarbon in liquid component at higher temperature.

Concerning the properties of generated gas from thermal conversion are evaluated by heating value or gross calorific specified which is energy released by burning per-unit volume. Generally, the heating value of fuel gases are in range of 3.7–120 MJ/m^3 (100–3,200 Btu/ft^3) [21].

2.6.2 Liquid

Liquid phases obtained from pyrolysis process are **a dark brown color** which mainly composed of oxygenated compounds phase an aqueous phase. The yield of this fraction is slightly decreased with an increasing of process temperature due to more broken of chemical bonds to form gas fraction at higher temperature. Usually the recovered condensable liquids are first centrifuged to remove aqueous phase. For organic phase is referred to crude oil which can be refined in order to identify boiling rang for classification type of fuel such as low molecular weight hydrocarbons (gases), gasoline and naphtha, kerosene , lubricating oils, and residue presented in Table 2.1.

Table 2.1 Component of distillation crude oil [22].

Fraction	Carbon Number	Boiling Rang (°C)	Applications
Gases	C_1-C_4	<0	Fuel gas
Gasoline and Naphthas	C_5-C_{12}	30-200	Engine Fuel
Naphtha	C_6-C_{10}	<210	Solvent feedstock
Kerosene	C_9-C_{15}	150-260	Jet fuel, solvent
Light gas oil	C_{13}-C_{18}	250-300	Diesel oil
Heavy gas oil	$>C_{22}$	300-370	lubricating oils
residual	$>C_{22}$	>370	Asphalt tar

A low molecular weight hydrocarbons are the fraction of gas consisted of 1-4 carbon atom per molecule. This fractions are the first refinery products at the top of the column tower They are transformed to gas to liquid by pressure applied to used as liquid petroleum LPG).

Gasolines are crude oil containing 5-8 carbon atom and boiling rang of 30-210ºC. This fraction can be used for spark ignition combustion engine such as automotive engine fuel as known standard benzene oil. Furthermore it can be upgraded by blend with alcohol (ethanol) to produce gasohol oil.

Naphthas are crude oil distilled between gasoline and kerosene rang. They are not fuel but rather used as industrial solvent feedstock.

Kerosenes are the colorless fraction consisting of 9-16 carbon atom distilled in the rang of 150-260ºC. They are used for a gas turbine fuel.

Light gas oil, well known as diesel oil consists of carbon 13-18 atom boiled in rang of 250-30ºC. There are two types of diesel oil used for combustion engine, depending on engine size; high speed and low speed automotive type.

Heavy gas oil is the fraction which boil in the 300-370ºC. It is used as lubricating oils.

Residues referred to alphas which boil after 370 ºC. due to long chain molecule of 22 carbon atom . This fraction can be blend to light fuel as gasoline.

The liquids used as fuel oil usually established by American Petroleum Institute (API) and American Society for Testing Materials (ASTM) are considered in terms of viscosity, flash point, pour point, specific gravity (API gravity), gross calorific value or hating value , and acid value. The typical properties of commercial fuels oil are summarized in Table 2.2.

Flash point is the lowest temperature for the vapor above the liquid to be ignited and exposed to a flame. This value is a significant parameter for fuel handling to prevent fire hazard. The flash point is normally measured by closed-cup testers according to ASTM D93.

Table 2.2 Typical properties of commercial fuels oil.

Properties	Diesel fuel oil [23]		Biodiesel [24]
	Automotive diesel	Industrial diesel	Methyl ester type
Flash point (°C)	>52	>52	40-70
Pour point (°C)	<10	<16	-
Viscosity (cP.)at 40°C	1.8-4.1	<8.0	3.5-5.0
Heating value (MJ/kg)	16-26	42-44	14-16
Specific gravity (g/cm^3) at 15°C	0.81-0.87	<0.92	0.8-0.9
Acidity (mg KOH/g oil)	-	<0.02	< 0.5
Cetane number	>47	>47	>51

Pour point is the lowest temperature that liquid fuel can be handled and free to flow without the formation to wax or crystal determined according to ASTM D99. If the temperature is below the pour point, the liquid fuel will be separated and become to solid and block the filter.

Viscosity of fuel oil refers to Kinematic viscosities concerning the resistance to shear or flow of fluid determined according to ASTM D445. It plays an importance role in the fuel injection system. If this value is high, it is difficult to inject.

Heating value or gross calorific value (GCV) is a quantity of heat per a unit mass released during combustion of fuel. This value can be measured Bomb calorimeter according to ASTM D1209 by and can be expressed in MJ/Kg, BTU/Lb, and Cal/g. This values is used to verify the efficiency of fuels for used as energy generation.

Specific gravity is the ratio of density of liquid fuel to density of pure water. It is measured to qualify liquid fuel used in petroleum industry commonly referred to API gravity according to ASTM D1298. Normally, the higher the API gravity the higher the fuel quality. The specific gravity value of fuel oil relates to hydrogen content and H/C ratio. In general, the larger gravity or H/C ratio of fuel, the better its combustion properties, the lower its viscosity, and of cause the lower its density [25].

Cetane number/octane number used to verify ignition quality of diesel oil and gasoline oil, according to ASTM D613 and ASTM D 2699, respectively. Fuel oils have high cetane/octane number indicated that the engine is easily to ignite at low temperature. However, if fuel oil has over cetane/octane it is not complete combustion leading to engine damaged.

Acidity or acid value Is one of significantly considered which may cause corrosion of oil tank and other components. It can be determined according to ASTM D664.

2.6.3 Solid Char

Solid residue referred to char which mainly consisted of fixed carbon or inorganic matter retained at the bottom of the reactor. Solid fraction concerns with process temperature, it is decreased with an increase of final temperature due to more releasing volatile matter. Solid chars obtained from pyrolysis of composite material can be further applied to activated carbon for biomass [19] or used them as reinforcement or filler to prepare new composite [26].

CHARPTER III

EXPERIMENTALS

3.1 Materials and Chemicals

3.1.1 Composite Wastes

There are ten different fiber reinforced plastic composite (FRP) wastes used in this research These wastes were generated from hand lay up and filament winding processes of pipe connector and conduit, respectively . They can be classified by resin matrix type into two systems , including unsaturated polyester and epoxy resin matrix. Each system was reinforced with two different glass fiber contents, approximately 30 wt.% and 60 wt.%, which were generated from hand lay up and filament winding processes, respectively. For unsaturated polyester system, it was separated into three types based on their chemical structure, being orthophthalic, isophthalic, and vinyl ester. Meanwhile, epoxy system was subdivided by the type of curing agent into two types, namely amine and anhydride. The characteristics of composite wastes are summarized in Table 3.1

3.1.2 Resin, Curing agent, and Chemical for Composites Preparation

Table 3.2 presents the resin, curing agent, and chemicals which were used as received to prepare new composites from original fiber and recovered fiber from pyrolysis process.

3.1.3 Original Fiber

E- Glass (125 μm) was purchased by From JUCHI Group, China.

3.1.4 Carrier Gas

Nitrogen gas (99.5%) was purchased from Thai Industrial Gases Public Company Limited, Thailand.

Table 3.1 Characteristics of composite waste samples.

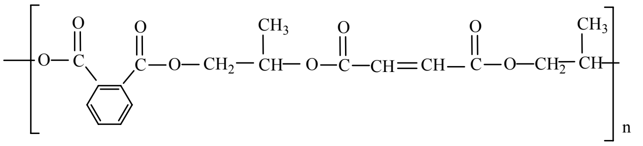
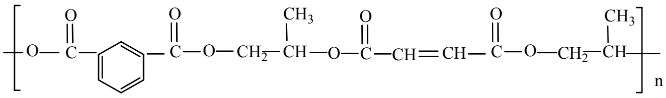
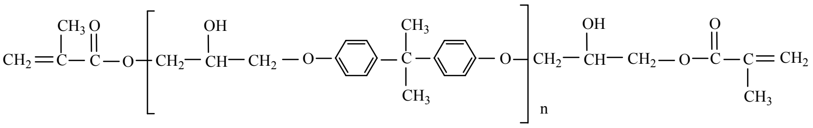
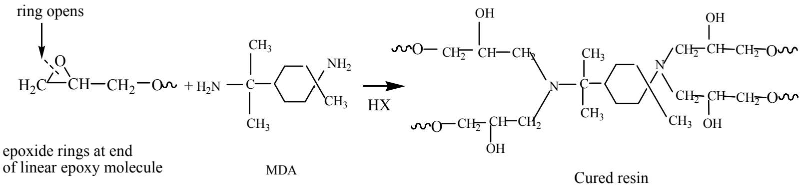
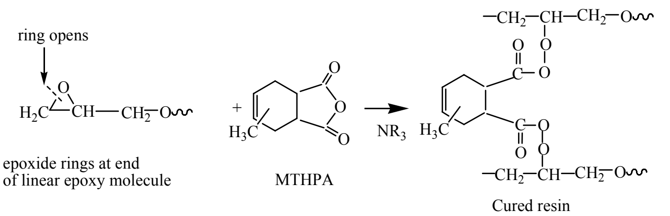
Item	Matrix system	Sample designation
Unsaturated polyester matrix system		
1. Orthophthalic (TP910)		Ortho 30%
2. Orthophthalic (TP910)		Ortho 60%
		
3. Isophthalic (F046)		Iso 30%
4. Isophthalic (F046)		Iso 60%
		
5. Vinyl ester (Derakane 411)		Vinyl 30%
6. Vinyl ester (Derakane 411)		Vinyl 60%
		
Epoxy matrix system		
7. Epoxy/Amine (DER331/1,8 Methane diamine (MDA))		Epoxy/MDA 30%
8. Epoxy/Amine (DER331/1,8 Methane diamine (MDA))		Epoxy/MDA 60%
		
9. Epoxy/Anhydride (DER331/Methyltetrahydrophthalic anhydride (MTHPA))		Epoxy/MTHPA 30%
10.Epoxy/Anhydride (DER331/Methyltetrahydrophthalic anhydride (MTHPA))		Epoxy/MTHPA 60%
		

Table 3.2 Listed of resin, and chemical for composite preparation.

Item	Matrix System	Trade named ®	Manufacturer	Functions
	Unsaturated polyester system			
1	Orthophthalic polyester	TP 910	Major Holdings	Resin matrix
2	Isophthalic polyester	F 046	Thai polyset	Resin matrix
3	Vinyl ester	Derakane-411	Dow Chemical	Resin matrix
4	Methyl Ethyl Ketone Peroxide	M 60	AKZO BOBEL	Catalyst
5	Cobalt naphthenate	Cobalt	OMG Group	Activator
	Epoxy Matrix System			
6	Epoxy resin (Diglycidyl Ether of bisphenol A)	DER 331	Dow Chemical	Resin matrix
7	1,8 Methane diamine (MDA)	H 3895	Air Products	Curing agent
8	Methyltetrahydrophthalic anhydride (MTHPA)	46Q	Lindride	Curing agent

3.2 Instruments and Equipments

3.2.1 Instrument for Characterization

The instruments used for characterization of composite waste samples and the products obtained from pyrolysis process are summarized in Table 3.3.

Table 3.3 List of experimental instruments for characterization

Instruments	Characterization	Material	Remark
1.Thermogravimetric analyzer (TGA[a])	- Proximate analysis - Thermal analysis	- Composite waste samples - Pyrolysis solid product	Figure 3.6
2. Fourier Transform Infrared Spectroscopy (FTIR[b])	Functional group	- Composite waste samples - Pyrolysis solid product	Figure 3.7
3. Elemental analyzer [c]	Elemental analysis	- Composite waste samples	Figure 3.8

Table 3.3 (continue) List of experimental instruments for characterization

Instruments	Characterization	Material	Remark
4. Scanning Electron Microscope (SEM [d])	Physical analysis	- Pyrolysis solid product - Fractured surface tested specimens	Figure 3.10
5. Centrifuge [e]	Separate water/oil	-Pyrolysis liquid product	Figure 3.11
6. Simulated distillation (GC [f])	Boiling range	-Pyrolysis liquid product	Figure 3.12
7. Automatic Bomb Calorimeter (Bomb calorimeter [g])	Gross calorific value (GCV)	-Pyrolysis liquid product	Figure 3.13
8. Gas chromatograph (GC [h])	Gas verification	- Pyrolysis gas product	Figure 3.14
9. Pensky-Martens Closed Cup	Flash point	- Pyrolysis liquid product	ASTM D93
10. Pour and Cloud Point Tester	Pour point	- Pyrolysis liquid product	ASTM D 97
11. Potentiometric Automati Titrator	Acidity	- Pyrolysis liquid product	ASTM D 644
12. Viscometer	Viscosity	- Pyrolysis liquid product	ASTMD 445
13. Digital Density Meter	Specific gravity	- Pyrolysis liquid product	ASTMD 4025

a: TGA, SDTA 851e ,Mettler Toledo, Switzerland.

b: FTIR, Spectrum One, Perkin Elmer, California, United States.

c: CHN/O analyzer, PE 2400 Series II, Perkin Elmer, Maryland , United States.

d: SEM, JSM 6480LV,JEOL, Japan.

e: Centrifuge C-28, BOECO, Germany.

f: GC-Simdist, CP-3800, Varian Les Ulis, France.

g: Bomb Calorimeter, AC-350, LECO, Orissa, United States.

h: GC, 8610C, SRI instrument, California, United States.

3.2.2 Equipments for Thermochemical Conversion by Pyrolysis Process

1. Quartz tube reactor which has 48 mm outside diameter and 300 mm long with socket 40/38 is shown in Figure 3.1 (a).

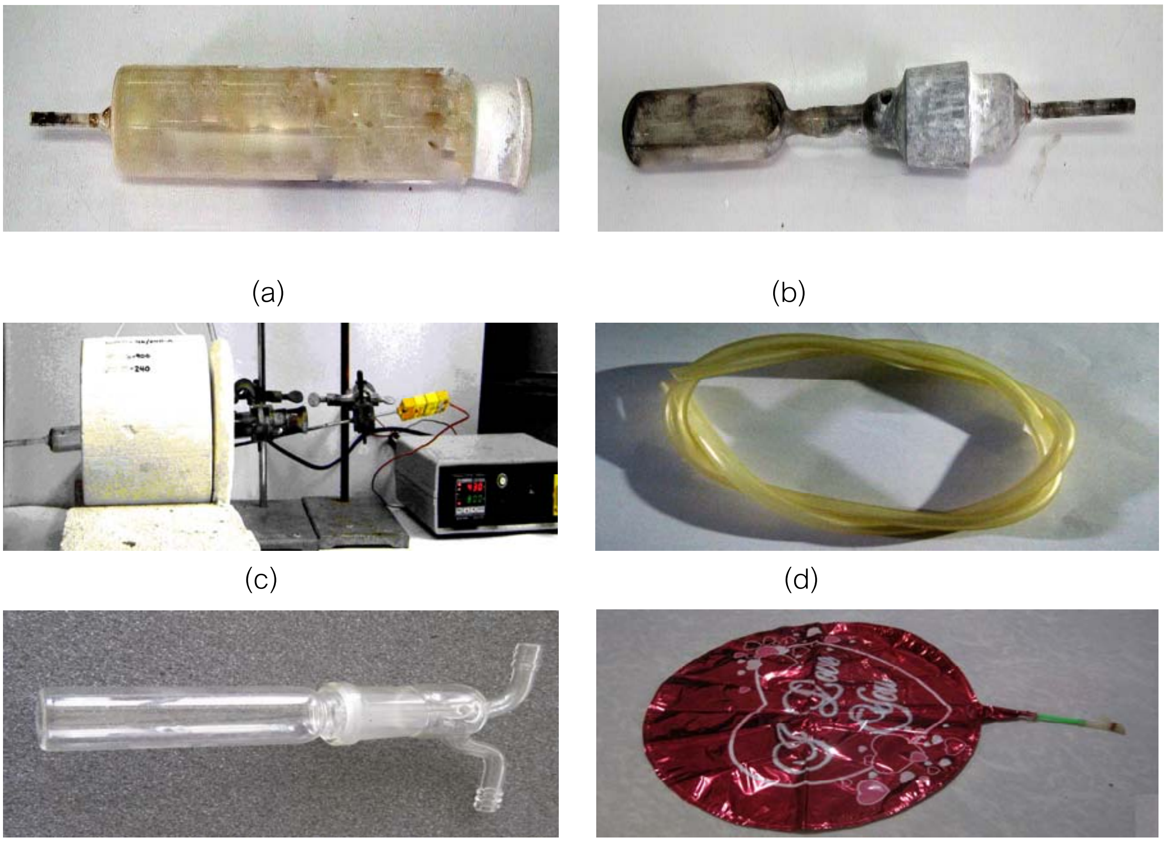
2. Quartz sample boat presented in Figure 3.1(b) was used for placing sample that will be pyrolyzed. It has 30 mm outside diameter and 300 mm long which can be placed the maximum weight of sample at 20 g per each run.

3. Tubular Electrical furnace which has 100 mm inside diameter and 150 mm long with temperature controller and a thermocouple was presented in Figure 3.1 (c).

4. Silicone line rubber, which was for gas passing though is shown in Figure 3.1 (d).

5. Borosilicate glass condenser which has 6.35 mm of inside diameter. It was used to trap evolution gas and condensed in to liquid phase at the bottom is presented in Figure 3.1 (e).

6. Gas sampling bag (general balloon foil), which can be contained at 6 L volumetric of gas, which was used to collect evolution gas of typical run is displayed in Figure 3.1 (f).



(a) (b)

(c) (d)

(e) (f)

Figure 3.1 Tubular tube reactor (a), quart sample boat (b), and horizontal electrical furnace with temperature controller and thermocouple (c), silicone rubber line(d), borolicate glass condenser (e), and balloon foil gas sampling bag (f).

3.2.3 Equipments for Preparation of New Composite

1. Conventional mixer presented in Figure 3.2 (a) was used to stir and disperse composite compositions such as resin, glass fiber, and additives into good mixing.

2. Teflon mold flexural and impact was used to fabricate and shape specimens according to ASTM D790-03 and D 256- 04, respectively, displayed in Figure 3.2 (b).

3. Convention oven (FAGOR Innovation) displayed in Figure 3.3 was used to cured epoxy/anhydride composite at the temperature of 150ºC for 15 min.

(a) (b)

Figure 3.2 Conventional mixer (a) and Teflon mold (b)

Figure 3.3 Convention oven (FAGOR Innovation).

3.3 Methodology

The flow chart of experimental procedure is summarized in Figure 3.4

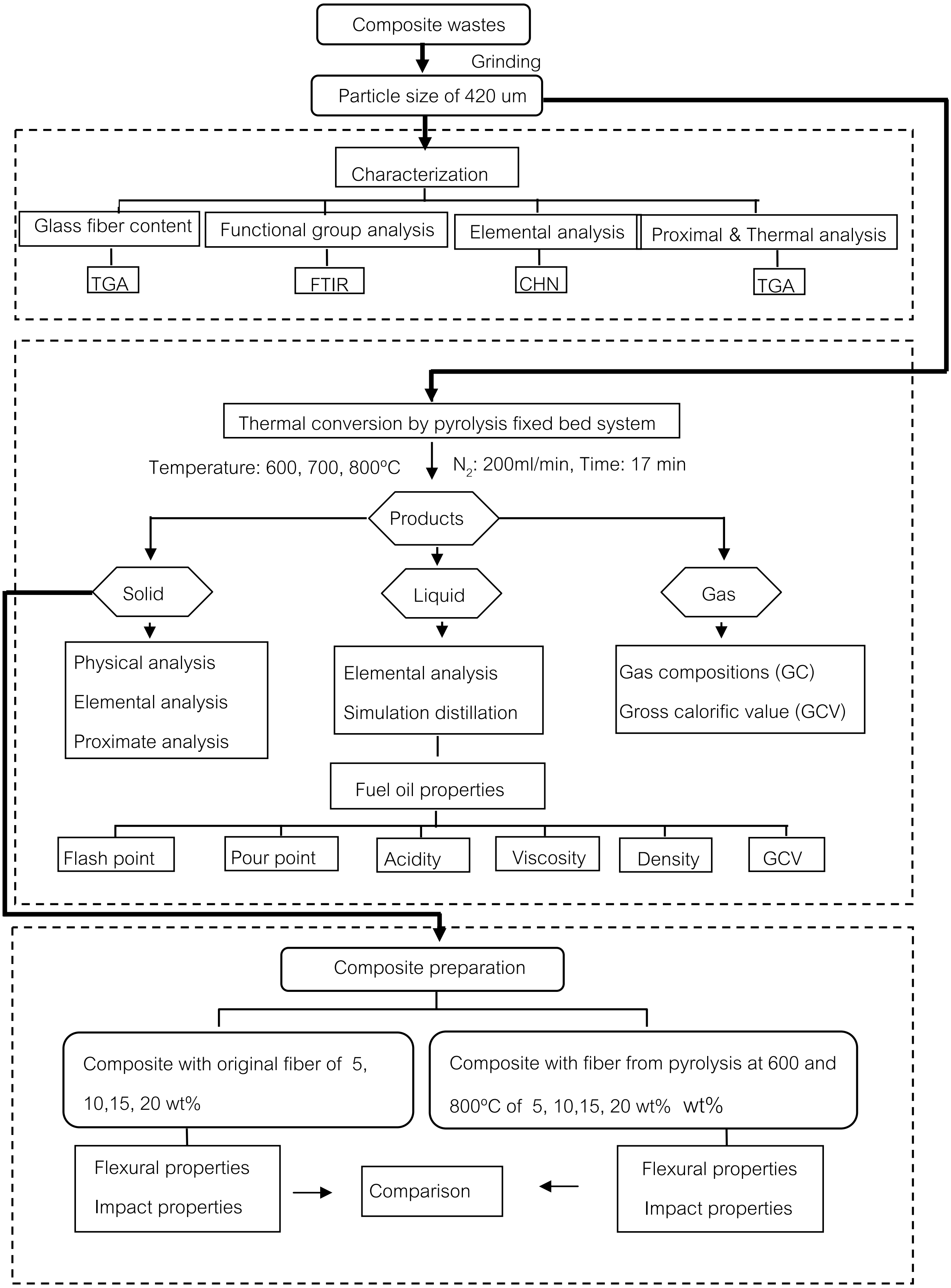


Figure 3.4 The flow chart of experimental procedure.

3.3.1 Preparation of Composite Waste Samples

The Composites wastes were ground into powder using biomass grinder in order to fit the composite wastes into the reactor and were then sieved into evenly approximate size of 420 um by standard screen Mesh No 40.

3.3.2 Thermal Conversion by a Fixed Bed Pyrolysis System

The schematic diagram of a horizontal fixed bed pyrolysis system is displayed in Figure 3.5. The Experiments were conducted by using horizontal quart tube reactor (25 mm id, and 300 mm long) at final temperature of 600, 700, and 800°C under nitrogen atmosphere at total flow rate of 200 ml/min. In typical run, 20 g of composite sample was placed into the quart sample boat connected with a series of ice-cooling column and gas sampling bag.

When the reactor was heated to the final temperature, the prepared quart sample boat was rapidly inserted into the center of the tubular reactor and maintained for 17 min. During process, the generated gases were first passed through the silicone line to ice-cooling column. In this step, some parts of gases were trapped and condensed to liquid product which were collected at bottom of Borosiligate glass condenser, while light gases or uncondensable gases were passed through and collected in gas sampling bag for further verified.

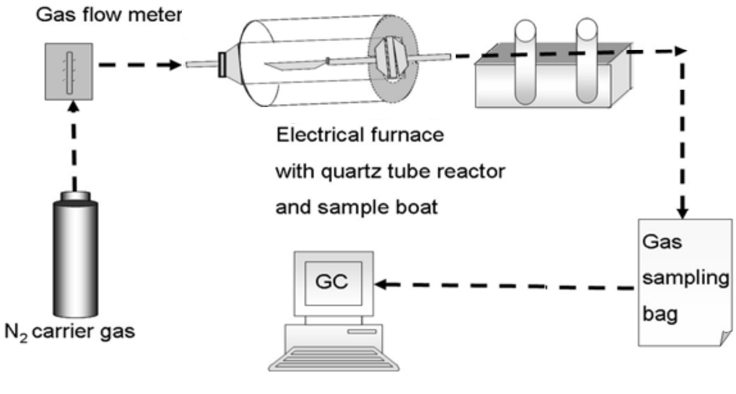


Figure 3.5 Schematic diagram of a horizontal fixed bed pyrolysis system.

After each experiment, the products obtained from pyrolysis of composite wastes consisting of solid, condensable liquid, and light gases were evaluated in terms of product yield or distributions. The solid residues remained in quartz sample boat and condensable liquids fractions were weighed in order to calculate products distributions, meanwhile gaseous products were evaluated by difference. The solid and liquid yield can be calculated by the following equation;

$$\text{Solid yield (wt.\%)} = \frac{\text{weight of solid residues}}{\text{weight of composite sample}} \times 100 \qquad (3.1)$$

$$\text{Liquid yield (wt.\%)} = \frac{\text{weight of liquid}}{\text{weight of composite sample}} \times 100 \qquad (3.2)$$

$$\text{Gas yield (wt..\%)} = 100 - \text{solid yield} - \text{liquid yield.} \qquad (3.3)$$

3.3.3 Preparation of New Composite by bulk molding compound (BMC) method

3.3.3.1 Preparation of Unsaturated Polyester Composites.

Three types of unsaturated polyester (i.e., orthophthalic, isophthalic, and vinyl ester resin) were prepared into composites by reinforced with original glass fiber and recovered glass fiber from pyrolysis process at 600°C and 800°C. Each type of resin was first mixed with cobalt naphthenate as an activator and then added glass fiber into the mixed resin at the ratio of 5, 10,15, and 20 wt% for an individual batch. The resin was stirred by using convention spiral mixer for 5 min and held at room temperature for 10 min in order to remove air bubble. After that, methyl ethyl ketone peroxide (MEKPO) was added into the mixture. and stirred for 3 min. The resin was then poured into Teflon mold and held at room temperature for 24 hr to completely cure the resin, before releasing from the mold. Table 3.3 is an example of weight ratio for preparation 100 g unsaturated polyester reinforced with glass fiber at the ratio of 5, 10,15, and 20 wt%.

Table 3.4 Compositions of 100 g unsaturated polyester composite.

Reinforcement phase	Matrix phase		
Glass fiber[a] (wt.%)	Resin[b] (g)	Cobalt[c] (g)	MEKPO[d] (g)
5	92.62	0.48	1.90
10	87.75	0.45	1.80
15	82.88	0.42	1.70
20	78.00	0.40	1.60

a: original or recycled fiber obtained from pyrolysis

b: ortho or iso or vinyl ester resin

c: 0.5 wt.% of total matrix weight

d: 2 wt.% of total matrix weight

3.3.3.2 Preparation of Epoxy Composites

The epoxy composites were prepared from both epoxy cured with amine and anhydride curing agents, at which each of them were reinforced with original glass fiber and recovered glass fiber from pyrolysis process at 600ºC and 800ºC. Table 3.5 presents weight ratio for the preparation of 100g epoxy composite at the glass fiber ratio of 5, 10, 15, and 20 wt%. The resin was first mixed with either original glass fiber or recycled fiber. After good dispersing, curing agent was then added and stirred by conventional mixer for 5 min before pouring the mixture into Teflon mold which was machined as flexural and impact specimens. For epoxy/amine system , the was allowed to fully cure at room temperature for at 24 hr before and releasing from the mold. Meanwhile, epoxy/anhydride system in Teflon mold was held at room temperature for 2 hr, and then heated at 150ºC for 15 min in conventional oven for fully cured and cooled down to room temperature before releasing from the mold. During the resin in Teflon mold was held at room temperature for 2 hr, the epoxy resin become more viscous, which could help to good dispersing and preventing of the accumulation or precipitation of glass fiber.

Table 3.5 Compositions of 100g epoxy composite.

Composite systems	Reinforcement phase	Matrix phase		
	Glass fiber[a] (wt.%)	Epoxy resin (g)	Curing agent (g)	
			MDA[b]	MTHPA[c]
Epoxy/amine	5	63.30	31.70	-
	10	60.00	30.00	-
	15	56.70	28.30	-
	20	53.30	26.70	-
Epoxy/anhydride	5	52.80	-	42.20
	10	50.00	-	40.00
	15	47.20	-	37.80
	20	44.50	-	35.50

a: original or recycled fiber obtained from pyrolysis

b: 50 wt.% of epoxy resin

c: 80 wt.% of epoxy resin

3.4 Characterizations and Testing

3.4.1 Characterization of Composite Waste Samples

3.4.1.1 Glass Fiber Content in Composite Waste Samples

Composite materials are composed of heterogeneously different phase components, therefore the total amount of glass fiber and organic matter contained in sample were be determined by thermogravimetric analyzer (TGA), SDTA 851e ,Mettler Toledo, Switzerland, presented in Figure 3.6, under air condition from an ambient to 900°C and maintained at this temperature for 10 min until no change in weight was observed. After resin matrix was burned out by oxidation reaction with oxygen under air atmosphere, the solid residues were referred to glass fiber containing in composite waste samples, which did not decompose under experimental conditions.

3.4.1.2 Functional Group Analysis

Fourier transform infrared spectrophotometer (FTIR) Spectrum One, Perkin Elmer, California, United States, which is displayed in Figure 3.7 was used to analyze the spectra of composite waste, solid residues, and liquid oil obtained from pyrolysis process in the wave length ranging of 4000-400 cm^{-1}at a resolution of 1 cm^{-1} The solid residues were first ground and then mixed with KBr. and further pressed into pellet form.

Figure 3.6 Thermogravimetric Analyzer (TGA), SDTA 851e ,Mettler Toledo, Switzerland.

Figure 3.7 Fourier Transform Infrared Spectrophotometer (FTIR) Spectrum One, Perkin Elmer, California, United states.

3.4.1.3 Elemental Analysis

The elemental analysis in terms of chemical compositions of composite waste samples, solid residue, and liquid oil obtained from pyrolysis process were determined by using Elemental analyzer, PE 2400 Series II, Perkin Elmer, Maryland , United States presented in Figure 3.8.

3.4.1.4 Proximate Analysis

Proximate analysis of composite waste samples were characterized in terms of moisture, volatile matter, fixed carbon, and ash contents using Thermogravimetric analyzer (TGA), SDTA 851e ,Mettler Toledo, Switzerland. displayed in . The temperature profile which was used to determine moisture, volatile matter, fixed carbon, and ash content is shown in Figure 3.9 , A sample was heated from 30 to 850ºC at a heating rate of 20ºC/min the weight changed at 100 ºC is the moisture content and continuously heated to 850ºC for 10 min to determine the amount of volatile matter. The sample was then cooled to 800ºC at at a heating rate of 20ºC/min under oxidizing atmosphere and held at this temperature until constant weight to examine fixed carbon. The remaining solid residue was referred to ash content.

Figure 3.8 Elemental Analyzer, PE 2400 Series II, Perkin Elmer, Maryland, United States

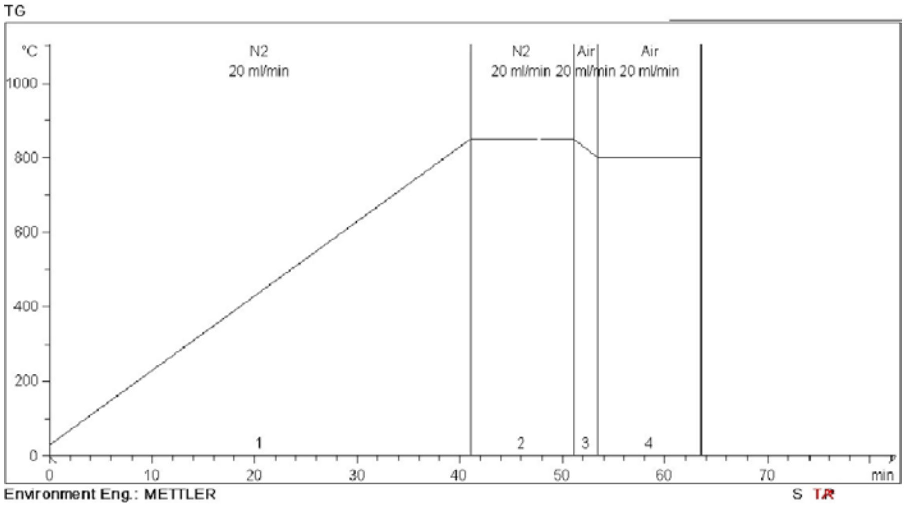


Figure 3.9 Temperature profile for proximate analysis of composite waste samples.

3.4.1.5 Thermogravimetric Analysis

The thermal degradation characteristic of composite samples was carried out using thermogravimetric analyzer (TGA), SDTA 851e ,Mettler Toledo, Switzerland, under inert nitrogen at flow rate of 20 ml/min. Individual run, composite sample was weighted for 10 mg. in alumina crucible. Dynamic experiments were performed at 5, 10, and 15°C /min from an ambient to 900 °C and held at final temperature for 5 min. The mass change of sample was continuously recorded as a function of temperature and time to produce thermogram (TG data) and the rate of weight loss (DTG data), respectively. The temperature at maximum weight loss was used to study kinetic using Arrhenius equation.

3.4.2 Characterization Products from Thermochemical Conversion by Pyrolysis Process

3.4.2.1 Characterization of Solid Residues

The solid residues obtained from pyrolysis were characterized in terms of physical appearance by Scanning electron microscope (SEM) JSM 6480LV, JEOL, Japan displayed in Figure 3.10 in order to observe the surface of recycled fiber after pyrolysis process. Furthermore, the solid residues were characterized the functional group, elemental and proximal analysis. The details of each characterization technique were similar to those previously mentioned.

Figure 3.10 Scaning Electron Microscope (SEM) JSM 6480LV, JEOL, Japan.

3.4.2.2 Characterization of Condensable Liquid Products

The condensable products derived from pyrolysis experiment were first centrifuged by using centrifuge, C-28, BOECO, Germany, presented in in Figure 3.11. for 30 min at 3000 rpm to separate aqueous phase from organic phase. Each phase was then weighed to determine its product yields. The oil phase which was referred to crude oil was indentify boiling distillation range by using Gas chromatography Simulated distillation GC-Simdist, CP-3800, Varian Les Ulis, France shown in Figure 3.12. Elemental analysis and goss calorific value (GCV) of liquid oil were analyzed using Elemental analyzer, PE 2400 Series II, Perkin Elmer, Maryland, United States, and using Automatic Bomb Calorimeter, AC-350, LECO, Orissa, United States, presented in in Figure 3.13, respectively. Functional group was studied using Fourier transform infrared spectrophotometer (FTIR). Furthermore, liquid oils were also characterized in terms of general fuel oil properties such as

- Flash point using Pensky- Martens Closed Cup (ASTM D93)
- Pour point using Pour and Cloud Point Tester (ASTM D97)

- Acidity by using potentiometric automatic titrator (ASTM D664)
- Kinematic viscosity determined at 40ºC using Viscometer (ASTM D445)
- Density by using Digital Density Meter (ASTM D4052)

Figure 3.11 Centrifuge C-28 (BOECO), Germany.

Figure 3.12 Simulated Distillation GC-Simdist CP-3800 Varian Les Ulis, France.

Figure 3.13 Automatic Bomb Calorimeter AC-350 LECO, Orissa.

3.4.2.3 Characterization of Gaseous Products

The collected gases were verified by using a gas chromatography (GC), 8610C, SRI instrument, California, United State, presented in Figure 3.14 equipped with a thermal conductive detector (TCD) and a flame ionized detector (FID) in order to identify gas compositions Meanwhile the percentage of individual gas was evaluated by volumetric of collected gas and GC quantifying. Furthermore the collected gases were evaluated from lower heating value ; LHV (MJ/m^3) which can by calculated by following equation [27]:

$$\mathrm{LHV}\ (\mathrm{MJ/m^3}) = \frac{12.64 \times [\mathrm{CO}] + 10.8 \times [\mathrm{H_2}] + 35.72 \times [\mathrm{CH_4}]}{\text{Total volume of gas (L/min)}} \qquad (3.4)$$

Where $[CO]$ is Volume of CO gas (L/min)

$[H_2]$ is Volume of H_2 gas (L/min)

$[CH_4]$ is Volume of CH_4 gas (L/min)

Figure 3.14 Gas Chromatography (GC) 8610C SRI Instrument, California.

3.4.3 Characterization of Composites Prepared from Original Glass Fiber and Recycled Glass Fiber from Pyrolysis Process

3.4.3.1 Flexural Properties

The flexural strength and flexural modulus of epoxy and unsaturated polyester reinforced with original glass fiber and recovered glass fiber obtained from pyrolysis process were tested by using a Universal Testing Machine (LR 100 N, LLOYD instrument United Kingdom, presented in Figure 3.15. The composite tested flat wise specimens were prepared by casting into Teflon mold having the size of 127 x 12.5 mm and 3 mm thickness according to ASTM D790-03 standard method. The specimen was placed on a support span the span to depth ratio of 16:1 (span length : thickness of specimens). A crosshead speed was ranged 1-1.5 mm/min depending on each the thickness of specimen the thickness which can be calculated by equation (3.5) according to ASTM D790-03. .At least five specimens of composite sample series were tested and the results were averaged to obtain the mean values.

$$R = \frac{ZL^2}{6d} \tag{3.5}$$

Where R is rate of crosshead motion (mm/min)

Z is rate of straining of the outer fiber, (mm/min), shall be equal to 0.01.

L is support span (mm.)

d is depth of beam or spcimn thickness (mm.)

Figure 3.15. Universal Testing Machine (LR 100 N, LLOYD Instrument, United Kingdom).

3.4.3.2 Izod Impact Properties

The impact resistance of composite sample prepared from original glass fiber and recovered fiber was measured by a Pendulum Impact Tester (B5102.202 2 J, Swick I, Germany) shown in Figure 3.16. The tested specimens were prepared by casting into Teflon mold having the size of 12.7 x 65 x 3 mm with a completely notched according to ASTM D 256-04 standard method. A pendulum having energies 2 J was found to be sufficient being used with the composite samples. At least five specimens of composite sample series were tested and the results were averaged to obtain the mean values.

Figure 3.16 Pendulum Impact Tester (B5102.202 2 J, Swick I, Germany).

3.4.3.3 Fractured Surface of Three-Point Bending Tested Specimens

The fractured surface of three point bending specimens was observed by Scanning electron microscope (SEM) as presented in Figure 3.10 to investigate the relationship between morphologies and strength of the composite samples.

CHAPTER IV

RESULTS AND DISCUSSION

The discussions of the experimental results in this work were classified into three sections. The first section reveals the characteristic of composite waste samples that used in this work in terms of the amount of glass fiber content, functional group analysis, elemental analysis, proximate analysis, and thermal decomposition behavior of composite waste samples. The second section shows the thermal conversion of composite wastes by a fixed bed pyrolysis system. This part presents the product distributions and the characteristic of pyrolysis products including of solid, liquid, and gaseous products in relation to pyrolysis temperature, type of unsaturated polyester resin matrix, type of epoxy curing agent, and glass fiber content. The last section is the preparation and properties of composites prepared from original glass fiber and recovered glass fiber from pyrolysis process, including the morphological appearance of the fractured surface from the three point bending test samples.

4.1 The Characteristics of Composite Waste Samples

4.1.1 Glass Fiber Content in Composite Waste Samples.

The amount of glass fiber content in each composite waste sample was determined by thermogravimetric analyzer (TGA) (TGA/SDTA 851e, Mettler Toledo, Switzerland) under air condition from an ambient to 900ºC and maintained at this temperature for 10 min until no change in weight was observed. After resin matrix was burned out by oxidation reaction with oxygen under air atmosphere, the solid residues were referred to glass fiber containing in composite waste samples, which did not decompose under experimental conditions. Table 4.1 shows the amount of glass fiber or solid residue of each composite sample. It was indicated that glass fiber content in the samples was closed to 30 and 60 wt. %.

Table 4.1 The Glass fiber content (wt. %) containing in composite waste samples

Raw materials/sample designation	Glass fiber content
Ortho 30%	29.27
Iso 30%	29.40
Vinyl 30%	30.20
Epoxy/MDA 30%	29.25
Epoxy/MTHPA30%	30.50
Ortho 60%	59.74
Iso 60%	60.44
Vinyl 60%	60.28
Epoxy/ MDA 60%	59.40
Epoxy/ MTHPA 60%	60.26

4.1.2 Functional Group Analysis

The FTIR absorption spectra of unsaturated polyester and epoxy composite waste samples are presented in Figure 4.1 and 4.2 , respectively. The major FTIR spectra of three types unsaturated polyester composite wastes were very similar appearing at the same regions, consisting of the strong absorption peak of carbonyl ester at 1730 cm^{-1} (C=O) and 1285 cm^{-1} (C-O), Especially, orthophthalic and isophthalic unsaturated polyester composite waste, their FTIR spectra were almost overlapped at the same region such as the presence of C-H aromatic stretching at 3030 cm^{-1}, aromatic C=C bending and alkylenyl C=C stretching at 1700-1500 cm^{-1}, and aromatic C-H bending 700 cm^{-1} which related to their similar chemical structure as presented in Figure 4.3 (a) and (b); whereas the absorption peak of vinyl ester composite waste was different from those of them in which it presented the strong peak at 2960 and 1636 cm^{-1} which generated from the vibration of C=C in the methylene and methacrylate group, as shown in Figure 4.3 (c). Furthermore, the absorption peaks of aromatic C-H bending at 700 cm^{-1} , aromatic C-H stretching at 3030 cm^{-1}, and 1508 cm^{-1} in vinyl ester composite waste were stronger than those of orthophthalic and isophthalic due to the higher amount of benzene ring in its repeating unit. In addition, the strong intensity at 3600- 3200 cm^{-1} of vinyl ester composite was attributed to the absorption peak of hydroxy groups (OH) on the dimethacrylate backbone.

However, it was indicated that there was no difference in absorption peak region of 30 and 60 wt.% of glass fiber composite wastes as revealed in Figure 4.1 (a) and (b), respectively, due to similar structure or functional group of the unsaturated polyester matrix.

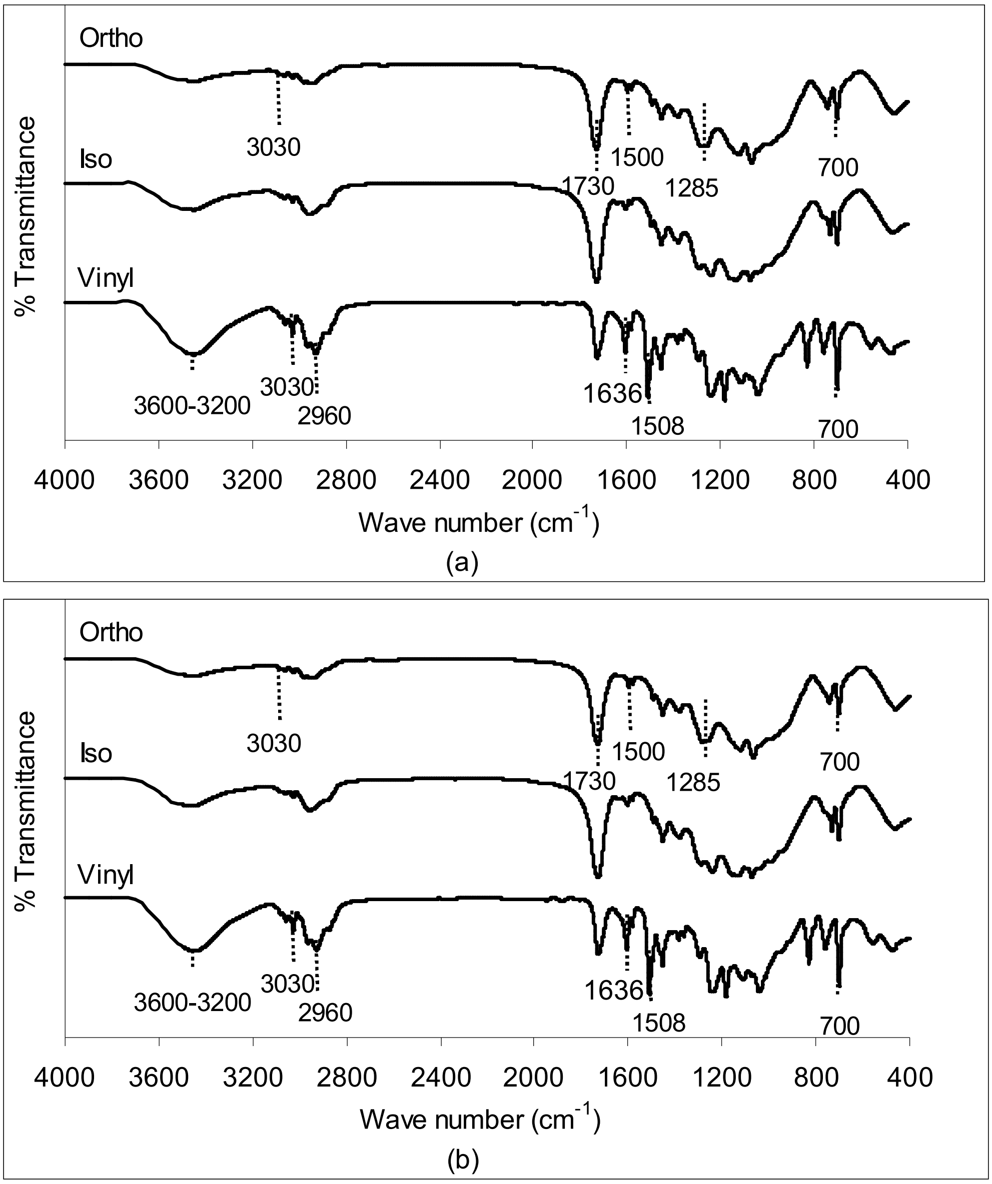
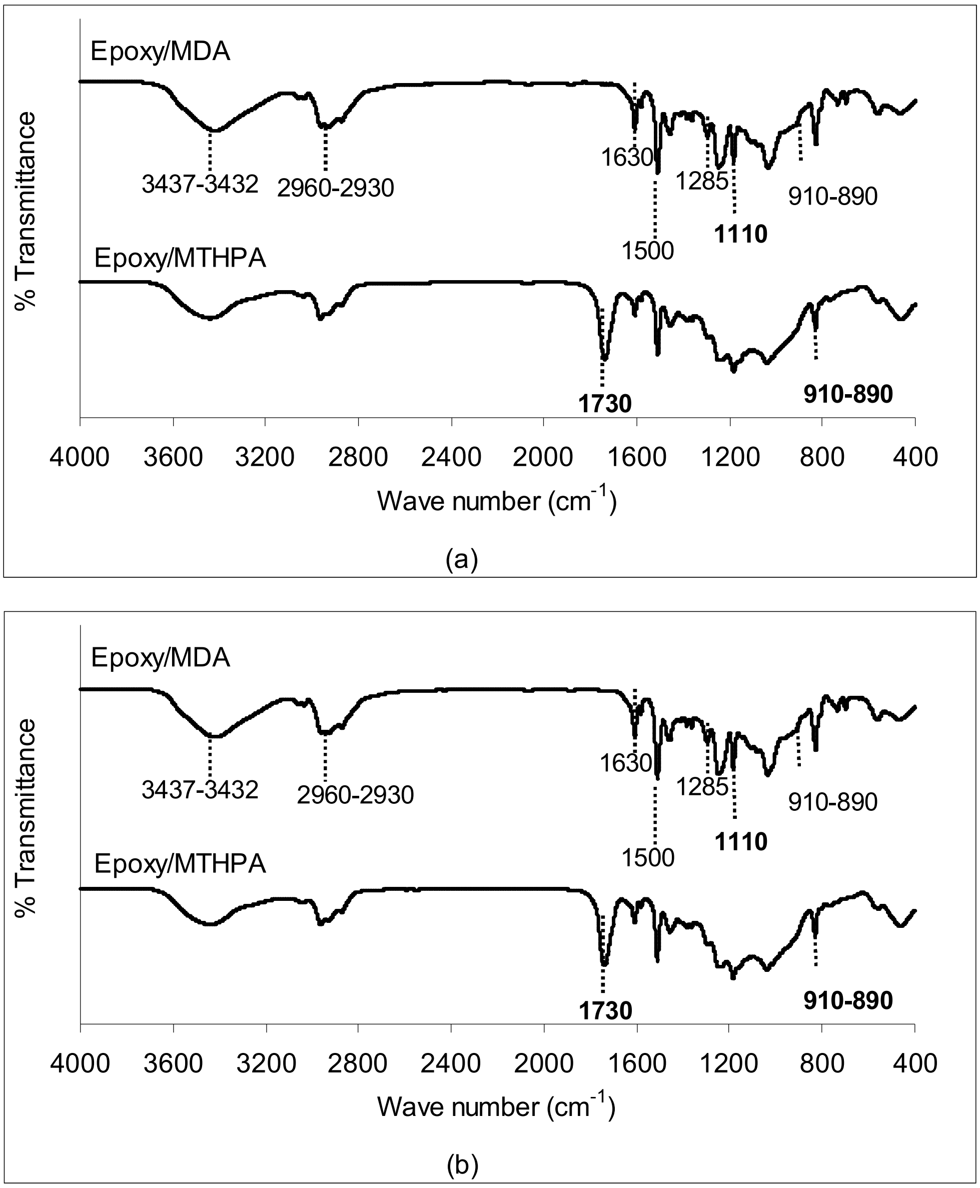


Figure 4.1 FTIR spectra of unsaturated polyester composite waste samples : (a) 30 wt% glass fiber and (b) 60 wt% glass fiber.

For the epoxy composite, the FTIR spectra of epoxy cured resin depended on the functional group of curing agent. Generally, the prominent absorption bands of epoxy resin presented at 910-890 and 1285 cm^{-1} (C-O stretching in epoxy or oxirane ring), 1630-1500 cm^{-1}(C-H bending in aromatic ring), 2930 and 2960 cm^{-1} (C-H stretching of the methylene and methyl group), and the broad peak at 3437- 3432 cm$^{-1.}$ (O-H stretching)



(a)

(b)

Figure 4.2 FTIR spectra of epoxy cured with amine (MDA) and anhydride (MTHPA) composite waste samples: (a) 30 wt.% glass fiber and (b) 60 wt.% glass fiber.

When epoxy was reacted with curing agent by ring opening, the intensity of absorption peak of C-O stretching t 910-890 cm^{-1} was decreased. However, the FTIR spectra of both epoxy cured with amine (MDA) and anhydride (MTHPA) matrix still presented the absorption peak which generated from the vibration in epoxy backbone such as 1630-1500 cm^{-1} (C-H bending in aromatic ring), 2960 and 2930 cm^{-1} (C-H stretching of the methyl and methylene group), and the strong broad peak at 3437-3432 cm$^{-1.}$ (O-H stretching).

In addition. Figure 4.2 (a) and (b) indicated that the appearance of C-N stretching at 1110 cm^{-1} was attributed to amine cured epoxy, while the strong carbonyl peak at 1730 cm^{-1} was used to identify the characteristic of anhydride cured epoxy. The chemical structure of epoxy cured with amine and anhydride was presented in Figure 4.4 (a) and (b), respectively. The C-O stretching t 910-890 cm^{-1} of epoxy cured with anhydride composite was stronger than that of the ones due to the higher C-O in anhydride curing agent. Similar to the spectra of unsaturated polyester composite, the spectra of epoxy reinforced with 30 and 60 wt% glass fiber presented in Figure 4.2 (a) and (b) were absolutely similar in their absorption peak region.

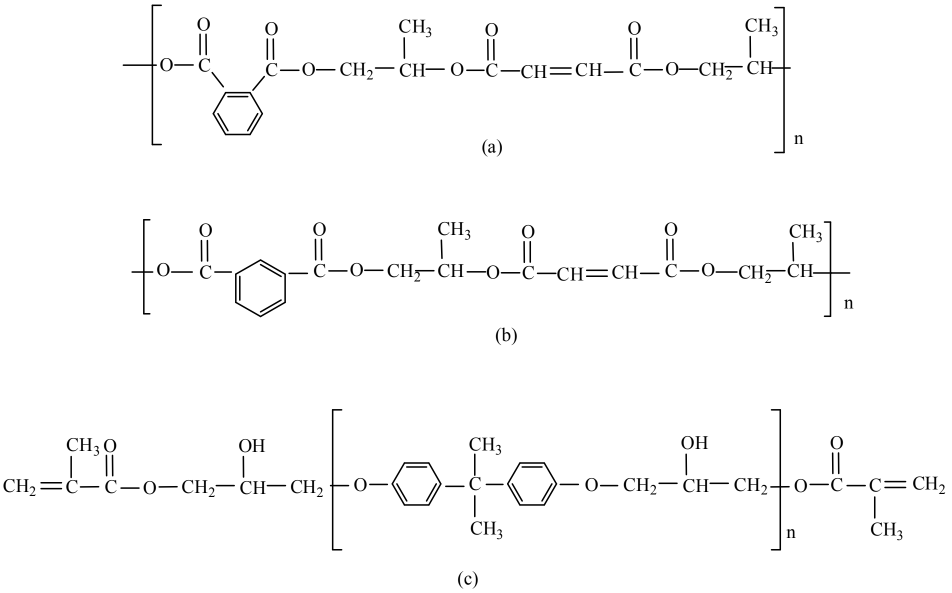


Figure 4.3 Chemical structure of unsaturated polyester resin: (a) orthophthalic polyester resin, (b) isophthalic polyester resin, and (c) vinyl ester resin.

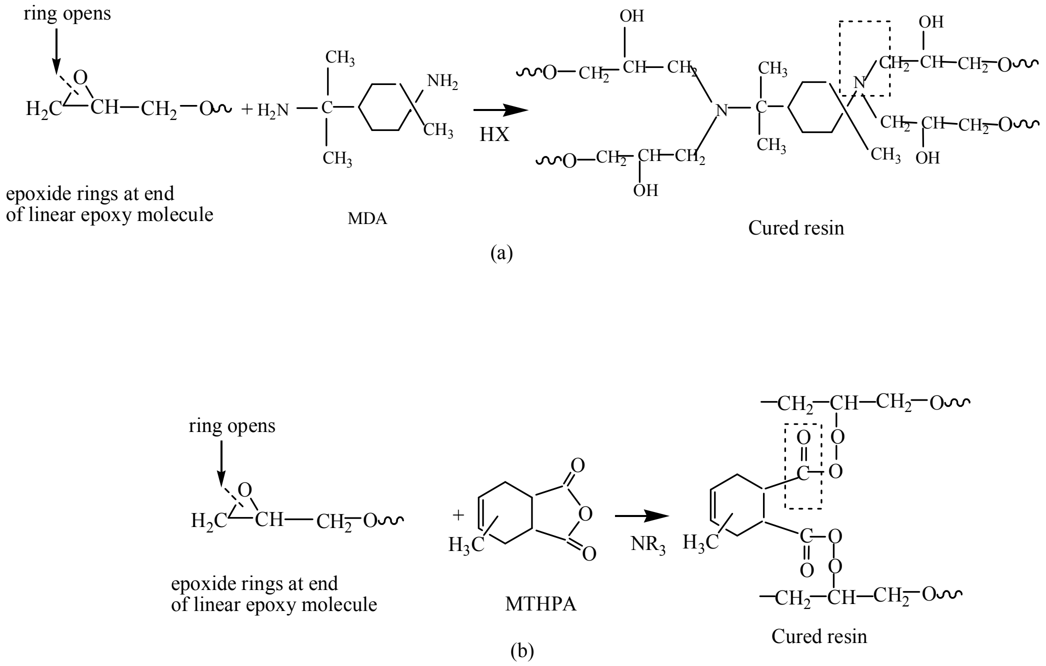


Figure 4.4 Chemical structure of epoxy cured resin: (a) Epoxy/amine (MDA) and (b) Epoxy/anhydride (MTHPA).

4.1.3 Elemental Analysis

The chemical compositions of composite samples were characterized by CHN analyzer LECO CHN-2000 as presented in Table 4.2. The percentage of CHN consisted in composite waste samples was used to evaluate the efficiency of pyrolysis process. It was indicated that how much chemical compositions in raw materials can be converted into solid, liquid, or gaseous product.

It can be seen from Table 4.2 that the chemical compositions consisted in composite samples depend on the percentage of glass fiber content. If the amount of glass fiber content in composite material was increased, the fraction of polymer matrix will be decreased resulting in the reduction of carbon, hydrogen, and nitrogen (CHN); while the amount of oxygen was increased because it was calculated from the difference in carbon, hydrogen, and nitrogen content. Both polymer matrices, unsaturated polyester and epoxy, mainly consisted of carbon, hydrogen, and oxygen. When theses elements were heated, they can be decomposed and turned into smaller molecules in terms of light gaseous molecules such carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), or hydrogen (H_2) and some amount of these molecules may be condensed into liquid phase which can be further applied to use as fuel oil.

Table 4.2 Elemental analysis of composite waste samples.

Composite Waste Samples	Chemical Compositions (wt.%)			
	C	H	N	O*
Ortho 30%	51.79	4.76	-	43.45
Iso 30%	47.93	4.83	-	47.24
Vinyl 30%	45.07	4.51	-	50.42
Epoxy/MDA 30%	51.73	6.07	1.52	41.28
Epoxy/MTHPA 30%	45.07	4.51	-	50.42
Ortho 60%	31.35	3.25	-	65.40
Iso 60%	30.08	2.97	-	66.95
Vinyl 60%	24.41	2.27	-	73.32
Epoxy/MDA 60%	28.51	3.10	0.93	67.46
Epoxy/MTHPA60%	25.41	2.27	-	72.32

* oxygen and Silicon in glass fiber (by difference)

4.1.4 Proximate Analysis

The proximate analysis in terms of moisture content, volatile matter, fixed carbon, and ash content of composite waste samples carried out by Thermogravimetric analyzer are presented in Table 4.3. The results indicated that all of unsaturated polyester and epoxy cured with anhydride composite samples consisted of small amount of moisture content. Meanwhile, epoxy cured with amine composites showed higher moisture content. This result was attributed from amine curing agent which consisted of hydrogen polar atom that are more active towards water or moisture.

Furthermore, the composite samples were mainly consisted of volatile matters which depended on glass fiber content. When the fraction of glass fiber in composite materials was increased, the fraction of polymer matrix was decreased resulting in the lower volatile matter. These parts were first volatilized and may be formed gaseous product for lighter molecule or condensed to liquid phase for heavier molecule under pyrolysis condition. The volatile matters generated from polymer matrix related to thermal stability of original material.

Table 4.3 Proximate analysis of composite waste samples

Composite Waste Samples	Proximate Analysis (wt. %)			
	Moisture	Volatile	FC*	Ash
Ortho 30%	0.50	70.18	0.03	29.29
Iso 30%	0.56	67.87	2.07	29.50
Vinyl 30%	0.55	66.98	2.17	30.30
Epoxy/MDA 30%	3.50	62.25	5.98	29.24
Epoxy/MTHPA 30%	0.90	61.84	6.81	30.45
Ortho 60%	0.35	39.80	0.01	59.84
Iso 60%	0.40	37.35	1.75	60.50
Vinyl 60%	0.42	37.1o	1.93	60.55
Epoxy/MDA 60%	2.40	34.74	3.36	59.50
Epoxy/MTHPA 60%	0.30	34.99	4.01	60.70

FC*: Fixed Carbon

It can be expected that under pyrolysis condition orthophthalic polyester matrix should be easily degraded and formed higher amount gas or liquid fraction than that of isophthalic and vinyl ester composite because of the presence of phthalic anhydride monomer in the orthophthalic polyester resin, which was low thermal stability. When heat was applied to orthophthalic unsaturated polyester, the phthalic anhydride was first started to degrade at lower temperature than the two other resin leading to the highest volatile matter and lowest fixed carbon.

In contrast, vinyl ester matrix yielded lower volatile matter and higher of fixed carbon upon heating because of its chemical structure was consisted of bisphenol A in the main chain. This structure was the reason for better thermal stability of vinyl ester matrix than that the orthophthalic and isophthalic polyester matrices; as a result, result, some amount of carbon can not be degraded under the same condition and remained in the form of solid residue as fixed carbon.

Additionally, the amount of volatile matter for epoxy cured with amine and anhydride were closed and than that of unsaturated polyester matrix. This result can be explained that unsaturated polyesters were comprised of styrene diluent monomer in order to reduce their viscosity for satisfied. Obviously, the ash content, non combustible residues or inorganic matters, in all composite samples were closed to the amount of glass fiber content in the composite wastes.

4.1.5 Thermogravimetric Analysis of Unsaturated Polyester Composite

Figure 4.5 and 4.6 show the TGA and DTG thermograms of unsaturated polyester reinforced with 30 and 60 wt.% glass fiber, respectively at a heating rate of 5, 10, and 15ºC/min. Obviously, all of them started to decompose approximately at 280ºC and ended at 455ºC, and this result is in accordance with those previously reported by Evan, et al. [28]. The weight loss profiles beyond 500 ºC were mostly constant due to the step of char formation.

According to Sidney [3], thermal degradation behavior of unsaturated polyesters crosslinked with styrene composite started by the volatilization of styrene and then decarbonylation of polyester main chain by random chain scission. Unsaturated polyester cured resins were degraded at the same interval temperature ranging from 200 to 500ºC, but with minor differences in maximum weight loss temperature between 340-450ºC which related to their chemical structure regarding to the substitution position of benzene ring. From the results, it was observed that orthophthalic matrix shows slightly lower initial and final decomposition temperatures and larger DTG curves than isophthalic and vinyl ester matrices composite. This was explained by Evan, et al. [28] that orthophthalic polyester consisted of branched chain phthalic anhydride which can easily release styrene monomer at slightly lower temperature. Additionally, Sidney [3] also stated that the substitution at iso or para position of benzene ring by using isophthalic acid or methacrylic acid in the isophthalic unsaturated polyester or vinyl ester resin resulted in the straight chain structure which showed better thermal stability than the orthophthalic polyester

The TGA data from Figure 4.5 and Figure 4.6 were summarized into Table 4.4 in order to show the effect of heating rate on thermal behavior of three types of unsaturated polyester composite wastes reinforced with 30 and 60 wt% glass fiber. It was showed that the major degradation temperature range started and ended at higher temperature heating rate increased. This characteristics were similar in all of the unsaturated polyester composite wastes reinforced with 30 and 60 wt% glass fiber.

Regarding to the effect of glass fiber content, it was observed from Table 4.4 that the presence of higher glass fiber content in unsaturated polyester composite resulted in the decreasing of the temperature at maximum weight loss (T_{max}). This result can be implied that the composite wastes reinforced with 60% glass fiber showed lower thermal stability than that of composite wastes reinforced with 30 wt% glass fiber. The presence of higher glass fiber content caused to higher local thermal conductivity resulting to start to degrade at lower temperature than those of the ones.

These the results are in agreement with those previously reported [29-32], which studied the effect of glass fiber content on the thermal behavior of glass fiber reinforced unsaturated polyester composite. They indicated that the presence of higher glass fiber content had impacted on the crosslinked density of cured network of unsaturated polyester composites by inhibiting process resulted in the decreasing in degree of cured unsaturated polyester resin [33]. As a results, their temperature at maximum weight loss were decreased comparing to those containing 30 wt% glass fiber.

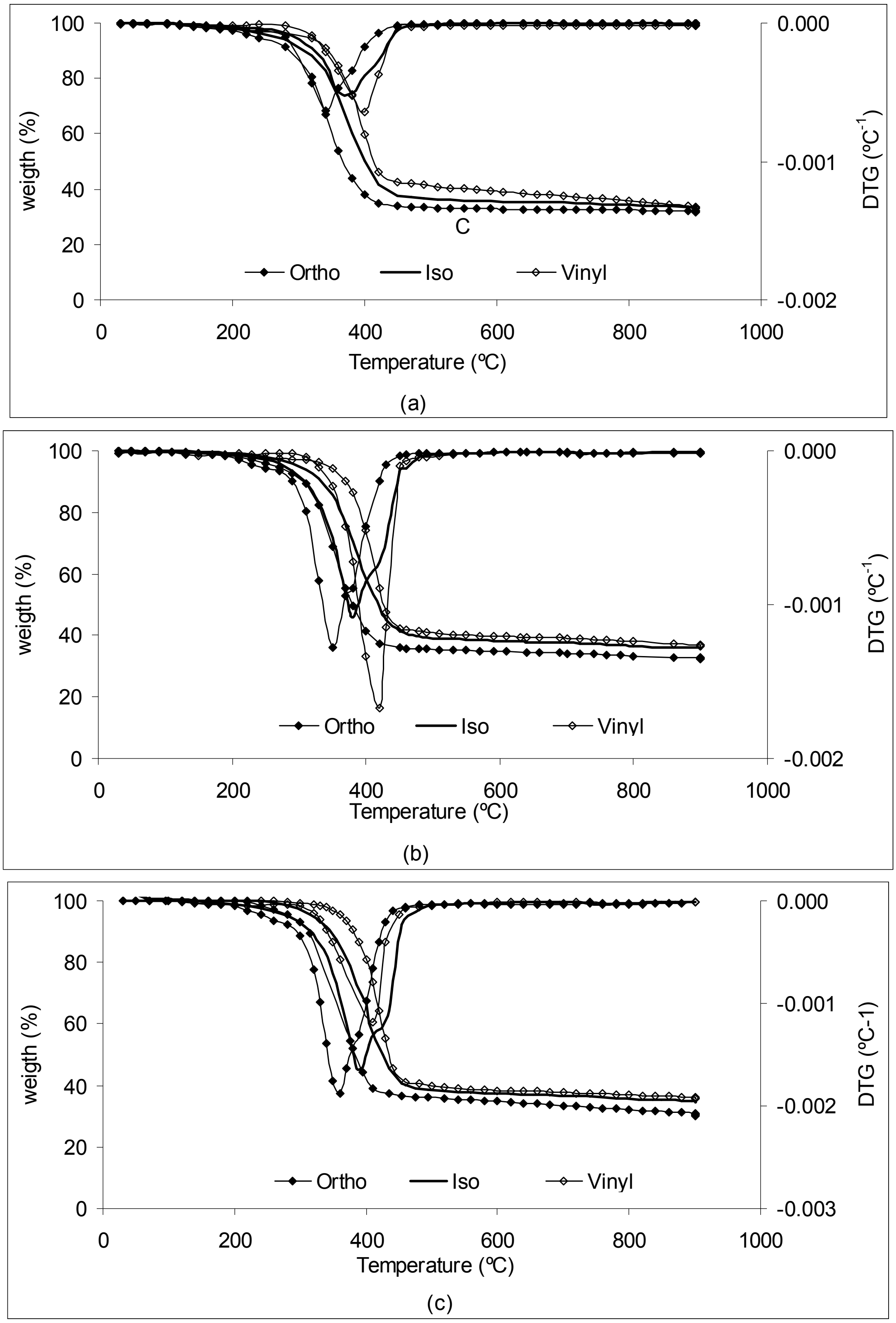


Figure 4.5 TGA and DTG thermograms of orthophthalic polyester, isophthalic polyester, and vinyl ester composite wastes reinforced with 30 wt.% glass fiber at three different heating rates : (a) 5ºC/min, (b) 10ºC/min, and (c)15ºC/min, respectively.

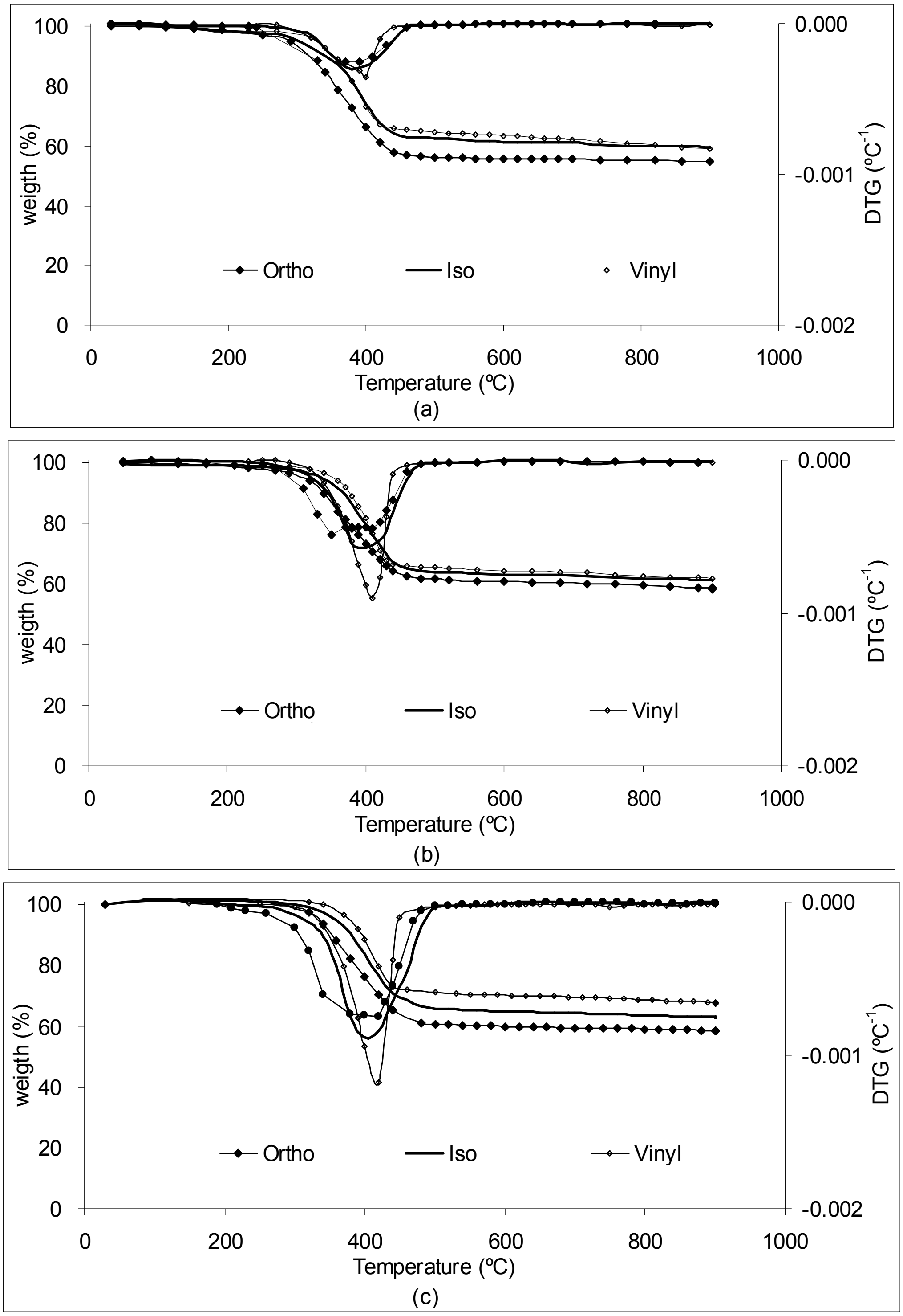


Figure 4.6 TGA and DTG thermograms of orthophthalic polyester, isophthalic polyester, and vinyl ester composite wastes reinforced with 60 wt.% glass fiber at three different heating rates : (a) 5ºC/min, (b) 10ºC/min, and (c)15ºC/min, respectively.

Table 4.4 Summarization of TGA thermograms of unsaturated polyester composite waste samples.

Composite waste samples	Heating rate (°C/min)	Temperature (°C)			Weight loss at T_{max} (wt%)
		Onset[a]	Endset[b]	Maximum[c]	
Ortho 30%	5	299.80	429.62	336.50	55.50
	10	310.30	441.68	448,00	56.62
	15	314.25	457.79	355.00	57.5
Ortho 60%	5	295.80	348.50	333.40	35.32
	10	302.02	394.80	344.90	37.20
	15	312.3	404.70	251.90	39.0
Iso 30%	5	328.70	434.50	370.70	54.00
	10	341.62	450.70	382.90	55.30
	15	346.50	457.50	390.60	58.45
Iso 60%	5	323.30	415.50	365.80	37.55
	10	336.25	431.00	377.90	38.20
	15	338.80	439.70	385.60	39.02
Vinyl 30%	5	358.90	429.34	405.00	50.40
	10	377.90	436.53	418.00	53.02
	15	379.60	446.82	425.00	55.30
Vinyl 60%	5	346.63	422.33	402.06	34.55
	10	358.91	434.00	415.05	36.57
	15	362.70	442.10	422.10	37.03

a: Onset of decomposition temperature (T_{onset}) b: Endset of decomposition temperature (T_{endset})

c: The temperature at maximum weight loss (T_{max})

4.1.6 Thermogravimetric Analysis of Epoxy Composite

The TGA and DTG thermograms at different heating rates are displayed in Figure 4.7 and 4.8, respectively. Clearly, the degradation step of cured epoxy composite wastes started by the dehydration of water and the elimination of secondary alcohohol before the scission of main chain at higher temperatures which was attributed to the major decomposition step [32]. The thermal degradation behavior of epoxy composite wastes depended on types of curing agents, glass fiber content, and heating rate which were similar to those unsaturated polyester composite wastes.

The epoxy cured with amine composite waste showed initial stage of weight loss between 130 and 200ºC due to elimination of absorbed moisture and small molecule of volatile product such as ammonia from amine fragmentation [32]. The major decomposition step derived from the cleavage of the weakest C-N crosslinked bonds and -C-O- bonds of epoxy main chain [33].

Meanwhile, the onset of major degradation step of epoxy cured with anhydride showed higher thermal degradation temperature than that of amine cured matrix composite. This was resulted from the breakdown of –C-O-C- which was the crosslinked bond of epoxy main chain - anhydride curing agent, and –C-O- of epoxy main chain. These two bonds had greater thermal stability than the C-N crosslinked bonds of amine cured epoxy composites. (more thermal stability bond).

The major decomposition temperature ranges of both epoxy cured with amine and anhydride depended on heating rate and glass fiber content as summarized in Table 4.5. Considering the effect of heating rate on weight loss profile of epoxy composite wastes, similar to unsaturated polyester composite wastes, as presented in Table 4.5 the onset , end set, and the temperature at maximum weight loss were shifted to higher as increasing heating rate. This may be related to the kinetic parameter which will be discussed shortly.

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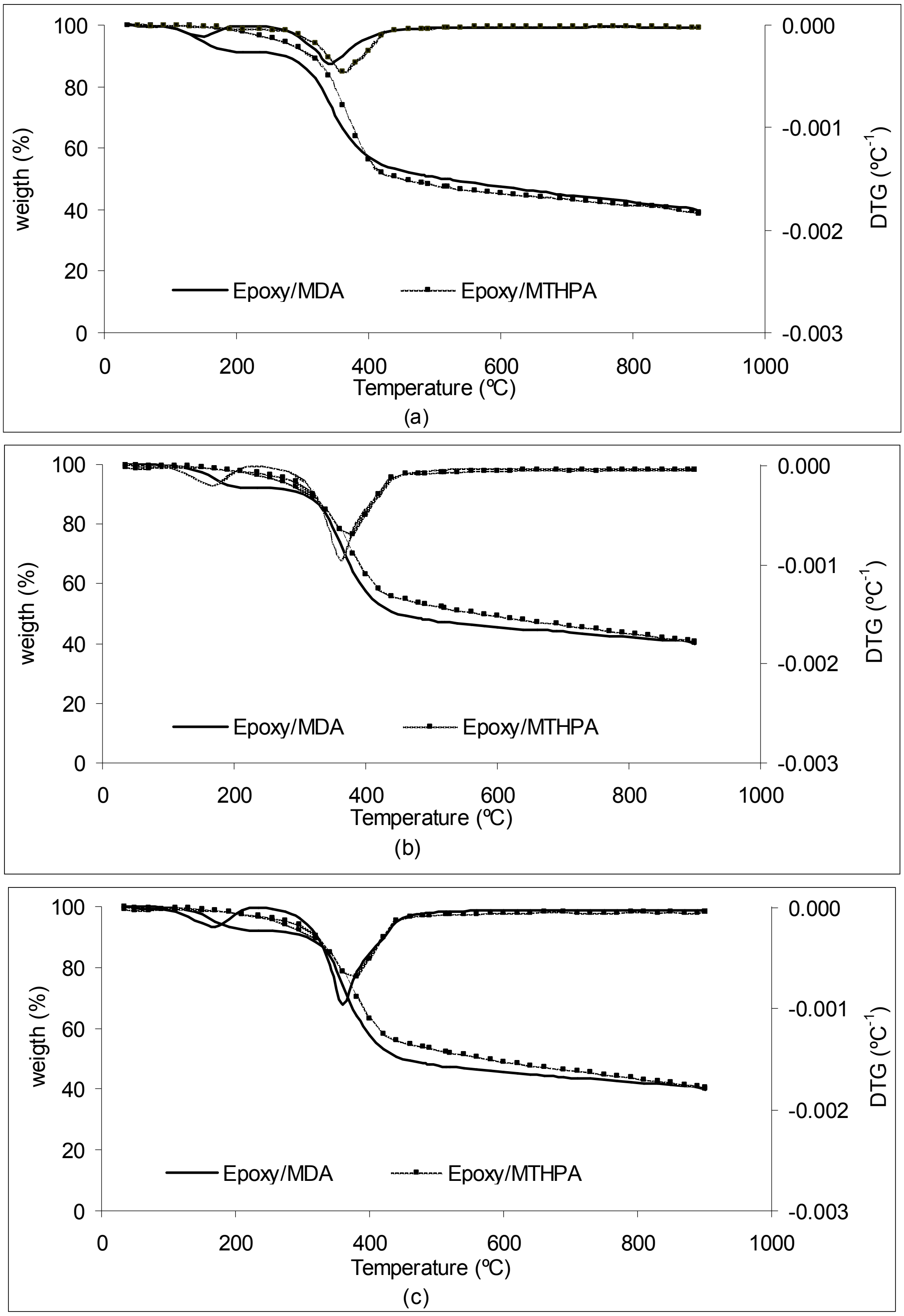


Figure 4.7 TGA and DTG thermograms of epoxy composite wastes cured with amine (MDA) and anhydride (MTHPA) reinforced with 30 wt.% glass fiber at three different heating rates : (a) 5ºC/min, (b) 10ºC/min, and (c)15ºC/min, respectively.

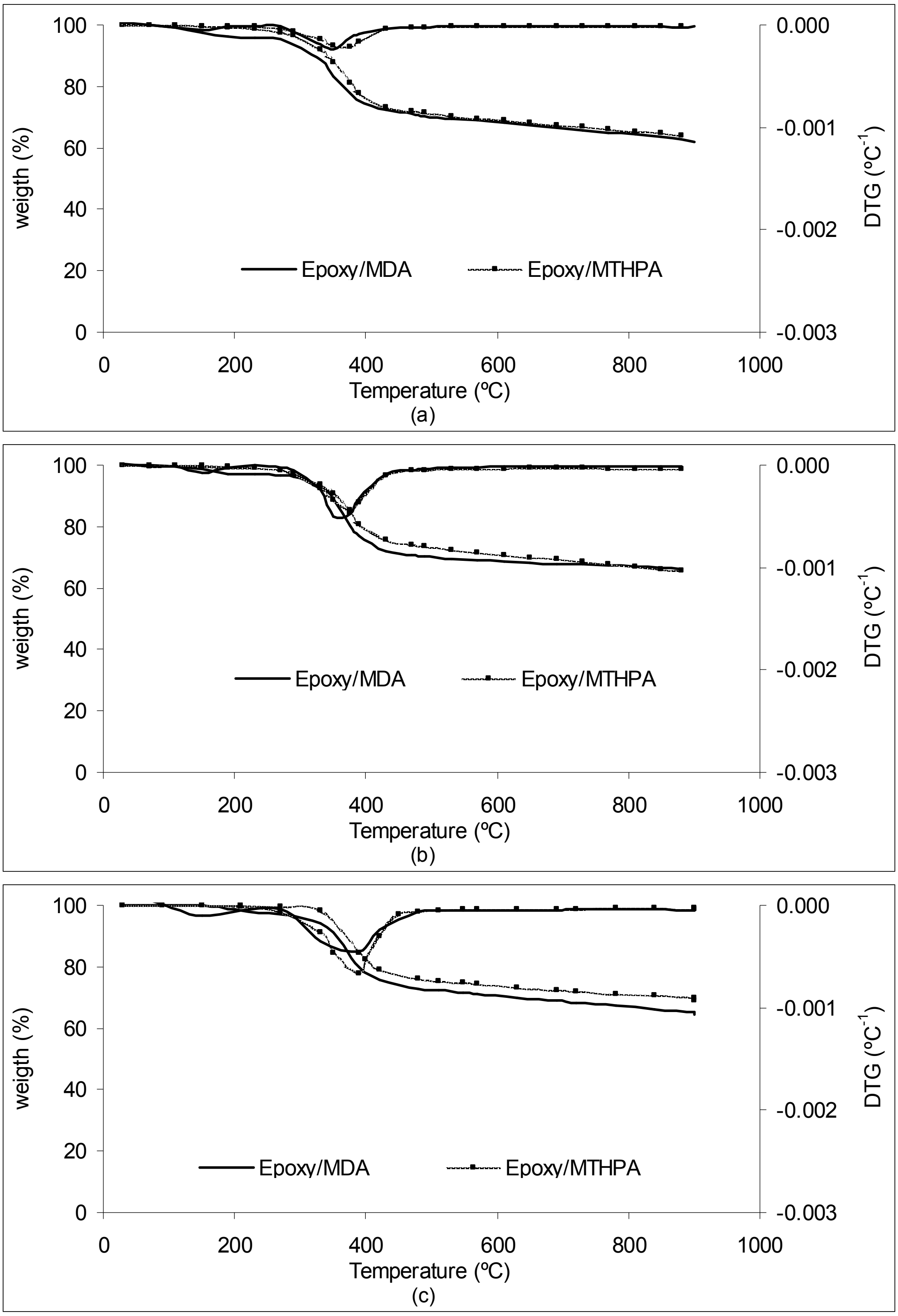


Figure 4.8 TGA and DTG thermograms of epoxy composite wastes cured with amine (MDA) and anhydride (MTHPA) reinforced with 60 wt.% glass fiber at three different heating rates : (a) 5ºC/min, (b) 10ºC/min, and (c)15ºC/min, respectively.

Regarding to the effect of glass fiber content, as presented in Figure 4.7 and 4.8 and summarized in Table 4.5.

Table 4.5 Summarization of TGA thermograms of epoxy composite waste samples.

Composite waste samples	Heating rate (ºC/min)	Temperature (ºC)			Weight loss at T_{max} (wt%)
		Onset[a]	Endset[b]	Maximum[c]	
Epoxy/MDA 30%	5	289.71	389.73	346.20	53.50
	10	308.53	404.41	361.83	55.08
	15	314.0	414.7	369.58	58.50
Epoxy/MDA 60%	5	262.89	388.80	345.91	24.02
	10	319.39	399.53	361.70	25.10
	15	305.0	418.91	366.16	27.32
Epoxy/MTHPA 30%	5	310.03	410.52	370.00	51.50
	10	320.10	420.55	381.01	53.03
	15	330.20	425.50	389.00	57.20
Epoxy/MTHPA 60%	5	300.02	411.00	367.00	22.05
	10	307.34	421.52	378.00	24.23
	15	313.74	423.33	386.01	25.31

a: Started to decompose temperature (T_{onset})　　b: Ended of decomposition temperature (T_{endset})

c: The temperature at maximum weight loss (T_{max})

The thermal degradation behavior obtained from epoxy reinforced with 60 wt% glass fiber composite waste was similar to that of 30 wt% glass fiber composite waste but the onset of major degradation temperature was lowered. This result is in agreement with Mijovic's work [34] whose indicated that the presence of glass fiber reinforcement had an effect on curing kinetic of epoxy composite by imposing restrictions on the molecular mobility of reactive group, resulting in lower reaction rate or longer time needed to complete curing reaction than that of neat epoxy resin. As a result, cured epoxy network structure was not completed. Consequently, the results suggested that the curing process of epoxy reinforced with glass fiber content system took longer to completely cure and achieve high crosslink density network than that of neat resin

4.1.7 Kinetic Study and Activation Energy (E_a) of Decomposition Process

The studies on degradation kinetics of composite waste samples provide some usefull data for their application in terms of thermal behavior such as the prediction of maximum service temperature which relates to their properties and lifetime. Activation energy is very simplified values that contribute to overall decomposition process.

Pyrolysis kinetic parameters of unsaturated polyester and epoxy reinforced with 30 and 60 wt.% glass fiber were investigated under nitrogen atmosphere by means of thermogravimetric measurements under non isothermal conditions from an ambient to 900°C at a heating rate of 5, 10, and 15°C/min. The activation energies of decomposition were determined by the application of the Arrehenius equation (Eq 4.2) and Kisssinger method [35]. This method used the temperature at maximum weight loss or maximum rate of conversion (T_{max} derived from DTG curves) to calculate the activation energy of decomposition process. The rate of conversion, $d\alpha / dt$, can be expressed by

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{4.1}$$

where

$$K(T) = A\exp\left(\frac{-E}{RT}\right) \tag{4.2}$$

Here,

$k(T)$	is the kinetic rate constant
A	is a pre-exponential factor
$f(\alpha)$	is the reaction function depending on the actual reaction mechanism
E	is the activation energy
R	is the gas constant
T	is the temperature in Kelvin, and
α	is the normalized fraction conversion.

Substitution of Eq. (4.2) into Eq. (4.1) gives the following equation:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (4.3)$$

According to Kissinger method, the degree of conversion at constant heating rate, $\beta = dT/dt$, and the rate of conversion at maximum weight loss temperature (T_{max}) is equal to zero , So, Eq. (4.3) can be expressed into the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (4.4)$$

Eq.(4.4) is the fundamental expressions of Kissinger method [35] used to calculate kinetic parameters performed by TGA. This method relates to the temperature at maximum weight loss, T_{max}, in which the rate of conversion under constant heating rate is constant, $(d\alpha/dt) = 0$, So Eq.(4.4) can be written after taking logarithms as following equation:

$$\ln\left(\frac{\beta}{T^2_{max}}\right) = \ln\frac{AR}{E} - \frac{E}{RT_{max}} \qquad (4.5)$$

For each conversion, $\ln(\beta / T^2_{max})$ is plotted vs. $1/T_{max}$ giving a straight line with a slope of $-E/R$.

Arrhenius kinetic parameters of unsaturated polyester and epoxy reinforced with 30 wt.% and 60 wt.% are plotted of $\ln(\beta / T^2_{max})$ against $1/T_{max}$ giving a straight line as shown in Figure 4.9 and 4.10, respectively. The activation energy can be calculated from the slope (m = -E/R). The activation energy (E_a) of thermoset composite decomposition can be used to compare the thermal stability of polymer matrix which related to the energy that polymer matrices needed to cleavage or break the chemical bonds. It can be implied that polymer having higher activation energy value be more thermally stable than the one with lower E_a value. The calculated activation energy by Arrhenius equation of all unsaturated polyester and epoxy composite wastes were ranged from 177 to 204 KJ/mol and 179-195 KJ/mol, respectively, as summarized in Table 4.6 which were closed to those previously reported by other researches [38-39].

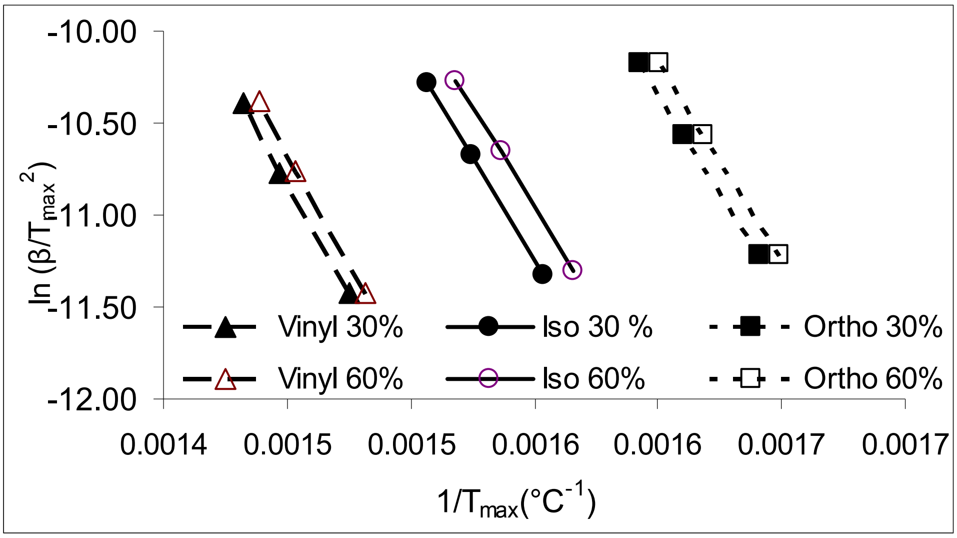


Figure 4.9 Arrhenius kinetic plot derived from TGA pyrolysis of unsaturated polyester reinforced with 30 and 60 wt.% glass fiber.

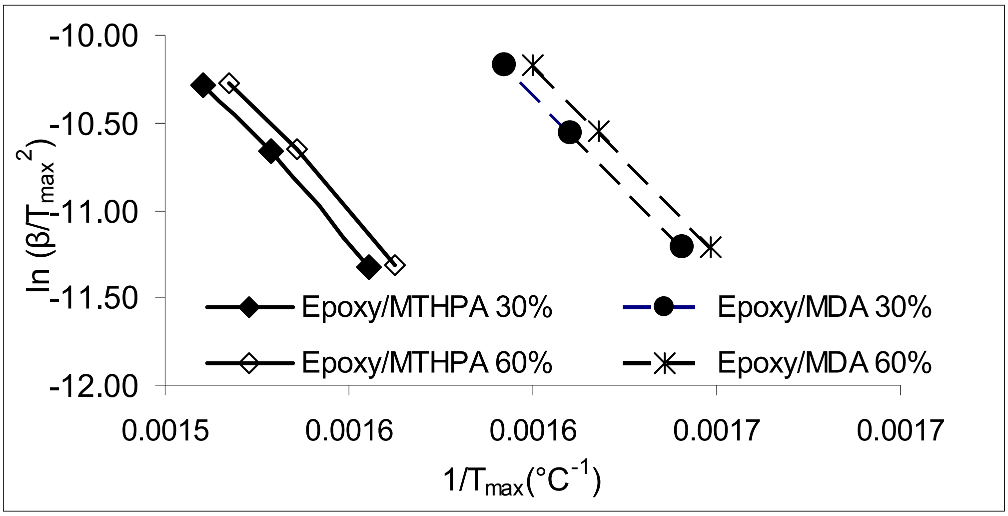


Figure 4.10 Arrhenius kinetic plot derived from TGA pyrolysis of epoxy cured with amine and anhydride reinforced with 30 and 60 wt.% glass fiber.

From the results of activation energies, it was found that the activation energy for decomposition of polymers is influenced by the chemical structure such as chain conformation, straight or branched chain or crosslinked network which decompose in a different manner when heated. Thermoplastic polymers are soften and melt before decomposing while thermoset plastic polymers are volatilized and formed char. The calculated activation energies of unsaturated polyester and epoxy composites from TGA and DTG thermograms were found to be dependent on the structure of crosslinked network and glass fiber content. Similary, Walczak [36] suggested that the activation energy of cured unsaturated polyester composite depended on their chemical structure and reinforcement content.

Comparing the effect of polyester matrix types, it was indicated the activation energy of polyester matrix associated with their decomposition steps and chemical structure. Orthophthalic polyester had lower activation energy and lager DTG peaks than isophthalic polyester and vinyl ester matrix because of the partial elimination of phthalic anhydride in branched chain. The similarity between isophthalic polyester and vinyl ester are their linear chain structure. However, the higher activation energy or thermal stability of vinyl ester matrix was due to the presence bisphenol A in the main chain and methacrylate at the end of vinyl ester backbone, which is a steric pendant group. In addition, vinyl ester resin has reactive double bonds (ester linkage) only at the end of chains, while the orthophthalic and isophthalic unsaturated polyesters have reactive double bonds distributed throughout the chain.

Table 4.6 The activation energies (KJ/mol) of unsaturated polyester and epoxy reinforced with 30 and 60 wt% glass fiber composite waste samples.

Composite Waste Samples	Activation Energies (KJ/mol)	
	30 wt% glass fiber	60 wt.% glass fiber
Ortho	179	177
Iso	186	184
Vinyl	204	202
Epoxy/MDA	181	179
Epoxy/MTHPA	195	193

For epoxy composite wastes, the activation energy of epoxy cured with different curing agent, amine (MDA) and anhydride (MTHPA), are presented in Table 4.6 indicated that Epoxy/MTHPA system required larger energy for breaking chemical bond in its network structure than epoxy/MDA system. As previously mentioned that the activation energy of decomposition process correlated with the strength or energy of chemical bonds, the chemicals having high chemical bonding needed higher energy to breakdown their bonding before degradation.

Regarding to the effect of glass fiber content, the activation energies for thermal degradation of unsaturated polyester and epoxy composite materials are decreased with the increase of glass fiber content. For example, the activation energies of epoxy cured with amine and anhydride in Table 4.6 showed that activation energies of Epoxy reinforced with 30 wt.% glass fiber were 181 and 195 KJ/mol, respectively. while, those of epoxy reinforced with 60 wt.% glass fiber were 179 and 193 KJ/mol.

These results are in agreement with corresponded with the research of Evans, [28], Barral [37], and Montserrat [38]. Furthermore, the activation energy of three type unsaturated polyester reinforced with 60 wt% glass fiber composite waste were higher than that of previously reported by Saetiaw [39] whose work showed the activation energies of the same types of unsaturated polyester reinforced with 70 wt % glass fiber composite waste under experimented condition. As previously discussed by Britoa [40] that an addition of metallic filler or glass fiber or filler like an addition of impurities into resin matrix which resulted in lower crosslinked density and lower thermal stability.

4.2 Thermal Conversion by Pyrolysis Process

This section presents the experimental results of thermal conversion by pyrolysis process of different composite wastes using a fixed bed reactor at the temperature of 600, 700, and 800ºC. The discussion on the obtained results is classified into two parts. The fist part shows the effects of pyrolysis temperature, unsaturated polyester type or epoxy curing agent, and the amount or glass fiber content in composite samples on product distribution. The second part presents the characteristics of pyrolysis product including solid, liquid, and gaseous obtained from different pyrolysis temperature and composite waste samples.

4.2.1 Product Distributions

When polymer matrices in composite waste samples, largely consisted of C-C bond skeleton, were subjected to pyrolysis at higher temperature, they will be degraded and fragmented into smaller hydrocarbons. Generally, the products derived from thermal conversion by pyrolysis were solid residues, condensable liquid (the main target product referred to pyrolysis oil), and gaseous products providing combustible fuel gases. The lighter molecules preferred to form the gaseous products, whereas heavier molecules would condense to liquid phase. The inorganic matters or other fixed carbon still remained in forms of solid residues. The total output of product by weight fractions is equivalent to total input raw material. The fraction of each product depended on both pyrolysis conditions (pyrolysis temperatures), and raw materials.

4.2.1.1 Effect of Pyrolysis Temperature on Product Distributions

. From the experimental results, the correlation between pyrolysis temperature and the distribution of products generated from pyrolysis of unsaturated polyester and epoxy reinforced with 30 wt% glass fiber can be plotted as shown in Figure 4.11. These results were averaged from 3 experiments having standard deviation of ± 0.5%. Obviously, decrease in solid weight resulted in the increase of liquid and gas weight. On the other hand, the reduction in liquid fraction when temperature increased from 600 to 800ºC resulted from greater cracking of chemical bonds into vapors fraction.

4.2.1.2 Effect of Different Type of Unsaturated Polyester Matrix and Epoxy Curing Agent on Product Distributions

Thermal decomposition of unsaturated polyesters composite waste was probably caused by free radical depolymerization. The process results from the parts of polymer. The rate of depolymerization of polymer chain depend on their structure which resulting in different thermal stability [41]. The weight fraction of solid, liquid, and gas products involved from pyrolysis of three types unsaturated polyester reinforced with 30 wt.% fiber under the same pyrolysis temperature from 600 to 800ºC are displayed in the Figure 4.12 (a-c), respectively.

It was indicated that there were negligible difference on the distribution of products obtained from different unsaturated polyester under the same condition due to the similarity of chemical composition of original monomer. The macromolecules of polyester backbone were formed by styrene crosslinked to dimensional matrix network. However there were some previous researches [28,29,40,42] reported on the relationship between chemical structure and thermal degradation behavior of unsaturated polyester. For example, Evans, et al. [28] studied the stability and the stage of degradation of unsaturated polyester of various structures such as branched chain

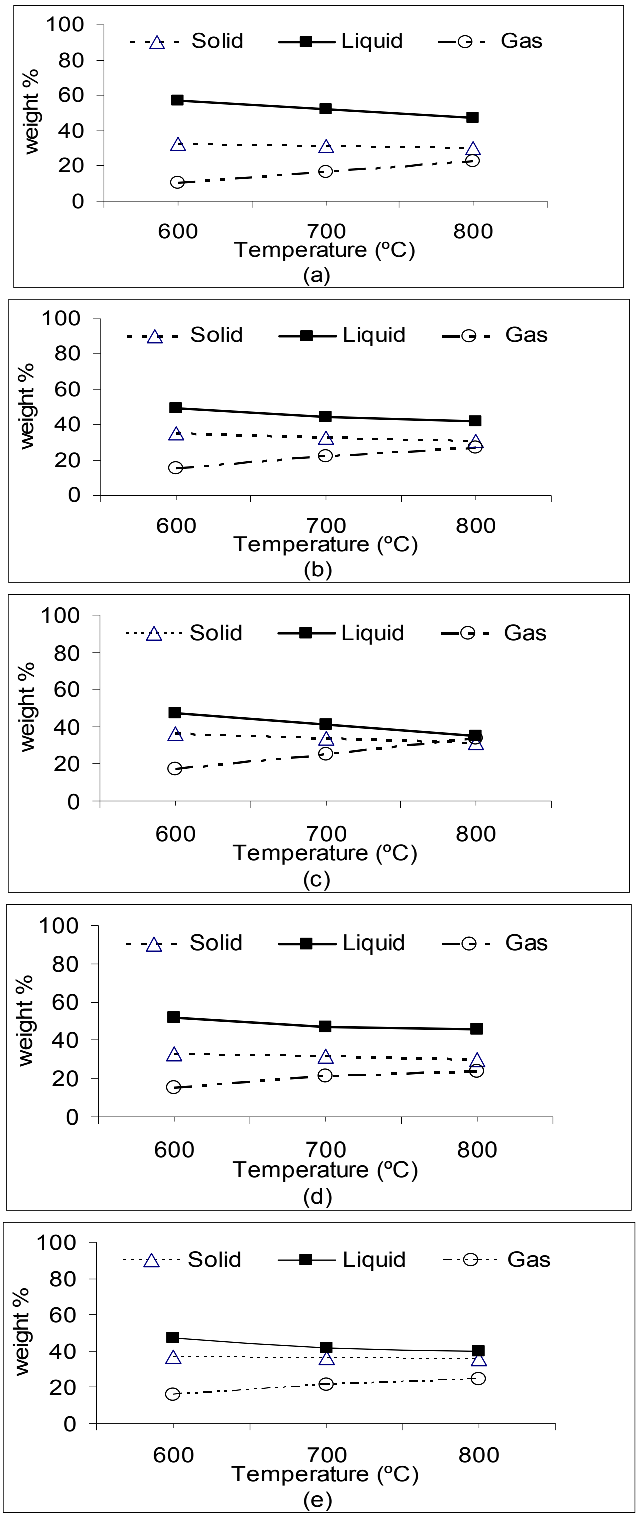
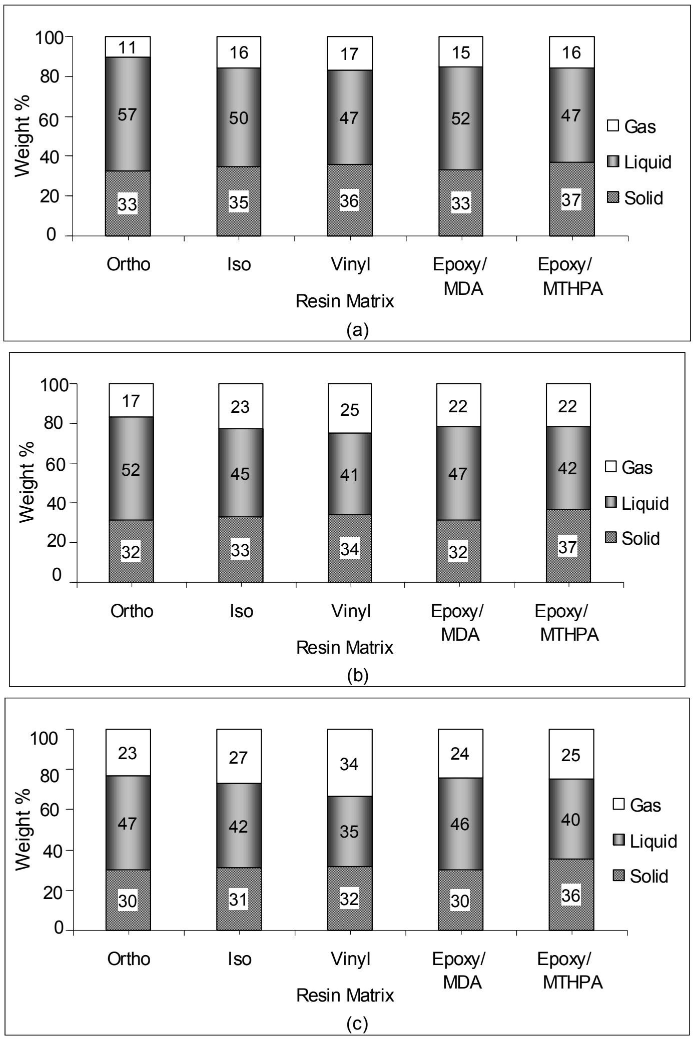


Figure 4.11 Effect of pyrolysis temperature on product yields from pyrolysis unsaturated polyester and epoxy reinforced with 30 wt% glass fiber; (a) orthophthalic, (b) isophthalic, (c) vinyl ester, (d) amine cured epoxy, and (e) anhydride cured epoxy composite waste with standard deviation of ± 0.5%



(a)

(b)

(c)

Figure 4.12 The products distribution of three types unsaturated polyester matrix and epoxy cured with amine (MDA) and anhydride (MTHPA) at pyrolysis temperature of (a) 600°C, (b) 700°C, and (c) 800°C.

glycol of propylene glycol-maleic anhydride-phthalic anhydride (orthophthalic polyester), aromatic of isophthalic and terephthalate ester using thermogravimetric analyzer. They indicated that isophthalic and terephthalate ester showed higher thermal stability than that of orthophthalic polyester due to the replacement of orthophthalic with iso or terephthalic structure which increased their thermal stability. For this reason, the liquid product of pyrolyzed orthophthalic polyester at 600°C was higher than that of iso and vinyl, while solid fraction was lower than other two resins.

On the other hand, iso and vinyl showed higher the fraction of gaseous product at 700 and 800ºC. It should be noted that ester bond (-COO-) in these matrices favored cracking into gaseous products at higher temperature. In terms of the distribution of products from pyrolysis of epoxy cured with Concerning the effect of the difference curing agent of epoxy matrix composite on the fraction of pyrolysis product also showed in Figure 4.12.

The properties of cured resins were related with chemical structure of their curing agent and also strongly depend on curing condition such as temperature. Maxwell, I.D and Richard, A.P [33] explained that crosslinked network structure of amine epoxy cured was heat sensitive due to presence of a small molecule such as ammonia, methane and nucleophilic nitrogen in the backbone leading to pyrolysis liquid fraction derived from epoxy/MDA system.

Under the same temperature slightly higher than that of epoxy/MTHPA system. pyrolysis were slightly higher epoxy/MTHPA system under the same pyrolysis condition. The fact that epoxy cured with anhydride gave lower exotherm during cure resulting in denser and brittle crosslinked network which improved its thermal stability than that of epoxy/MDA network.

4.2.1.3 Effect of Glass Fiber Content on Product Distributions

The products distribution derived from pyrolysis unsaturated polyester and epoxy reinforced with different fiber content were considerably different on the fraction pyrolysis products as compared in Figure 4.13(a-c)

It showed that the solid, liquid and gas fraction obtained from pyrolysis composite wastes consisted of 30 and 60 wt% glass fiber at pyrolysis temperature of 600ºC showing similar trends that of 700 and 800ºC. It was clear that the increase of fiber loading from 30 to 60 wt% results in the decrease of liquid and gas fraction due to the reduction of the organic content which can be degraded and volatilized to gas before condensed to liquid phase.

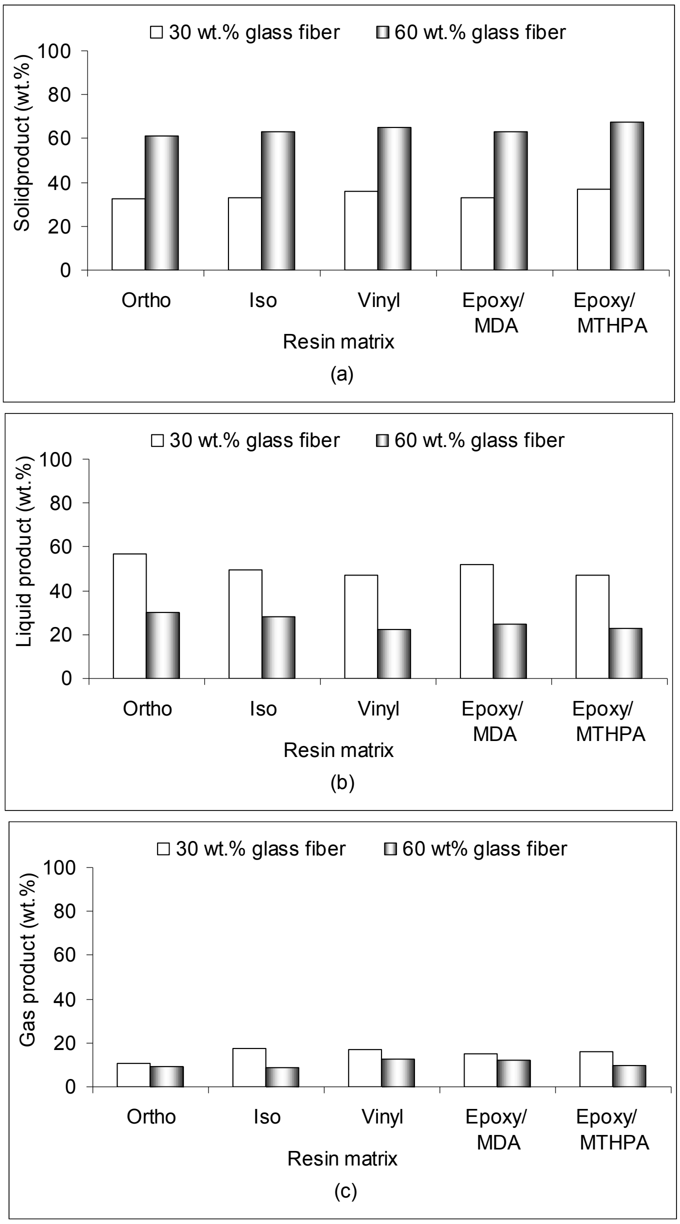


Figure 4.13 The comparison solid (a), liquid (b), and gas (c) fraction derived from pyrolysis of composite waste consisted of 30 and 60 wt% glass fiber at pyrolysis temperature of 600°C.

4.2.2 Characterization of Pyrolysis Products

This section presents the characteristic of pyrolysis products including solid, liquid, and gas obtained from pyrolysis of different polymer matrix at pyrolysis temperature of 600, 700, 800°C.

4.2.2.1The Characteristic of Solid residues

The solid residues retained in quartz sample boat after finished run were brittle black. They were analyzed in terms of physical appearance, functional group, elemental and proximate analyses.

Physical Appearance of Solid Residues

Due to the large number of different the SEM images from Scanning Electron Microscope (SEM, JEL JEM-6480 LV) of residues from pyrolysis process, therefore, only ten images from pyrolysis process of 60 wt.% glass fiber composite wastes at 600 and 800ºC were chosen for discussion as presented in Figure 4.14 and 4.15, respectively.

They are used to indicate the influence of different polymer matrix, pyrolysis temperature on appearance of solid char. Figure 4.14 and 4.15, indicated that such residues mainly composed of glass fiber and small amount of carbonaceous or coke-like materials derived from polymer matrix degradation during pyrolysis and may continue to repolymerize to gaseous phase by secondary reactions which corresponded with Lopez, et al.[43].

There was no significant difference on morphology appearance among various types polymer matrix. However, it seems that SEM micrographs in Figure 4.14 (a) and (b) of pyrolysis residue from orthophthalic polyester, and epoxy/MDA showing lower amount of carbonaceous materials covered on fiber surface than that of other resins which corresponding to higher liquid fraction.

The influence of pyrolysis temperature on physical appearance of solid residues can be compared and shown as SEM micrograph of solid residues at pyrolysis temperature of 800ºC (Figure 4.15). It was observed that the pyrolytic carbon slightly decreased with increasing temperature from 600 to 800ºC, but still well covered on fiber surface.

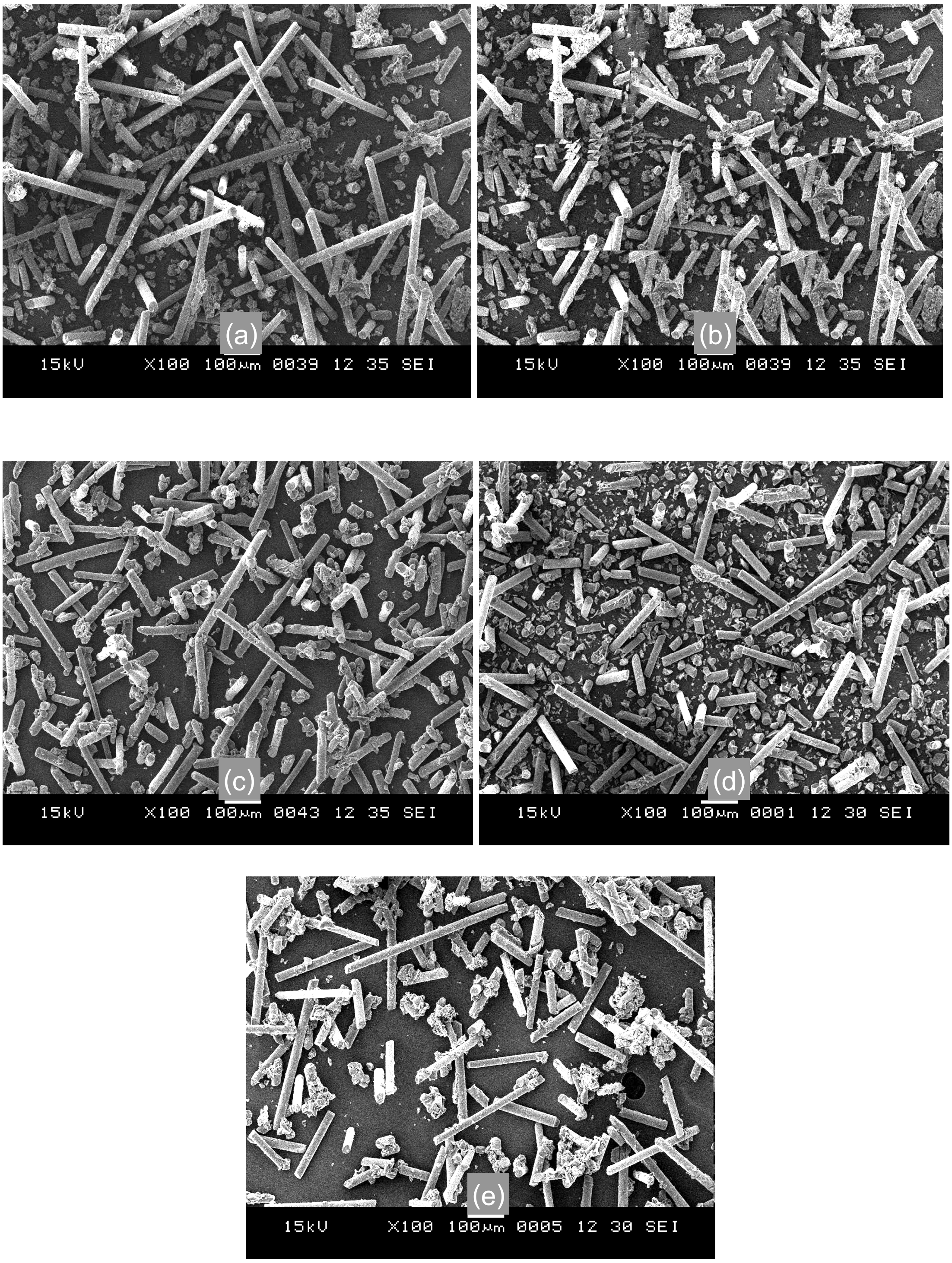


Figure 4.14 SEM micrograph of solid residues from pyrolysis of unsaturated polyester and epoxy reinforced with 60 wt.% glass fiber at temperature of 600ºC: (a) orthophthalic, (b) isophthalic, (c) vinyl ester, (d) epoxy/MDA, and (e) epoxy/MTHPA.

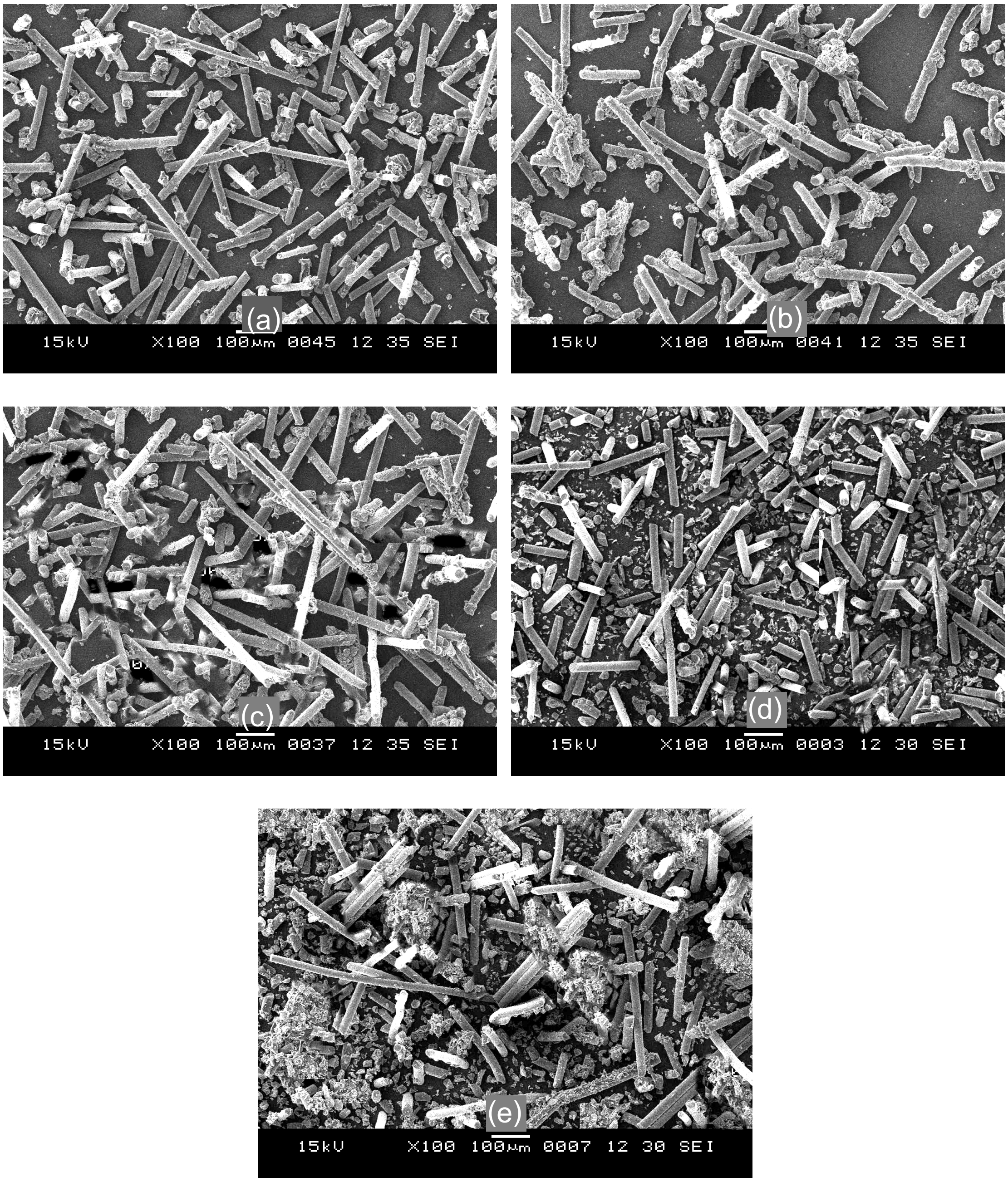
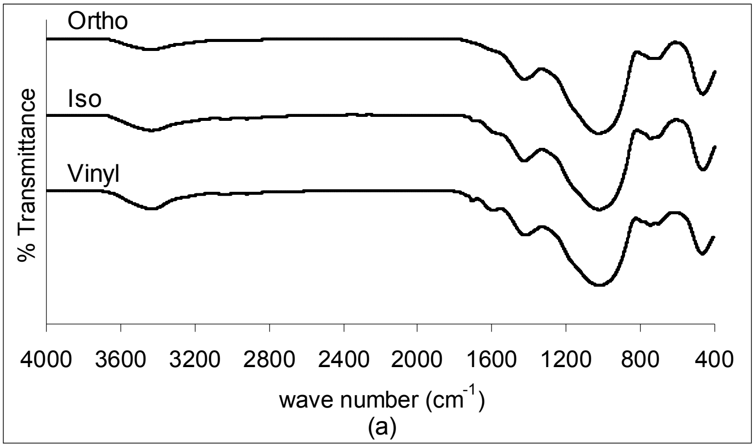


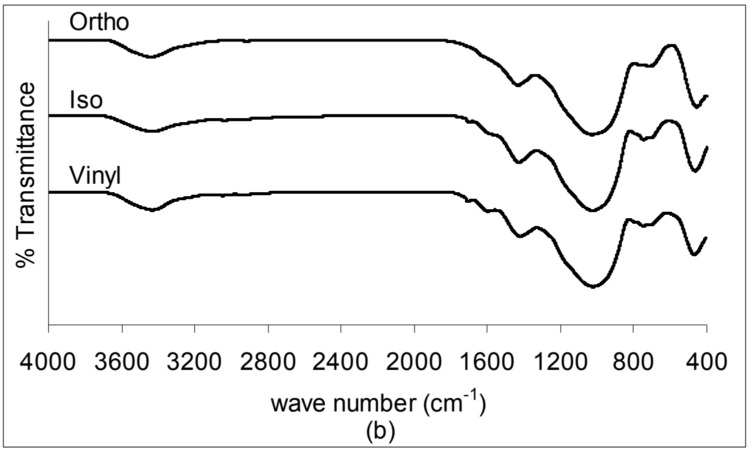
Figure 4.15 SEM micrograph of solid residues from pyrolysis of unsaturated polyester and epoxy reinforced with 60 wt.% glass fiber at temperature of 800ºC: (a) orthophthalic, (b) isophthalic, (c) vinyl ester, (d) epoxy/MDA, and (e) epoxy/MTHPA.

Functional Group Analysis of Solid Residues

The characterization in terms of functional group of resin matrix retained on glass fiber surface of solid residues which obtained from pyrolysis process at different temperature from 600 to 800°C were investigated by using FTIR Perkin-Elmer Spectrum and presented in Figure 4.16.



(a)



(b)

Figure 4.16 FTIR spectra of solid residues obtained from pyrolysis of three types unsaturated polyester reinforced with 30 wt.% glass fiber composite waste at temperature of (a) 600 °C, and (b) 800°C.

The FTIR spectra of solid residues obtained from pyrolysis of polymer matrix reinforced with 30 and 60 wt.% glass fiber composite wastes were quite similar. Hence, this section should be presented only the spectra of solid residue from pyrolysis process of unsaturated and epoxy reinforced with 30 wt% glass composite waste at the temperature of 600 and 800°C as given in Figures 4.16 and 4.17. It was observed that FTIR spectra of solid residue of different types of unsaturated polyester and epoxy matrix were similar which presented the broad absorption peak at 3760 cm^{-1} and 1085 cm^{-1} resulting from the vibration of Si-OH and SiO_2 in glass fiber, respectively [44,45]. Additionally, there were no evidence of absorption peak of carbonyl ester (-COO-) at 1730 and carbon nitrogen (C-N-) at 1100 cm^{-1} presented in unsaturated polyester and amine cured epoxy composite, respectively. It was implied that these chemical bonds were appreciably converted which may either be condensable liquid or gas formed.

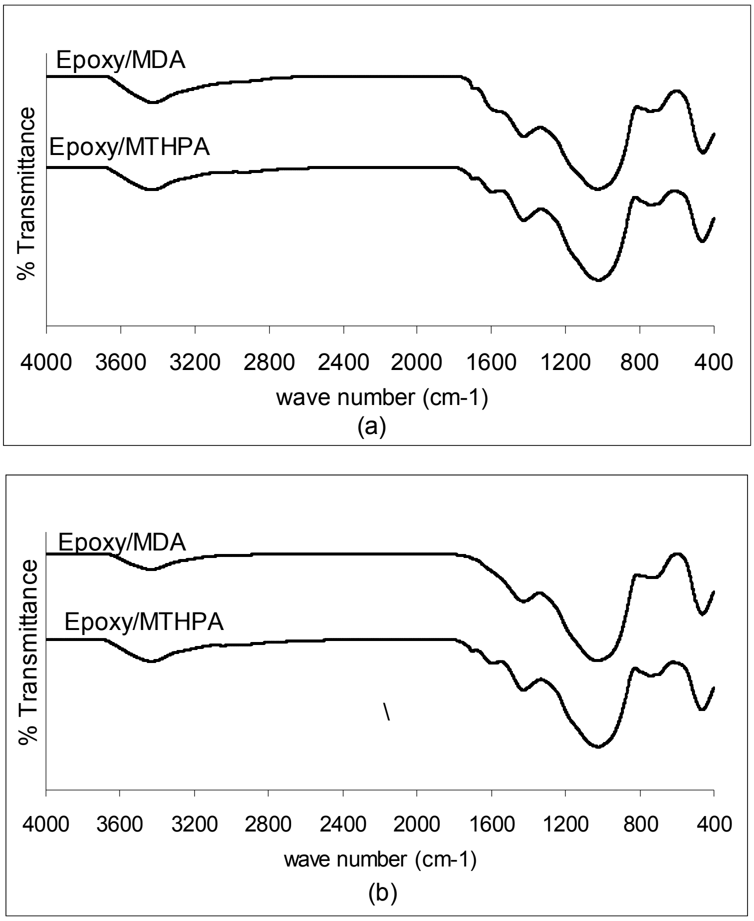


Figure 4.17 FTIR spectra of solid residues char obtained from pyrolysis of epoxy cured with amine and anhydride composite waste at temperature of (a) 600 °C, and (b) 800°C.

Considering the influence of pyrolysis temperature on solid residues, the spectra attributed to there are no significant on thermal degradation of polymer matrix after the temperature increased from 600°C to 800°C. This is due to the fact that residues solid char were mainly glass fiber. The indicative chemical bonds in polymer matrix were first degraded at temperature of 600ºC, while some segment still remained and covered on glass fiber surface as seen from SEM micrograph before further converted by secondary decomposition at higher temperature.

Elemental Analysis of Solid Residues

The Elemental analysis results of solid residues from pyrolysis process of unsaturated polyester and epoxy reinforced with 30 and 60 wt.% glass fiber composite wastes at temperature of 600, 700, and 800ºC were determined by ECO CHN-2000 analyzer and presented in Table 4.6. The results indicate that the amount of carbon and hydrogen slightly decreased in correlation with the increase of pyrolysis temperature. The amount of oxygen, calculated by difference, increased suggesting that such residues mainly comprised of inorganic matter in formed of glass fiber.

However, the percentages of carbon and hydrogen obtained from series of unsaturated polyester and epoxy showed little different difference types of unsaturated polyester resin matrix related with thermal stability of each type of resin matrix. Orthophthalic polyester composite presented lowest the amount of carbon and hydrogen, while vinyl ester showed highest carbon and hydrogen percentages. These results corresponded with activation energy of composite waste sample. This is because chemical structure of vinyl ester resin is epoxy and unsaturated of polyester.

The elemental analysis results of solid char from pyrolysis of epoxy cured with amine were little less than that of epoxy cured with anhydride which related with the lower in dissociation energy bond of C-N and N-H network of amine cured epoxy than C-O in anhydride cured epoxy [5] resulting in epoxy cured with amine can be more degraded and less in carbon composition in solid char.

The chemical composition in solid residue from pyrolysis of 60 wt.% glass fiber showed similar trend of decreasing carbon and hydrogen with the increase of temperature related the amount of carbon and hydrogen in original feedstock composite waste.

Table 4.7 Elemental analysis (wt.%) of solid residues obtained from pyrolysis process of composite wastes with 30 and 60 wt% glass fiber.

Solid residues	Temperature (°C)	30 wt% glass fiber				60 wt% glass fiber			
		C	H	N	O*	C	H	N	O*
Ortho	600	6.55	0.07	-	93.38	2.62	0.00	-	95.77
	700	5.46	0.05	-	94.49	2.18	0,00	-	97.82
	800	5.26	0.01	-	94.73	2.10	0.00	-	97.90
Iso	600	9.07	0.19	-	90.91	3.62	0.07	-	96.31
	700	7.09	0.13	-	92.79	2.83	0.04	-	97.09
	800	5.35	0.12	-	94.52	2.15	0.03	-	97.82
Vinyl	600	11.03	0.23	-	88.97	4.19	0.09	-	95.72
	700	10.47	0.22	-	89.31	3.97	0.08	-	96.11
	800	8.75	0.19	-	91.02	3.41	0.07	-	96.52
Epoxy/ MDA	600	10.40	0.32	0.35	88.93	3.64	0.14	0.10	96.22
	700	8.36	0.23	0.15	91.26	2.92	0.09	0.06	97.17
	800	6.38	0.11	0.12	93.39	2.23	0.04	0.04	97.73
Epoxy/ MTHPA	600	12.40	0.63	-	86.97	4.21	0.25	-	95.54
	700	10.36	0.26	-	89.38	3.52	0.10	-	96.38
	800	6.38	.0.17	-	93.47	2.23	0.06	-	97.71

*: oxygen and others (by difference)

Proximate Analysis of Solid Residues

Proximate analysis in terms of volatile matter and fixed carbon and ash content in solid residues from pyrolysis of composite wastes were performed by thermogravimetric analyzer and presented in Table 4.8. The results show similar trend as elemental analysis. There were some amount of volatile matter and fixed carbon remained in residues as presented in SEM micrograph in Figure 4.14, especially vinyl

Table 4.8 Proximate analysis (wt.%) of solid residues obtained from pyrolysis process of composite wastes with 30 and 60 wt% glass fiber.

Solid residues	Temperature	30 wt% glass fiber			60 wt% glass fiber		
	(°C)	VM[a]	FC[b]	Ash	VM[a]	FC[b]	Ash
Ortho	600	5.23	0.52	94.25	2.42	0.20	97.38
	700	5.20	0.20	94.60	2.25	0.15	97.60
	800	5.13	0.13	94.74	2.20	0.07	97.73
Iso	600	8.02	1.92	90.06	2.64	0.28	97.08
	700	5.33	1.52	93.15	2.40	0.23	97.37
	800	4.93	1.34	93.73	2.30	0.13	97.57
Vinyl	600	10.35	2.00	87.65	2.72	0.45	97.08
	700	8.82	1.87	89.31	2.50	0.40	95.74
	800	7.91	1.55	90.54	2.38	0.32	96.68
Epoxy/MDA	600	9.29	1.80	88.91	2.72	0.31	96.97
	700	7.28	1.73	90.99	2.50	0.20	97.30
	800	5.83	1.32	92.85	2.38	0.32	97.47
Epoxy/MTHPA	600	11.47	2.23	86.30	4.80	0.68	96.50
	700	9.85	1.85	88.30	4.40	0.47	95.13
	800	5.15	1.50	93.35	4.03	0.35	95.62

a: Volatile matter

b: Fixed carbon

and epoxy cured with and hydride. This may be concerned with the thermal behavior of thermoset plastic which cannot melt or remold like thermoplastic, but it degraded and formed brittle char covering fiber surface. However, the lowest volatile mater and fixed carbon in residue char due to the not heat stable of phthalic anhydride in its polymer chain with the increase of condensable liquid fraction at 600°C. It should be concerned with this resin start to degrade at lower temperature. The proximate analysis results of 60 wt.% glass fiber solid residue seems to indicate that such residue hardly contained of volatile and fixed carbon. It should be concerned with the higher loading glass fiber resulted in lower crosslinked density network.

4.2.2.2 The Characteristic of Condensable Liquids

The condensable liquids obtained from pyrolysis of composite wastes were viscous dark brown liquid as shown in Figure 4.18. They were first centrifuged at 3000 rpm for 30 min. to separate aqueous phase or water in such liquid. After water was removed, organic phases were then analyzed the functional group, the chemical composition, simulated distillation and fuel properties.

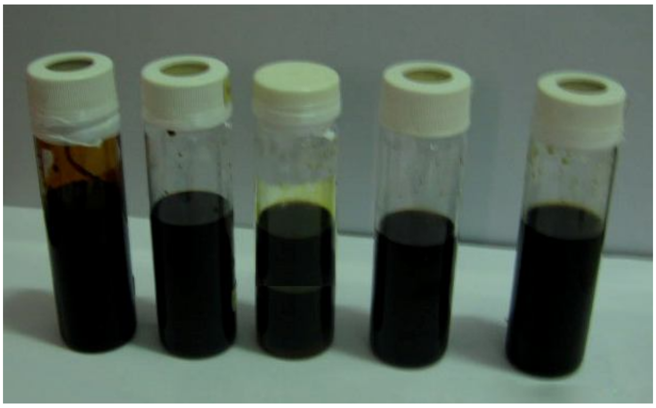


Figure 4.18 Condensable liquid obtained from pyrolysis composite wastes.

Functional Group Analysis of Condensable Liquids

The FTIR spectra produced from pyrolysis oil of unsaturated polyester composite reinforced with 30 wt.% glass fiber composites waste at pyrolysis temperature of at 600 and 800°C are presented in Figure 4.19 (a) and (b).

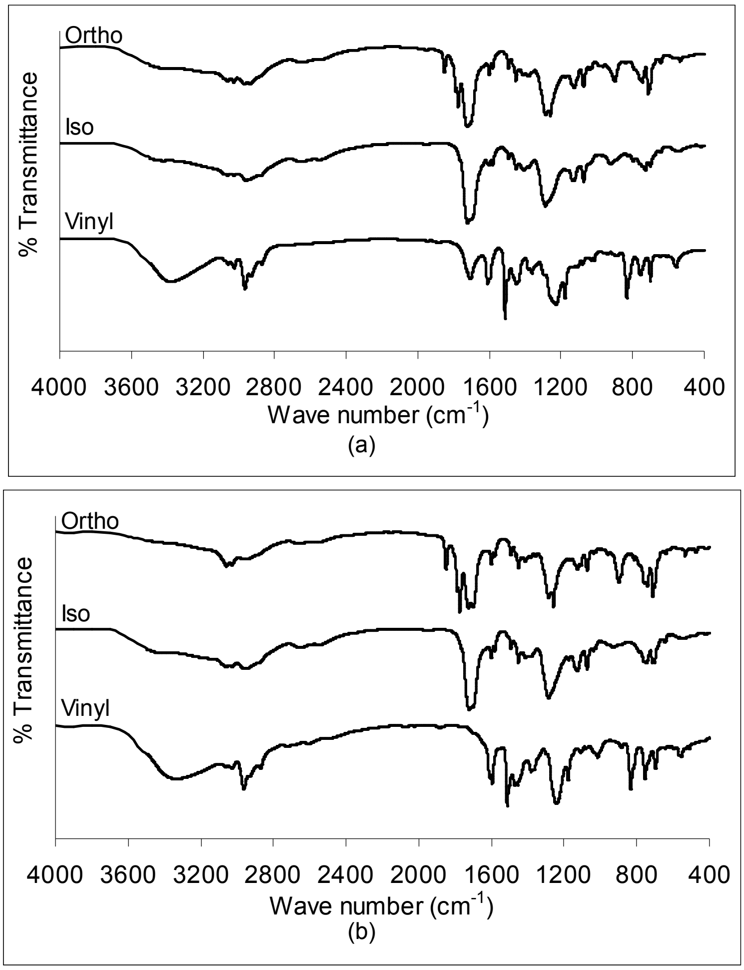


Figure 4.19 FTIR spectra of pyrolysis liquid oil obtained from pyrolysis of unsaturated polyester reinforced with 30 wt.% glass fiber composite waste at temperature of (a) 600 °C, and (b) 800°C.

The distinguished strong peaks were the broad peak at 3432-3437 cm^{-1} derived from O-H stretching of alcoholic compounds consisting of the breadth peaks which indicated to carboxylic groups. The prominent absorption peaks at 1730 and 1285 cm^{-1} were assigned to C=O and C-O stretching of carboxylic or ester compounds and may be used to identify oxygenated compounds in the decomposition products of polyester. The presence of sharp peaks at 1500-1600 and 700-910 cm^{-1} corresponded to skeletal vibrations and C-H bending of aromatic rings. The ratio of methyl groups (CH_3) at 2930 cm^{-1} to methylene groups (CH_2) at 2960 cm^{-1} was rather low which indicated a high proportion of methylene groups in the oil [46]. These spectra suggested that the oil composed mainly of aromatic structure and oxygenated compounds derived from the chain scission of crosslinked bond and the breakdown of ester group (COO).

The effect of glass fiber content on FTIR spectra of pyrolysis liquid oil obtained from pyrolysis of unsaturated polyester reinforced with 30 and 60 wt % glass fiber under the same pyrolysis temperature of 700 °C are presented in Figure 4.20 (a) and (b), respectively.

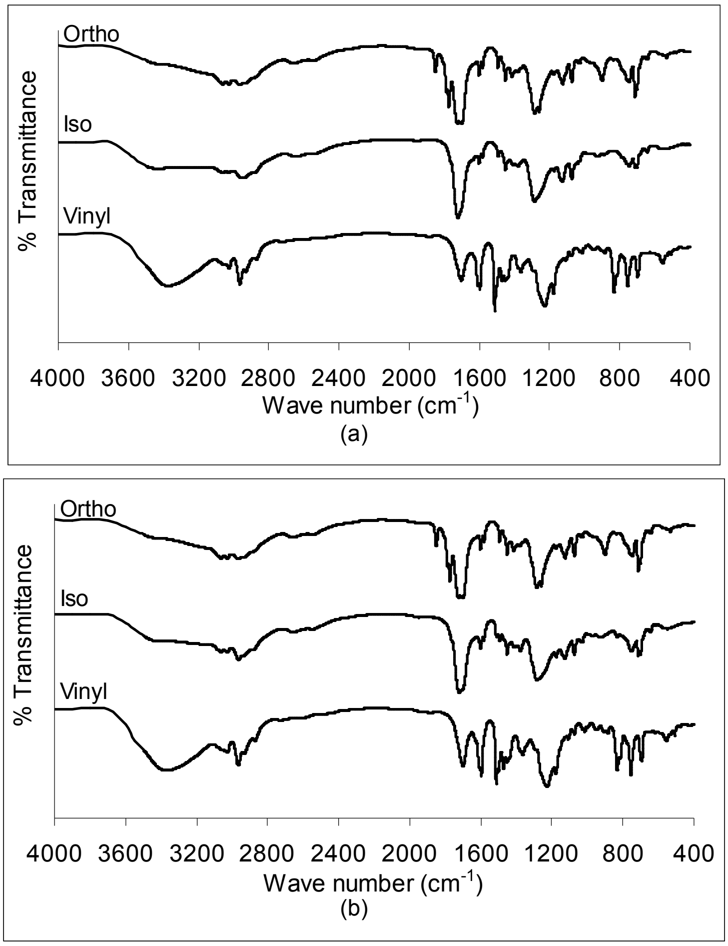


Figure 4.20 FTIR spectra of pyrolysis liquid oil obtained from pyrolysis of unsaturated polyester composite waste at temperature of 700°C: (a) 30 wt.% glass fiber, and (b) 60 wt.% glass fiber.

From Figure 4.19 and 4.20, it can be suggested that pyrolysis temperature did not have significant correlation with aromatic content. The chemical structure of unsaturated polyester matrix on the their composition of liquid oil similarly composed of aromatic and oxygenated compound but it may be different in its weight fraction which corresponded with Torres, et al. [13,15].

Functional group analysis of liquid oil from pyrolysis of epoxy composite at 600 and 800°C are presented in Figure 4.21 (a) and (b), respectively.

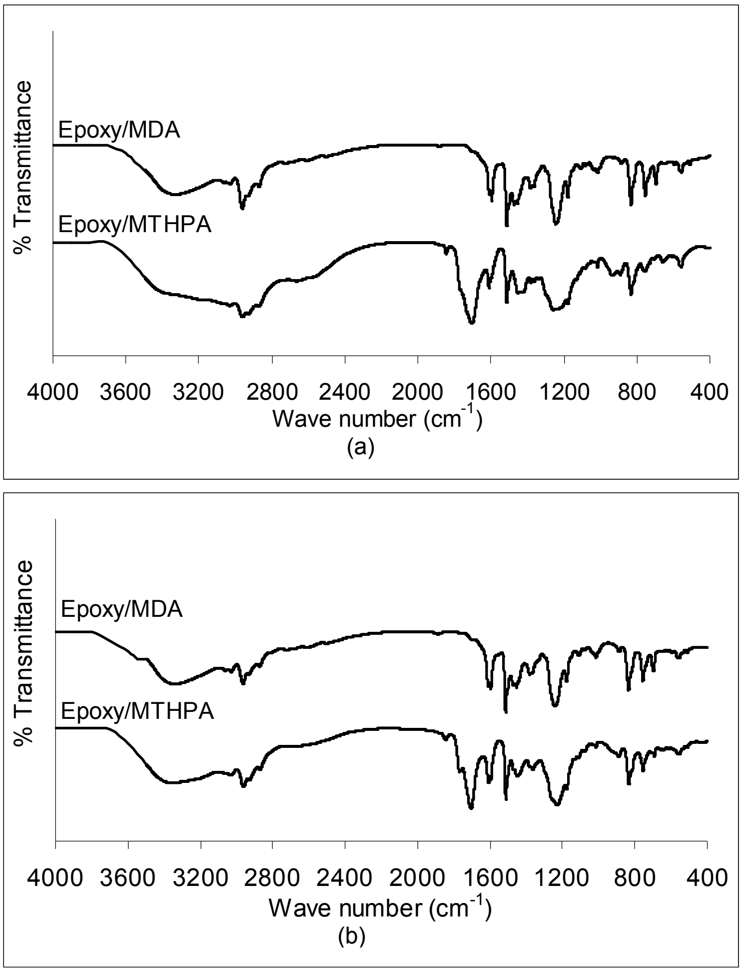


Figure 4.21 FTIR spectra of pyrolysis liquid oil obtained from pyrolysis of amine and anhydride cured epoxy reinforced with 30 wt.% glass fiber composite waste at temperature of (a) 600 °C, and (b) 800°C.

It was indicated that their compositions were similar to those seen from polyester due to the presence of the broader peak from O-H stretching of alcoholic compounds at 3432-3437 $cm^{-1}$and aromatic absorption peak at 1500-1630 cm^{-1}. However, it was seen that the ratio of groups (at 2930 cm^{-1}) to methylene groups (at 2960 cm^{-1}) and methyl groups was rather higher than unsaturated polyester, suggesting greater aliphatic chain.

The comparison of FTIR spectra of pyrolysis liquid oil of amine and anhydride cured epoxy is displayed in Figure 4.22. Both materials has similar alcoholic and oxygenated compound. Though, each one presented its characteristic absorption peak derived from the breakdown of chemical bonds in curing agent such as the presence of absorption peak C-N bond at 1100 cm^{-1} for amine curing and carbonyl ester C=O at 1730 and 1285 of C-O four anhydride structure.

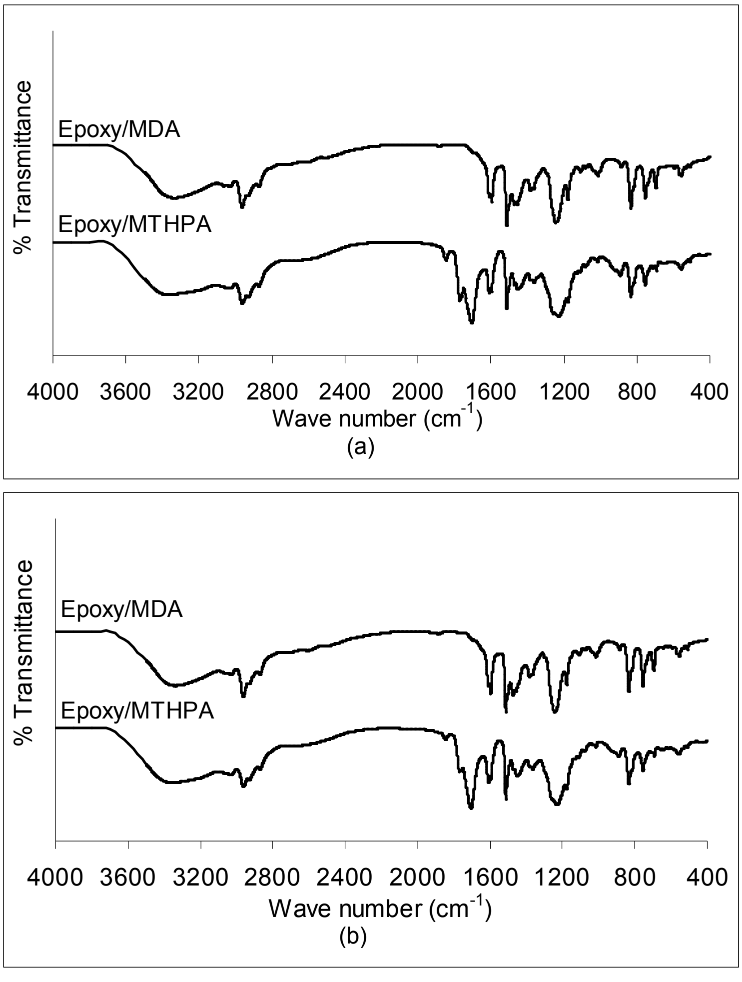


Figure 4.22 FTIR spectra of pyrolysis liquid oil obtained from pyrolysis of amine and anhydride cured epoxy composite at temperature of 700 °C: (a) 30 wt.% glass fiber composite waste, and (b) 60 wt.% glass fiber.

Elemental Analysis of Condensable Liquids

After the water in condensable liquid was removed by centrifugation, the organic phase, referred to liquid oil, was analyzed for the amount of chemical composition using LECO CHN-2000 analyzer and calculated for atomic ratio of hydrogen to carbon (H/C), and oxygen to carbon (H/C). Additionally, the liquid oil were measured for gross calorific value (GCV) by bomb calorimeter. These results are summarized in Table 4.9 and 4.10, respectively.

Table 4.9 Elemental analysis, water content, and gross calorific value (GCV) of condensable liquids obtained from pyrolysis process of composite wastes with 30 wt.% fiber.

Resin Matrix	Temperature (ºC)	Elemental Analysis (wt %)				Atomic ratio		Water (wt%)	GCV (MJ/kg)
		C	H	N	O*	H/C	O/C		
Ortho	600	72.00	6.42	-	21.58	1.07	0.22	5.0	28.20
	700	74.00	6.27	-	19.73	1.02	0.20	4.8	29.60
	800	75.30	6.20	-	14.43	0.99	0.18	4.5	30.60
Iso	600	67.53	7.40	-	25.07	1.31	0.28	3.80	25.90
	700	68.41	6.27	-	24.26	1.29	0.27	3.65	26.30
	800	70.62	6.57	-	23.04	1.08	0.24	3.10	27.70
Vinyl	600	79.34	7.40	-	12.88	1.18	0.12	4.50	29.20
	700	80.3	7.33	-	11.49	1.22	0.11	4.30	29.80
	800	81.72	6.34	-	10.31	1.17	0.09	3.90	30.70
Epoxy/ MDA	600	77.08	8.41	2.45	12.06	1.31	0.12	5.0	33.60
	700	77.18	8.09	2.42	12.31	1.26	0.12	4.8	33.90
	800	78.53	7.66	2.63	11.18	1.17	0.11	4.5	34.60
Epoxy/ MTHPA	600	71.74	7.53	0	20.73	1.26	0.22	3.6	29.20
	700	73.98	7.35	0	18.67	1.19	0.19	3.4	29.80
	800	80.00	7.25	0	12.75	1.09	0.12	3.0	30.70

*: oxygen and others (by difference)

Table 4.10 Elemental, water content, and gross calorific value (GCV) of condensable liquids obtained from pyrolysis process of composite wastes with 60 wt.% fiber.

Resin Matrix	Temperature	Elemental Analysis (wt %)				Atomic ratio		Water	GCV
Liquid	(°C)	C	H	N	O*	H/C	O/C	(wt%)	(MJ/kg)
Ortho	600	72.19	7.74	-	21.00	1.11	0.21	4.20	25.90
	700	73.65	6.24	-	20.11	1.02	0.20	4.00	27.70
	800	75.09	5.93	-	18.98	0.95	0.19	3.5	29.20
Iso	600	73.51	6.98	-	19.51	1.14	0.20	3.40	29.50
	700	74.53	6.66	-	18.81	1.09	0.19	3.12	29.60
	800	76.31	6.56	-	17.13	1.03	0.17	2.80	29.80
Vinyl	600	78.00	7.34	-	14.70	1.13	0.14	4.0	30.60
	700	78.12	7.18	-	14.60	1.10	0.14	3.8	30.70
	800	80.16	6.99	-	12.85	1.05	0.12	2.5	31.70
Epoxy/MDA	600	76.33	9.55	2.11	12.01	1.50	o.12	4.80	32.40
	700	77.00	9.28	2.11	11.61	1.42	0.11	4.50	33.90
	800	78.39	8.19	2.38	11.04	1.25	0.10	4.10	34.40
Epoxy/MTHPA	600	73.50	7.09	-	19.41	1.16	0.20	3.2	33.60
	700	75.00	7.02	-	17.98	1.12	0.20	2.8	34.30
	800	76.00	6.24	-	17.76	0.99	0.20	2.5	34.30

*: oxygen and others (by difference)

It was observed from Table 4.8 and 4.9 that the difference among resin matrices and glass fiber content did not strongly effect the chemical composition of condensable liquids and their GCVs. The amount of carbon increased as function temperature corresponded with the decrease of carbon in solid residue. Hydrogen and hydrogen composition decreased as the increase of temperature due to further vapor to gas phase resulting in the higher in GCV. H/C atomic ratio obtained from pyrolysis oils of orthophthalic polyester composite were rather low (~1.0-1.1) which corresponded with Torres, et al. [14] who suggested that such oil is mainly of aromatic compound. Whereas other matrices showed more H/C atomic ratio (~1.2-1.3), suggesting that the oils were less aromatics and more aliphatic hydrocarbon chain. In addition, it was suggested that water content in pyrolysis liquids were ranged of Torres, et al. [14] derived from the breakdown of COOH and may be from condenser system.

Simulated Distillation of Condensable Liquids

In order to evaluate the utility of fuel oil, the pyrolysis liquid oils derived from pyrolysis temperature of 600°C of 30 wt.% glass fiber composite waste, the highest liquid yields, were selected to distill for analysis of the boiling point range of the products as crude petroleum oil by using GC Simulated Simulation CP3800. The distillation results are presented in Figure 4.23.

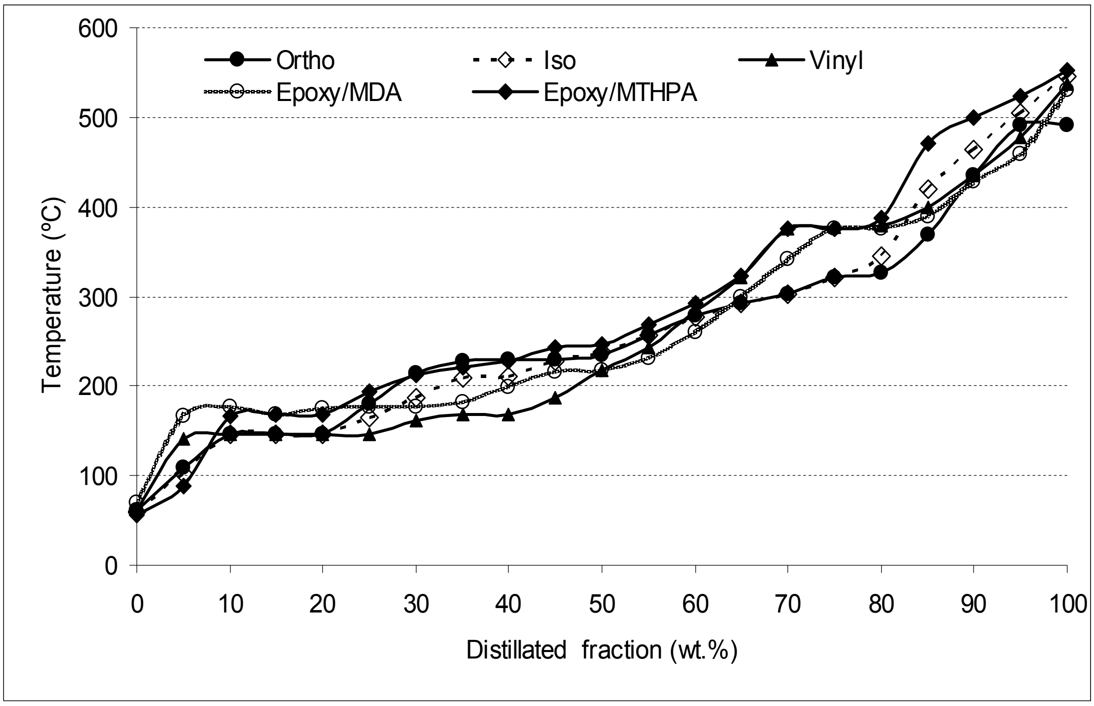


Figure 4.23 Distillated fractions of pyrolysis liquid oils obtained from pyrolysis of unsaturated and epoxy reinforced with 30 wt.% glass fiber composite waste at temperature of 600 °C.

From the distillation curve in Figure 4.23, boiling point ranges of fuel product fractions are summmarized in Table 4.11. It shows that such liquid oil mainly consisted of hydrocarbon distillated of the boiling point range between 30 and 200 which referred to the fraction of gases consisting of 1-4 carbon atoms and gasoline or naphtha which can be used for commercial petrol. This fraction is rich in aromatic. It was suggested that the liquid remained largely comprised of stable aromatic structure corresponded with the results of elemental analysis which showed H/C atomic ratio ranging between 1.0-1.1 (range of aromatic structure). However, the initial boiling of pyrolysis oil derived from pyrolysis of orthophthalic unsaturated polyester composite was 60ºC which is better than that reported by Torres, et al [13,14]. The oils having high initial boiling point temperature (70ºC) may cause problems during engine starting and warming up. Therefore, it should be mixed with light hydrocarbon fraction before used as petrol oil.

Table 4.11 The Distillated products of pyrolysis liquid oil obtained from pyrolysis of unsaturated and epoxy reinforced with 30 wt.% glass fiber composite waste at temperature of 600 ºC.

Distillated products	Boiling range (ºC)	Distilled fraction (wt.%)					Utility
		Ortho	Iso	Vinyl	Epoxy/MDA	Epoxy/MTHPA	
Gases/Naphtha	30-200	28	32	47	40	26	Gasoline oil
Kerosene	200-250	26	21	9	18	25	Kerosene oil
Light gas oil	250-300	15	15	7	7	11	Diesel oil
Heavy gas oil	300-370	17	7	6	8	8	Lubricant oil
Residue	>370	14	25	31	31	27	Asphalt

Furthermore, Table 4.11 also suggested that the distillated fraction is related to the type of resin. For polyester matrices, their thermal degradation were initiated by random scission of ester linkage and then further cracked into smaller molecule which may be in various forms such as phthalic anhydride ($C_6H_4(CO)_2O$), terephthalic acid (HOOC-ph-COOH), carbon dioxide(CO_2), propylene glycol ($HOCH_2CHOHCH_3$), propylene ($CH_2=CH-CH_3$), and methane (CH_4) according to Sarah [47]. According to Maxwell and Richard [33] the degradation products of amine cured resin occurred from the initial cleavage of the weakest C-N bonds and O-CH_2- were hydrogen, methane propene, ammonia, methylamine, trimethylamine, water, phenol. Whereas the products generated from thermal degradation of epoxy cured with anhydride were suggested by Vlastaw, A. S. [32] which started by the dyhydration of water and further decomposed into carbon dioxide, toluene, pyridiene, acetone, methyl formate, hexatriene, methyl acetone, and butadiene.

In addition, the pyrolysis liquid oils, derived from pyrolysis temperature of 600°C of 30 wt.% glass fiber composite waste, were also analyzed for the general properties of liquid fuel such as flash point, pour point, viscosity gross calorific value (GCV) specific gravity, and acidity and compared to other fuels as presented in Table 4.12. Pour point and viscosity of liquid oil derived from pyrolysis process of ortho and iso phthalic unsaturated polyester composite waste were clearly lower than that of vinyl or epoxy composite. This is because the oil of ortho and iso phthalic polyester mainly consisted of waxy crystal compound than that of vinyl or epoxy composite. It can be observed that the fuel properties of pyrolysis vinyl oil were ranged between ortho or iso phthalic unsaturated polyester and epoxy resin which corresponded with Cunliffee, et al. [48]. As mentioned in chapter II, vinyl ester resin was the modified resin of unsaturated polyester and epoxy resin which essentially comprise an epoxy-based and crylic ester end groups.

Table 4.12 also showed acid value of pyrolysis oil from unsaturated polyester. Flash point of pyrolysis oil of ortho or iso unsaturated polyester and vinyl ester were lower than that of epoxy and convention fuel oil. Scheirs and Kaminsky [46] explained that the original feed stock of unsaturated polyester contained styrene monomer which was sensitively ignitable material. However, Cunliffe and Williams [16] suggested that these pyrolysis oils can be recycled as chemical feedstock for polyester resin production process.

From comparison on acidity of condensable liquid oil derived from pyrolysis process of unsaturated, epoxy composite wastes and conventional oil, it can be seen that the liquid oil from ortho and iso phthalic polyester are significantly greater than that of epoxy and conventional oil. Recalling to the chemical compositions of pyrolysis liquid presented in Table 4.9, two of these oils largely consisted of oxygen content with may be in formed of acid (COOH). The presence of high acidity in liquid oil resulted in low gross calorific value and may cause corrosion of engine tank and formation of gum.[49]

Table 4.12 Fuel properties of pyrolysis liquid oil obtained from pyrolysis of unsaturated and epoxy reinforced with 30 wt.% glass fiber composite waste at temperature of 600ºC compared to other conventional fuels.

Properties: Unit:	Flash point (ºC)	Pour point (ºC)	Viscosity[a] (CPs.)	GCV[b] (MJ/kg)	SG[c] (g/cm^3)	Acidity (mgKOH/oil)
ASTM	D6450	D97	D 445	D240	D4052	D644
This research						
Ortho	44.4	<-20	21.5	29.4	1.3	141.2
Iso	45.3	<-20	19.5	25.9	1.1	155.1
Vinyl	36.4	3	15.3	33.5	1.1	34.8
Epoxy/MDA	84.0	3.1	74.7	37.2	1.1	8.81
Epoxy/MTHPA	84.3	7.9	70	34	1.2	88.2
[9][d]	26	NR[e]	3.9	33.6	0.83	NR[e]
[28][f]	>52	<10	1.8-4.1	16-26	0.81-0.87	NR[e]
[29][g]	40-70	NR[e]	3.5-5	14-16	NR[e]	<0.5

a: @40ºC

b : Gross calorific value

c: Specific density at15ºC

d: Liquid oil obtained from pyrolysis of 30 wt.% glass fiber orthophthalic polyester at 450ºC

e: Not recommend

f: Automotive diesel oil

g: Bio diesel

4.2.2.3 The Characteristic of Gaseous Product

The gaseous products from pyrolysis of composite wastes collected in gas sampling bags were analyzed and quantified by Gas chromatography (GC) SRI 8610C. The analysis results of evolution gases from pyrolysis process of unsaturated polyester reinforced with 30 and 60 wt.% glass fiber composite wastes in relation to final pyrolysis temperature are presented in Figure 4..24 and 4.25, respectively. It was demonstrated that product of gases were rich in carbon dioxide (CO_2); 60-70 vol.% which directly derived from the breakdown of ester bonds (-COO-) with resin, methane(CH_4); 30-40 vol.%, and some amount of carbon monoxide (CO), and hydrogen (H_2).

The influence of final temperature on gas composition, Figures 4.24 and 4.25 show that carbon dioxide decreased with the increase of pyrolysis temperature from 600 to 800ºC due to secondary decomposition into carbon monoxide. Significant increased of carbon monoxide resulted from both secondary reaction decomposition of carbon dioxide and carbonization of atomic structure in solid residue at elevated temperature. Further cracking of evolved volatile matter [15] also resulted in greater yield of methane and hydrogen.

Gaseous products generated from pyrolysis of epoxy composite waste are shown in Figure 4.26 which largely consisted of methane gas (50-60 vol.%) derived from the breakdown of alkyl groups in the epoxy chain [6,15,16], carbon dioxide (40-50 vol.%), carbon monoxide (3-5 vol.%) and some amount of hydrogen gas (0.1-0.2 vol%)

The comparison of gross calorific value (GCV) of generated gas from various resin matrix reinforced with 30 and 60 wt.% glass at pyrolysis temperature from 600 to 800ºC are displayed in Figure 4.27 (a-c).

It can be seen that the GCVs of evolution gases from composite consisted of 30 wt.% glass fiber were slight higher than that of 60 wt.% glass fiber, resulting from larger in volumetric gas evolution. The GCVs of nitrogen free gaseous product involved from pyrolysis 30 wt.% glass fiber reinforced unsaturated polyester composite wastes were ranging from 12-14 MJ/m^3 and comparable to previous literature [13,15].

The GCVs of gas obtained from pyrolysis of epoxy cured amine and anhydride composite waste shown in Figure 4.27 were no significantly different (17-21 MJ/m^3) which clearly higher than that of unsaturated polyester composite due to greater methane gas..

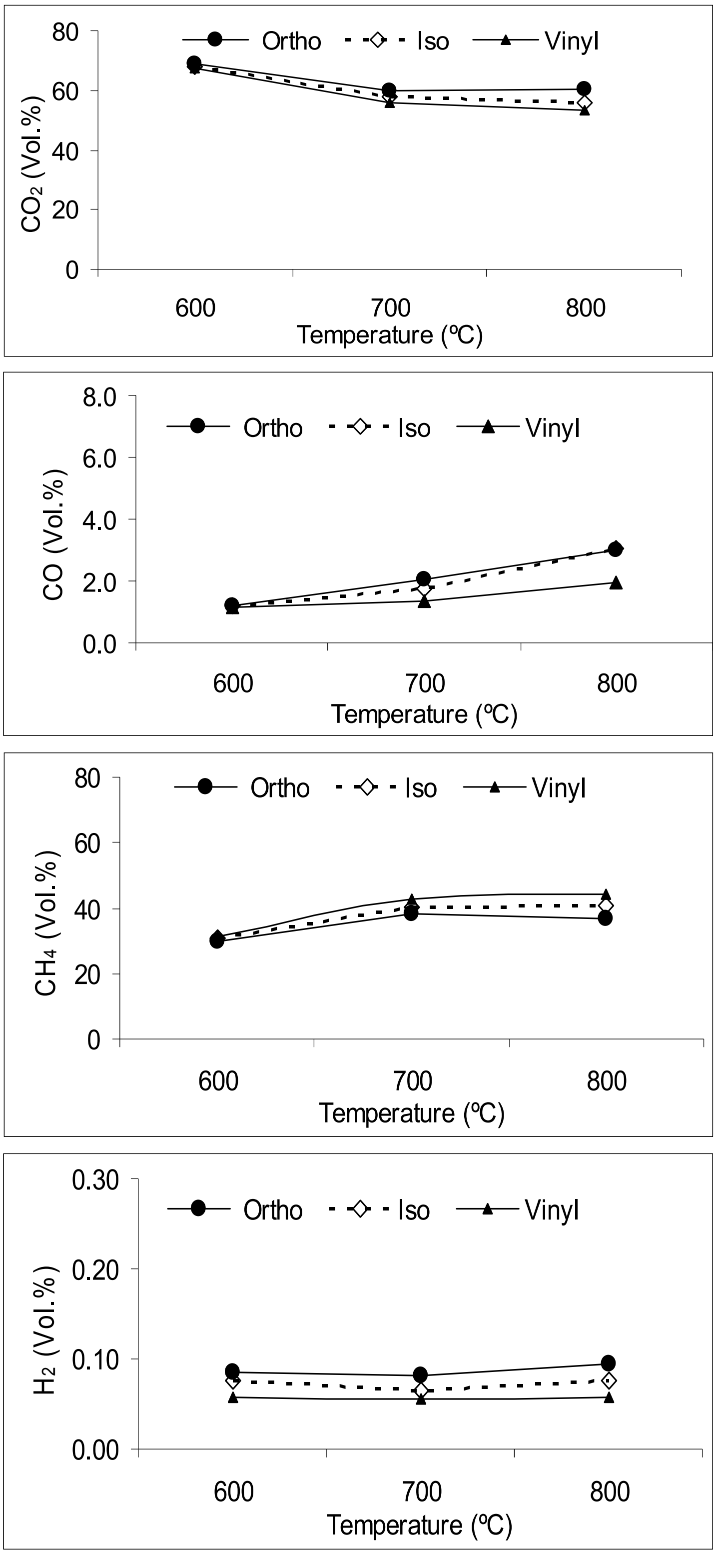


Figure 4.24 Gaseous product (nitrogen free) involved from pyrolysis process of three types unsaturated polyester reinforced with 30 wt% glass fiber composite wastes.

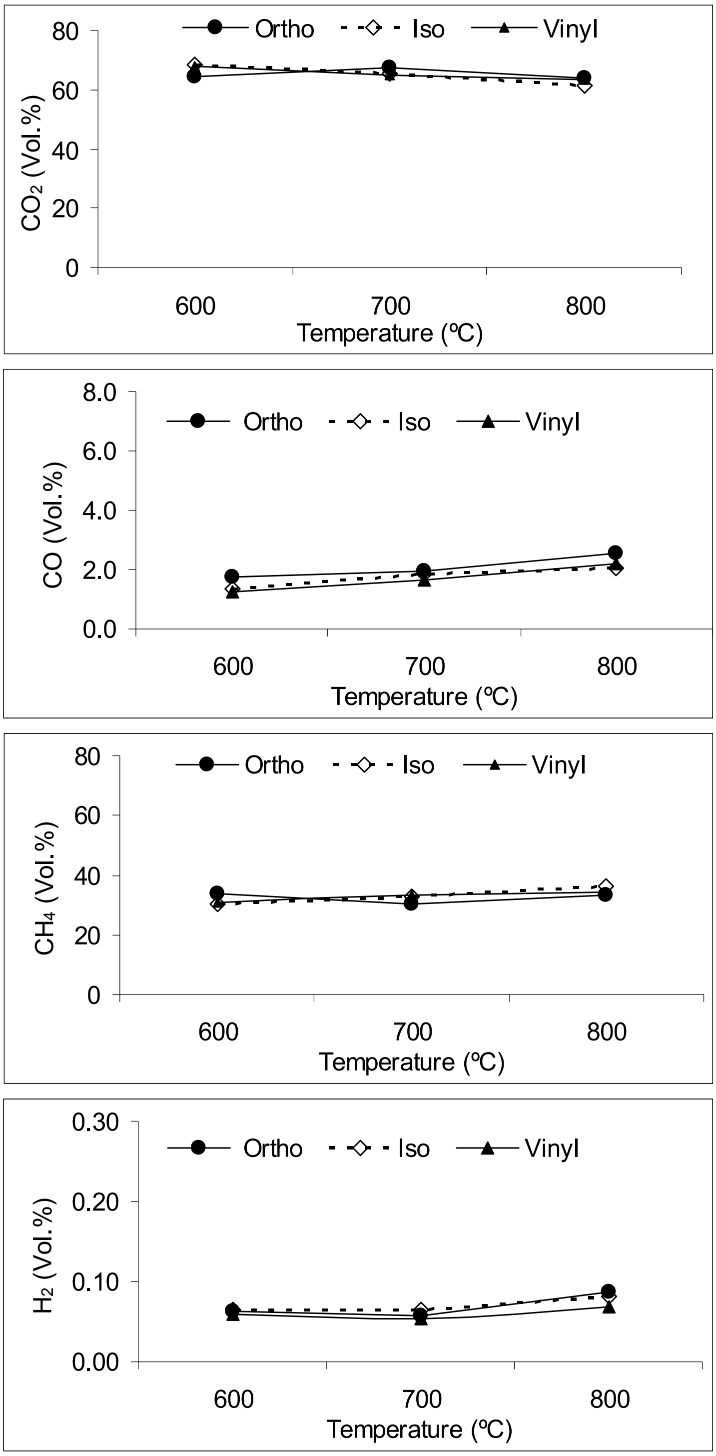


Figure 4.25 Gaseous product (nitrogen free) involved from pyrolysis process of three types unsaturated polyester reinforced with 60 wt% glass fiber composite wastes.

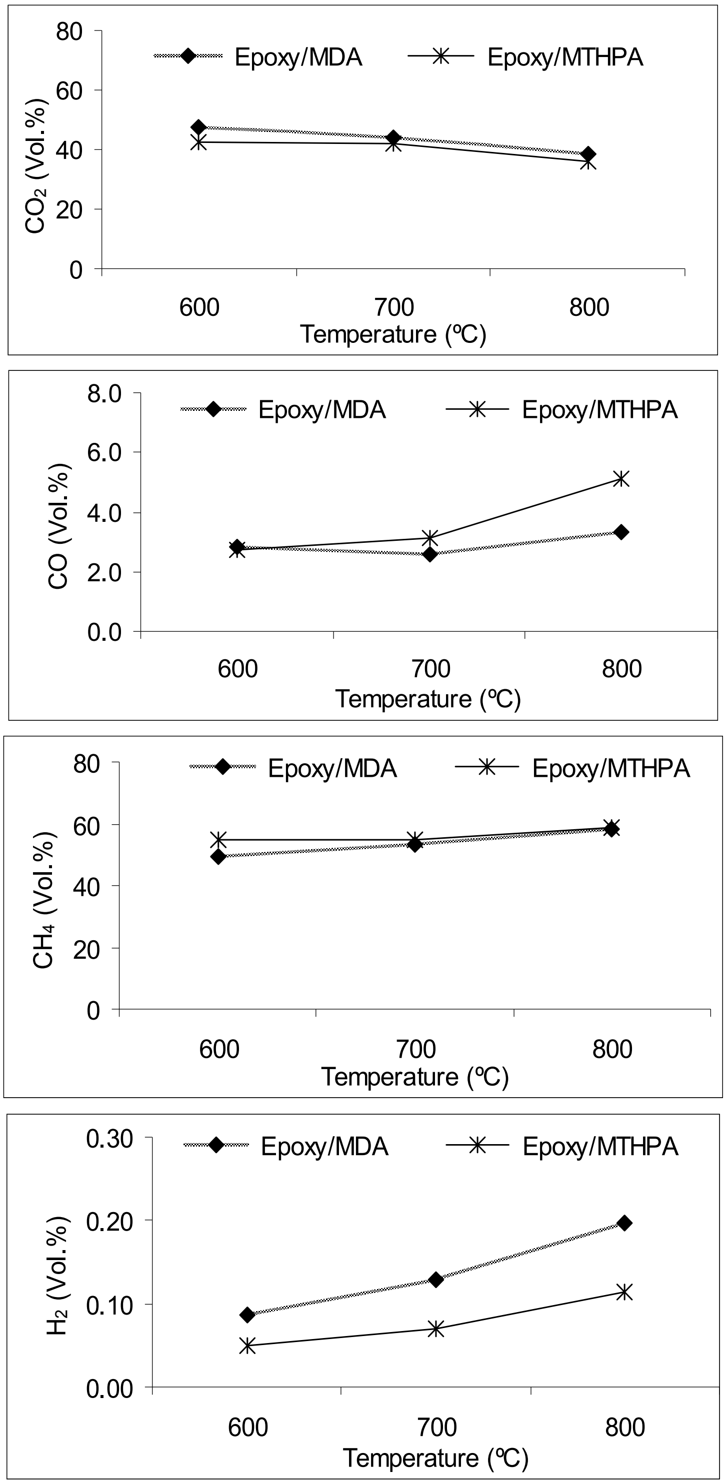


Figure 4.26 Gaseous product (nitrogen free) involved from pyrolysis process of amine and anhydride cured epoxy reinforced with 30 wt% glass fiber cured composite wastes.

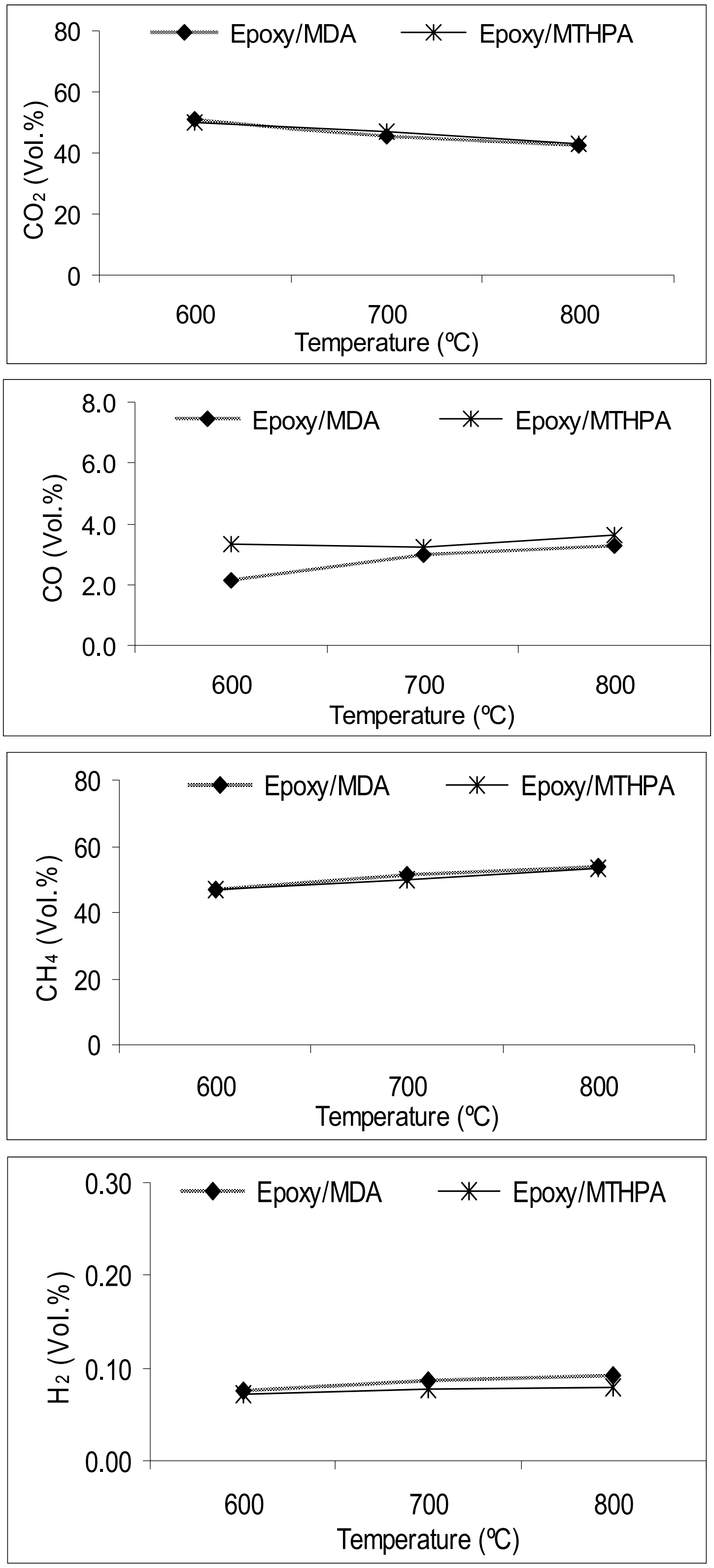


Figure 4.27 Gaseous product (nitrogen free) involved from pyrolysis process of amine and anhydride cured epoxy reinforced with 60 wt% glass fiber cured composite wastes.

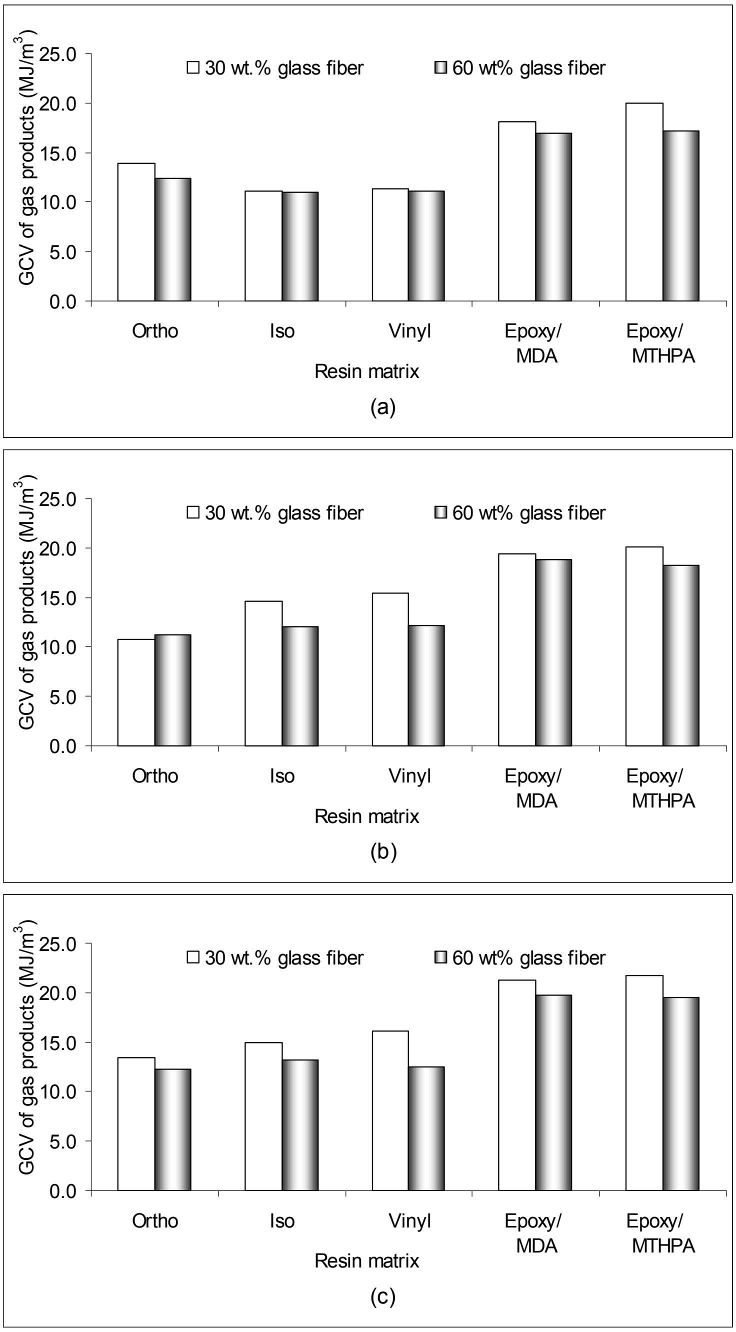


Figure 4.28 The comparison of nitrogen free gross calorific value (GCV) of gaseous products obtained from pyrolysis of unsaturated polyester and epoxy reinforced with 30 and 60 wt% glass fiber at pyrolysis temperature of (a) 600°C, (b) 700°C, and (c) 800°C.

4.3 Characterization of Composites Prepared from Original Glass Fiber and Recycled Glass Fiber from Pyrolysis Process

This section presents the mechanical properties in terms of flexural and impact properties of composite prepared from original glass fiber (125 μm) and recycled glass fiber (mean length of 130-200 μm and particle size of 420 μm) obtained from pyrolysis of 60 wt.% glass fiber composite waste samples at temperature of 600 and 800 °C in order to investigate the effect of pyrolysis temperature and the proportion of recycled fiber that can be used for replacing original fiber with no significant effect on mechanical properties . The proportion of fibers was varied from 5 to 20 wt. % of the total composite weight. Furthermore, the fractured surface of three-point bending test specimens was observed by Scanning Electron Microscope (SEM) to investigate the relationship between interfacial bonding of fiber- matrix and strength.

4.3.1 Flexural Properties

The flexural properties in terms of flexural strength and flexural modulus of unsaturated polyester and epoxy reinforced with original glass fiber and recovered glass fiber obtained from pyrolysis process were tested by using a Universal Testing Machine (LLOYD LR 100 N) in form of flat wise specimens according to ASTM D790-03 standard method for three point bending test.

4.3.1.1 Flexural Strength

The flexural strength of bulk molding compound (BMC) unsaturated polyester reinforced with original and recycled glass fiber at various content varied from 5 to 20 wt.% are presented in Figure 4.29. The results showed that vinyl ester resin had higher flexural strength than isophthalic and orthophthalic polyester resin about 9 and 27%, respectively, which can be related to their its fracture surface morphology by SEM images in Figure 4.30 (a-c). It was revealed that fracture surface of vinyl ester and isophathalic polyester cured resin matrix showed rib-like of fracture path propagation, especially vinyl ester resin, while orthophthalic polyester resin showed smooth and presence of spot which was defection area leading to lower flexural strength than the other two resins.

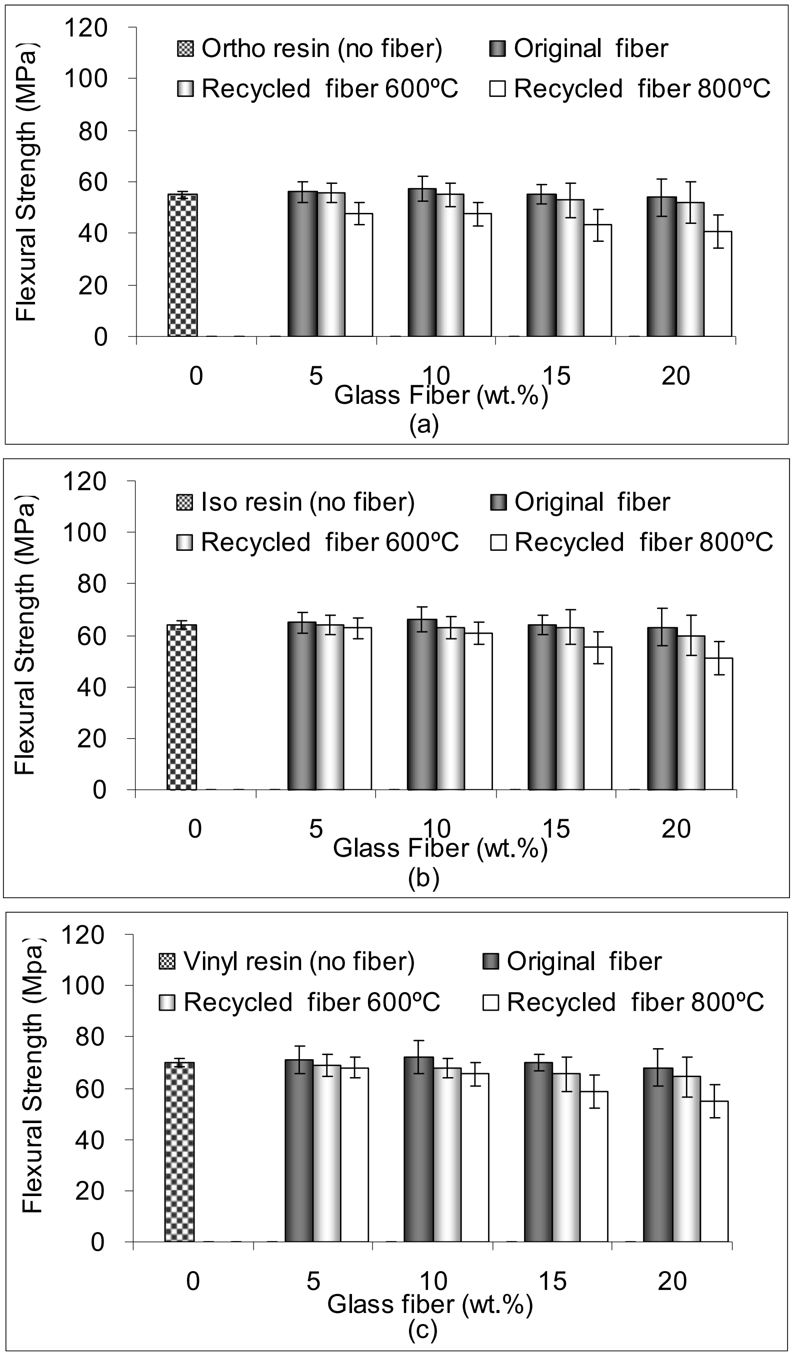


Figure 4.29 Effect of glass fiber content on flexural strength of unsaturated polyester resin and BMC composite: (a) orthophthalic polyester, (b) isophthalic polyester, and (c) vinyl ester composites.

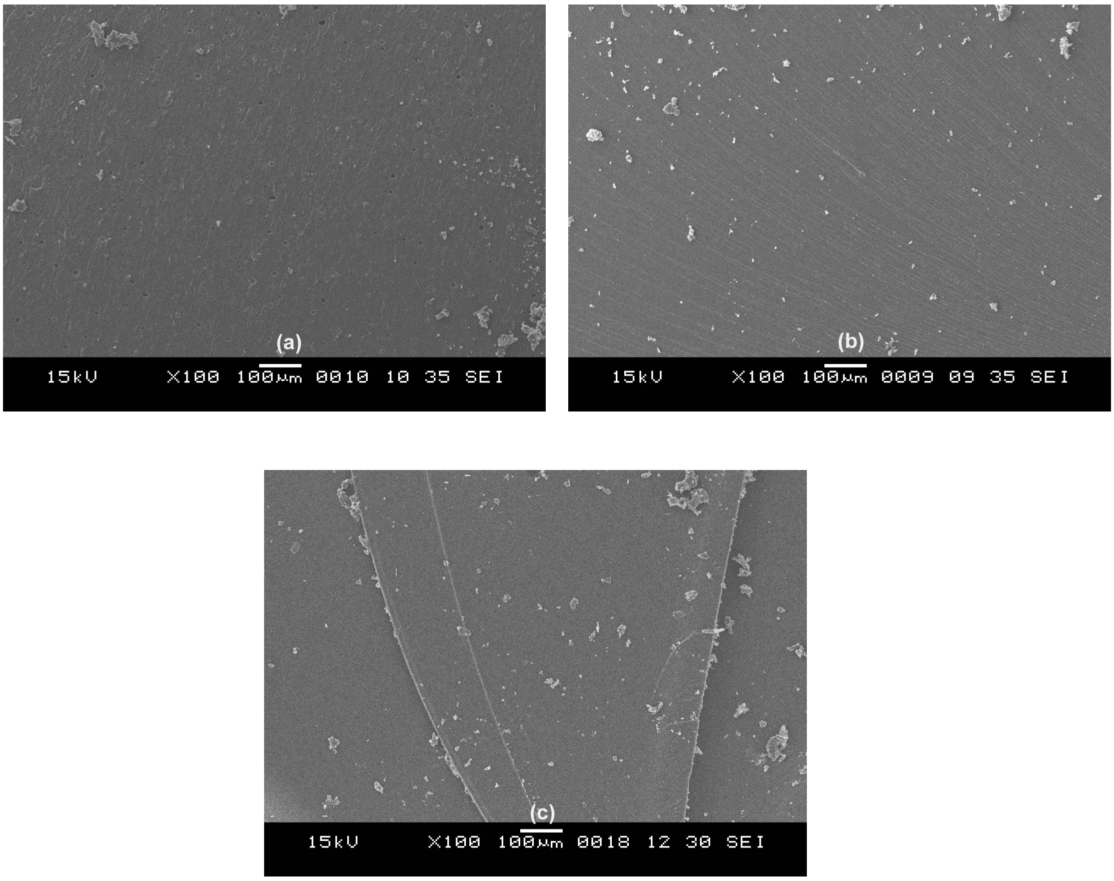


Figure 4.30 SEM micrographs of fracture surface from three point bending test specimens of unsaturated polyester resin: (a) orthophthalic polyester, (b) isophthalic polyester, and (c) vinyl ester resin.

This is resulted from the difference in their chemical structure which are presented in Figure 4.31 It can be seen that the chemical structure of vinyl ester resin consisted of bisphenol A in its straight main chain which is very stiff and strong and high rigidity structure resulting in higher flexural strength than the other two resins. Visco, et. al. [50] indicated that the steric hindrance structure of orthophthalic polyester resulted in lower density structure which attributed to its lower flexural strength comparing to the isophthalic polyester resin. In addition, The chemical structure of isophthalic polyester showed higher symmetry than that of orthophthalic polyester, leading to higher strength when applied stress.

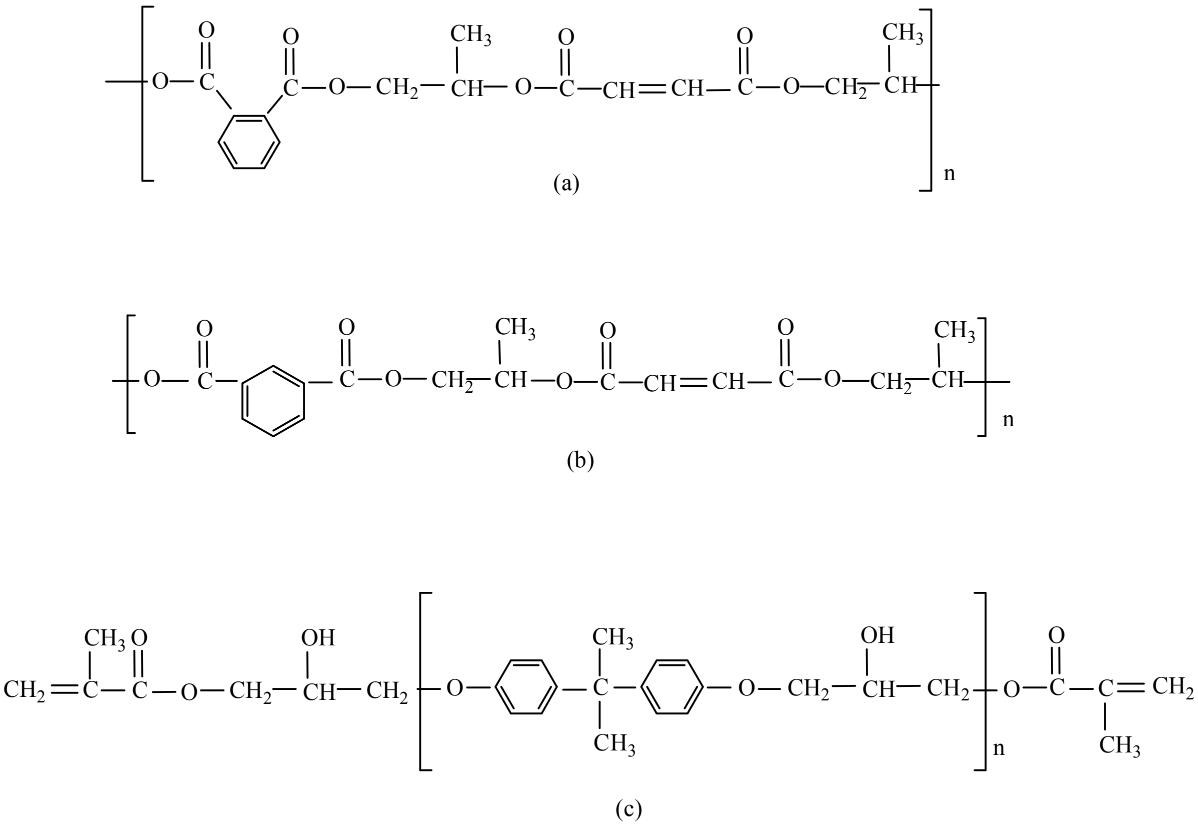


Figure 4.31 Chemical structure of three types unsaturated polyester resin: (a) orthophthalic polyester, (b) isophthalic polyester resin, and (c) vinyl ester resin.

For the effect of different curing agent on flexural strength of epoxy resin, as presented in Figure 4.32, it was found that the amine (MDA) cured epoxy resin had lower flexural strength than of and anhydride (MTHPA) cured epoxy resin of about 20% which was resulted from a few reasons. Firstly, because amine curing agent had higher viscosity (400 centipoise, cps.) than anhydride curing agent (260 cps) which affected to the homogeneity of resin mixed at room temperature. Secondary, the pot life of resin mixed with amine curing was short which resulted in the fast and into high exothermic reaction, In additin, unreacted molecules may be presented which were trapped into network structure during curing reaction as white haze sports, contributing to weak point when applying load as shown in SEM image in Figure 4.33 (a) Finally, is due to its chemical structure was cycloaphthic amine which preeminently showed in terms of toughness .While anhydride curing which low viscosity and can be reacted with epoxy resin at high temperature (150°C) leading to more homogeneity of resin mixed as the results from SEM image in Figure 4.33 (b) Furthermore, the presence of benzene ring in its structure as shown in Figure 4.34 providing good flexural strength.

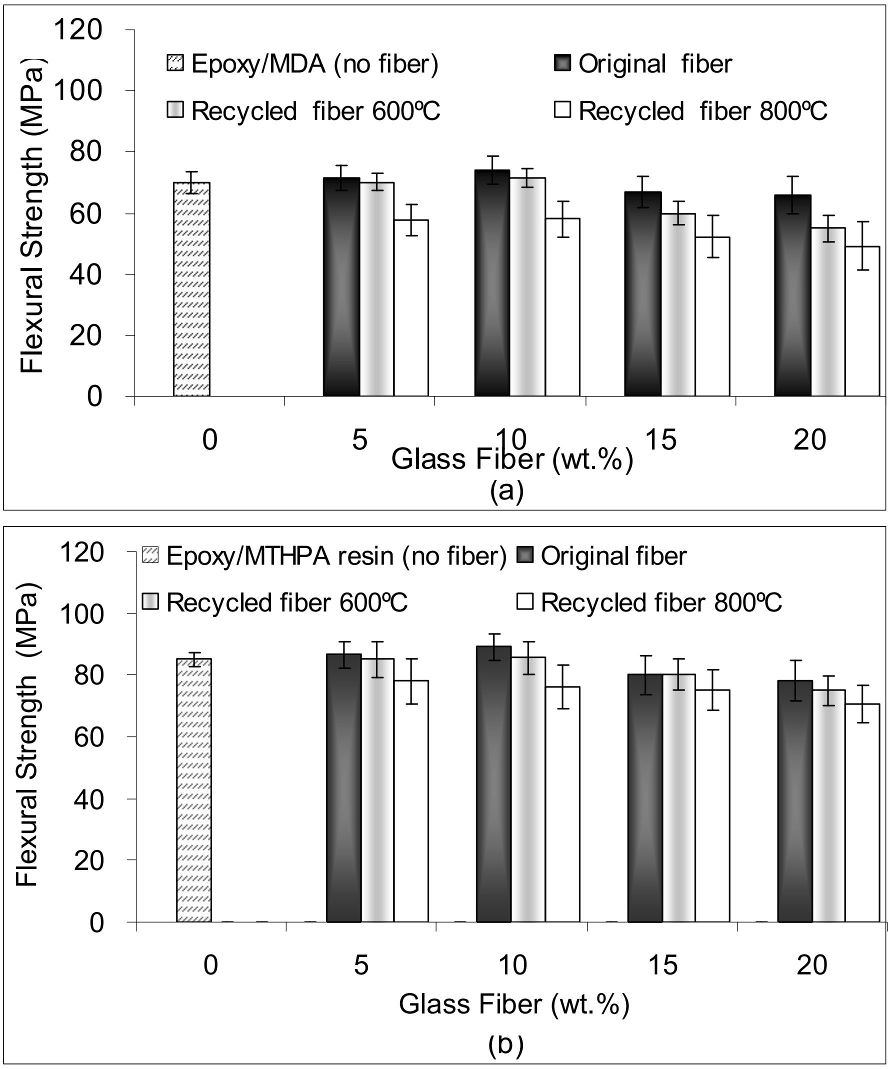


Figure 4.32 Effect of glass fiber content on flexural strength of epoxy resin and BMC composite: (a)epoxy/MDA, and (b) epoxy/MTHPA composites.

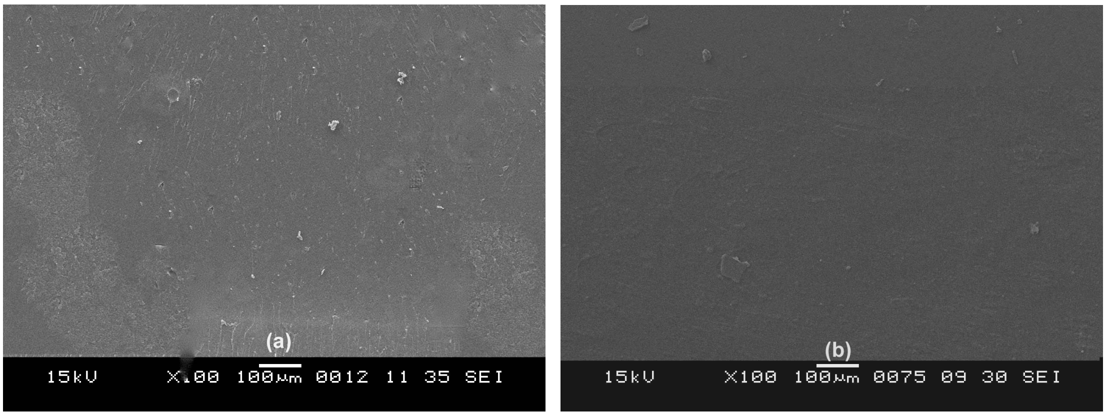
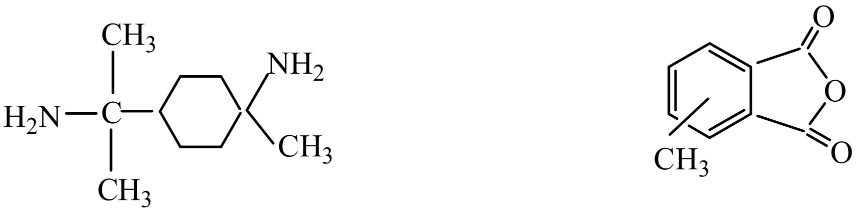


Figure 4.33 SEM micrographs of fracture surface from three point bending test specimens of of epoxy resin: (a) epoxy/MDA and (b)epoxy/MTHPA.



MDA MTHPA

Figure 4.34 Chemical structure of Methanediamine (MDA) and Methyltetra hydrophthalic anhydride (MTHPA).

According to rule of mixture [10], it was observed from Figure 4.29 and 4.32 that the flexural strength of both BMC composites containing original glass fiber were increased 2-5 % when glass fiber content was significantly increased from 5 to 10 wt% but it was slightly decreased (1-2%) when the original glass fiber content was increased to 20 wt% This result may be affected from the agglomeration of original glass fiber as presented in SEM images in Figure 4.35 and 4.36, resulting in the reduction of strength at fiber fraction from 15 -20 wt%. However, their flexural strength was shill higher than that of neat resin and no significant effect from the difference types of unsaturated polyester and epoxy curing agent was observed.

Considering the flexural strength of both BMC composites reinforcing with recycled glass fiber from pyrolysis process at temperature of 600 and 800°C, unlike the

BMC composites having original glass fiber, upon increasing recycled glass fiber content, their flexural strength was decreased. In addition, it was found that the flexural strength of both BMC composites containing 20wt% recycled glass fiber at 800°C were clearly lower than that of the BMC composites containing original glass fiber (10 - 15%) and recycled fiber 600 °C(3-7%). It can be seen from SEM images in Figure 4.37 and 4.38 respectively, that the fracture surface of the unsaturated polyester and epoxy composites prepared from recycled glass fiber at 600 and 800°C showed poor interfacial bonding between matrix and glass fiber as evidenced by the presence of many holes. Particularly, the composites containing recycled glass fiber at 800°C showed several tiny holes greater than the ones with recycled glass fiber at 600°C.

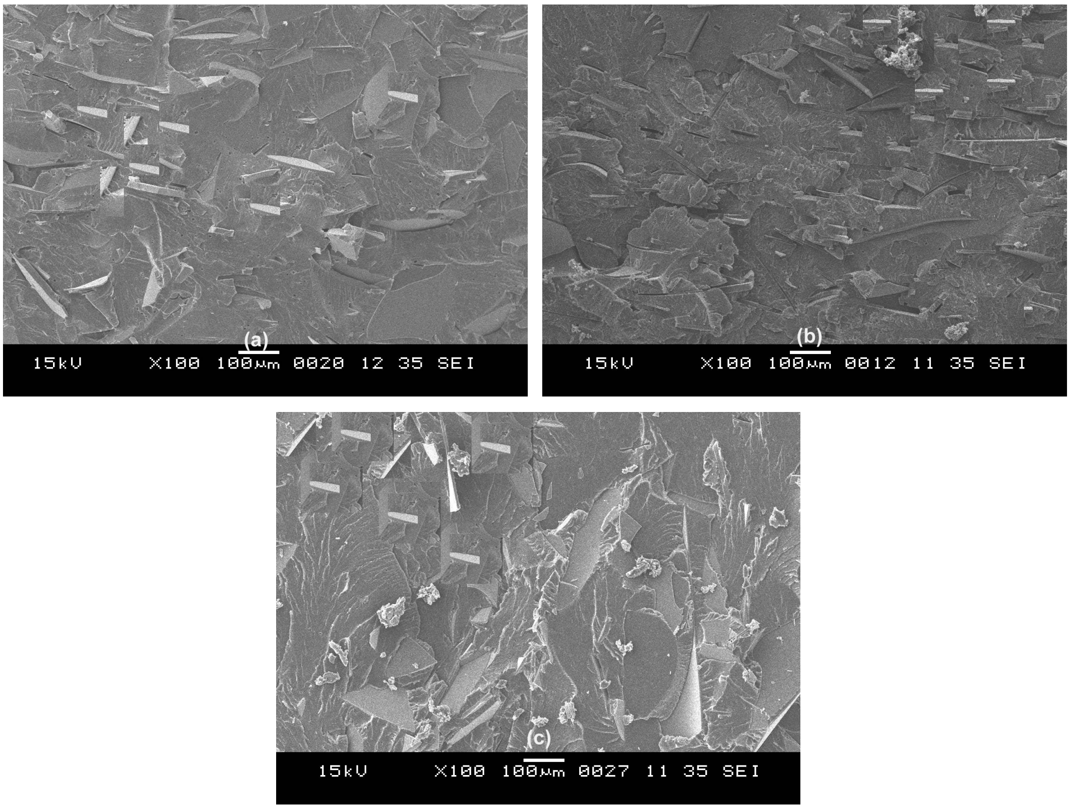


Figure 4.35 SEM micrographs of fracture surface from three point bending test specimens of unsaturated polyester composite: (a)orthophthalic polyester with 15 wt% original glass fiber, (b) isophthalic polyester 15 wt% original glass fiber, and (c) vinyl ester 15 wt% original glass fiber composites.

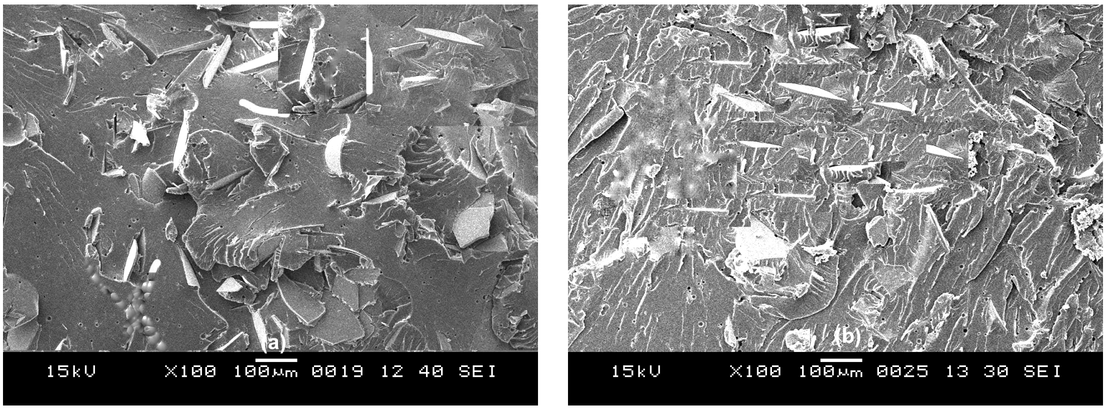


Figure 4.36 SEM micrographs of fracture surface from three point bending test specimens of epoxy composite: (a) Epoxy/MDA with15 wt% original glass fiber, (b) Epoxy/MTHPA with15 wt% original glass fiber composites.

These holes and voids were resulted from the lack of adhesion between the two phases; as a result, the pulled out of fiber under load was occurred which was more clearly observed in recycled glass fiber 800ºC as presented in Figure 4.37 and 4.38 (b).This is an important factor having impact on mechanical strength of composite material. The reduction in strength of BMC composites with recycled glass fiber may be. resulted from the breakage of fiber during applied load due to thermal degradation by pyrosis process Moreover, the coupling agent of glass fiber, which was widely used for unsaturated polyester and epoxy resin as presented in Figure 4.39, was probably degraded at these pyrolyzed tem perature, leaving the recycled glass fiber without any surface treatment, which was usually helped promoting the interfacial adhesion between matrix and fiber.

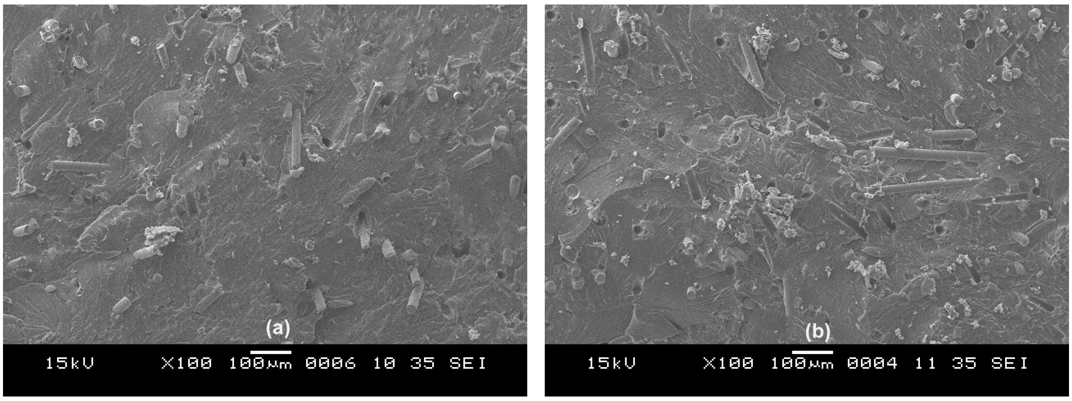


Figure 4.37 SEM micrographs of fracture surface from three point bending test specimens of (a) orthophthalic polyester with 15 wt% recycled glass fiber (600°C) composite and (b) orthophthalic polyester with 15 wt% recycled glass fiber (800°C) composite.

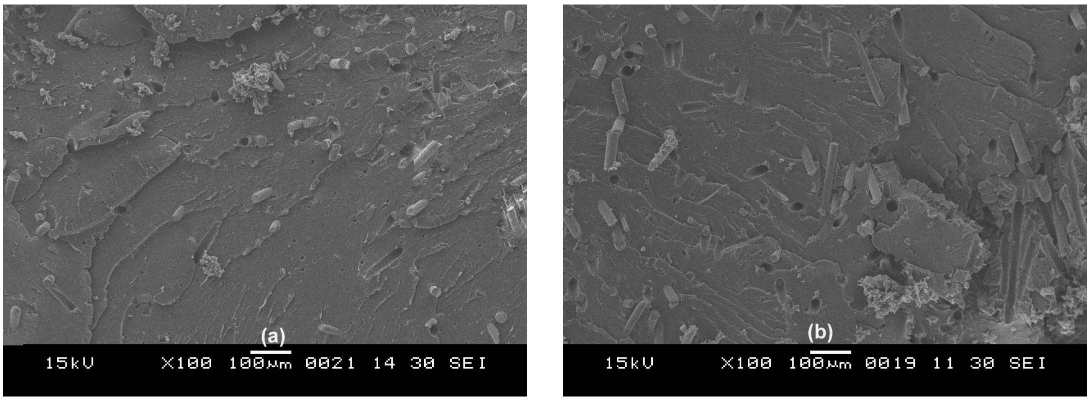
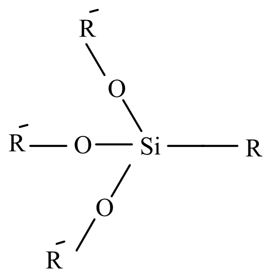
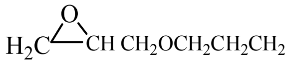


Figure 4.38 SEM micrographs of fracture surface from three point bending test specimens of (a) epoxy/MDA with 15 wt% recycled glass fiber (600°C) composite and (b) epoxy/MDA with 15 wt% recycled glass fiber (800°C) composite.



Where R is CH_2 or CH_3

R´ is



$H_2C(O)CH\ CH_2OCH_2CH_2CH_2$ for epoxy marix, and

CH_2=CH for unsaturated polyester matrix

Figure 4.39 Typical coupling agent for unsaturated polyester and epoxy resin base [53].

4.3.1.2 Flexural Modulus

The flexural modulus of three types unsaturated polyester resin matrix is presented in Figure 4.40.similar to flexural strength, their modulus values were different depending on their chemical structure. Vinyl ester resin had higher flexural modulus value than isophthalic and orthophthalic polyester resin about 25 and 65 %, respectively. This result was clearly attributed to the effect of chemical structure as previously mentioned on flexural strength.

Similar to flexural strength, the flexural modulus of epoxy resin matrix was significantly affected from the different curing agent as previously discussed. It was found from Figure 4.41 that epoxy cured with anhydride curing agent showed ap proximatly 15% higher in flexural modulus than that of epoxy cured with amine about 15 %.

Considering the flexural modulus of all BMC composites containing original glass fiber, it was found that their modulus was increased with increasing original glass fiber content, suggesting that BMC composites became stiffer, similar to other previous works [52-53].

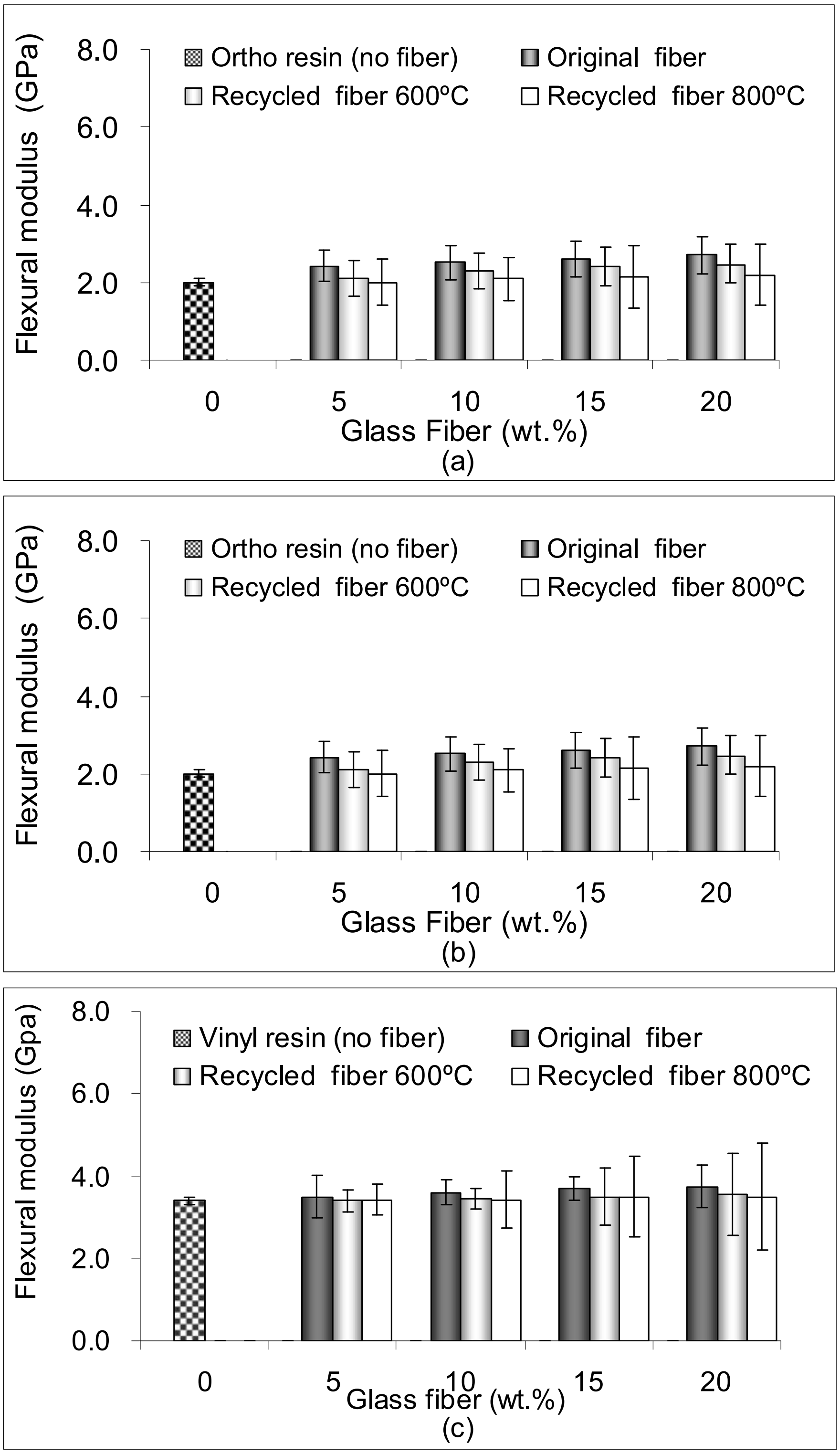


Figure 4.40 Effect of glass fiber content on flexural modulus of unsaturated polyester resin and BMC composite:(a) orthophthalic polyester, (b) isophthalic polyester, and (c) vinyl ester composites.

This is also based on rule of mixture which was proved that the elastic modulus of composite related to elastic moduli of fiber and matrix and their volume fraction of reinforcement material. The increase in flexural modulus of each unsaturated polyester containing original glass fiber was different depending on type of unsaturated polyester matrix.

Comparing with the resin matrix (o wt% fiber), it was found that the flexural modulus of orthophthalic polyester composite was significantly increased from 20 to 35 % when the original glass fiber was increased from 5 to 20 wt% While it was increased from 10 to 20 % for isophthalic unsaturated polyester matrix and from 6 to 10% for vinyl ester resin matrix. Similarly, the increase in flexural modulus of epoxy composite depended on type of curing agent the flexural modulus of Epoxy/MDA composites was increased from 7 to 25% when the original glass fiber was increased from 5 to 20 wt% compared to neat resin. While those of epoxy/MTHPA were increased from 2-20 %. The significantly increased in flexural modulus may by resulted from the stiffness of original glass fiber.

Regarding to the effect of recycled glass fiber, it was found that the flexural modulus of both BMC composites showed similar trend as the ones with original glass fiber that the flexural modulus was increased as increasing of recycled glass fiber content. However, the percentage of increasing in the flexural modulus was significantly depended on pyrolyzed glass fiber temperature. It was found that the recycled glass fiber at 800°C. had less effct on in creasing in flexural less than that of recycled glass fiber 600°C, which was affected from the loss of sizing during pyrolysis at higher temperature.

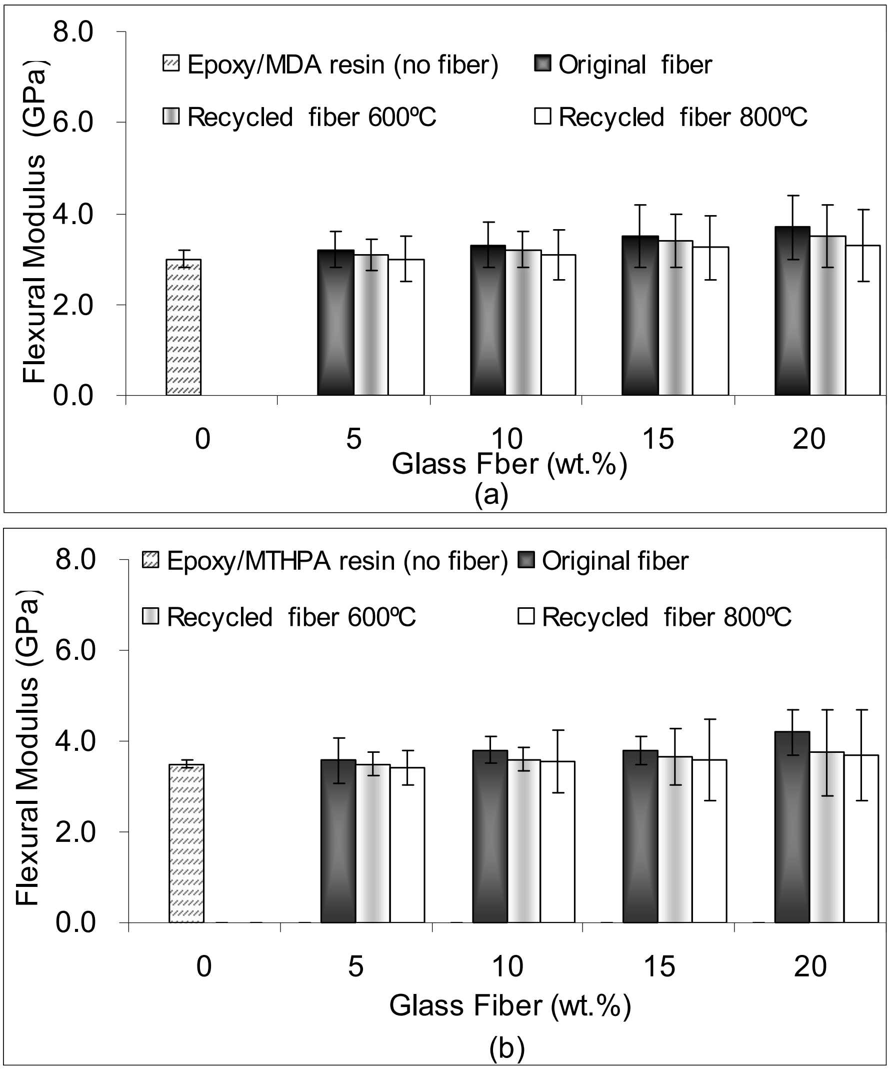


Figure 4.41 Effect of glass fiber content on flexural modulus of epoxy resin and BMC composite: (a) epoxy/MDA and (b) epoxy/MTHPA composites.

4.3.2 Impact Properties

The impact properties of unsaturated polyester and epoxy resins and their BMC composites carried out by impact tester (Zwick) according to ASTM D256-04 were presented in Figures 4.42 and 4.43, respectively. Similar to flexural properties, the impact strength of vinyl ester matrix was greater than that of isophthalic and orthophthalic approximately 7 and 25 % respectively. This is due to the effect of chemical structure of vinyl ester which was based on a bisphenol A backbone as previously mentioned. On the other hand the impact strength of epoxy cured with MDA was higher than that of epoxy cured with MTHPA because of the cycloaliphatic amine structure of MDA which contributing to better toughness of the epoxy composite than the one wilh MTHPA which had rigid structure of benzene ring.

The impact strength of both BMC composites containing original fiber and recycled fiber tended to decrease with higher glass fiber loading, suggesting that the composites became more brittle upon increasing glass fiber content. This is due to the stiffness of the fiber comparing to the matrix.

Considering the impact strength of BMC composites containing original glass fiber, the results showed that the addition of 5 wt % glass fiber had no influence on their impact strength values. This result was found in both systems. Further loading the glass fiber resulted in the decrease in impact strength, owing to the agglomeration of glass fiber leading to the increase of localized stress and reduction of the elasticity of matrix material. As a result, the impact strength was decreased. Another possible reason also was discussed by Surai, et. al. [54] that the particle of reinforcement in the scale of micrometer led to the generation of crack around reinforcement and short energy distance for energy dissipation, whereas the high volume fraction of nanoparticle size can be used to improve toughness of brittle plastic because of the dense of interfacial region. Therefore, the impact strength of BMC composites containing original glass fiber (125 μm) may be affected from the length of glass fiber, resulting in the decrease of strength values.

Regarding to the effect of recycled glass fiber obtained from pyrolysis process on the impact strength of BMC composites, it can be seen from Figure 4.40 and 4.41 that the impact strength of both BMC composites containing recycled glass fiber at 600 and 800ºC showed similar trend that the impact strength was decreased with the addition of recycled glass fiber and was lowered than that of neat resin and BMC composite with original glass fiber. This result was agreed with previous research reported by Marco, et al. [26].

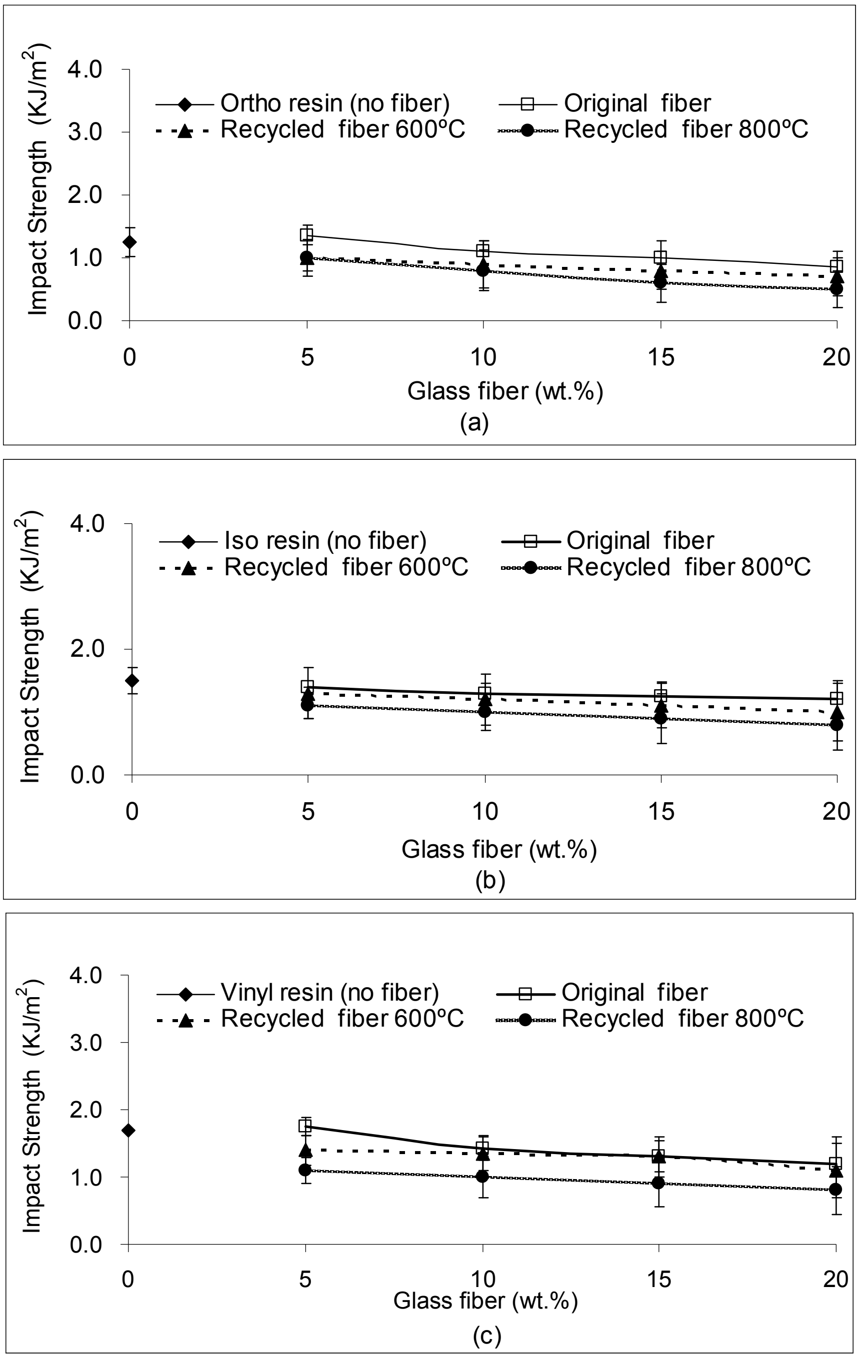


Figure 4.42 Impact strength of unsaturated palyester resin and BMC composites in relation to weight fraction of glass fiber (a) orthophthalic polyester, (b) isophthalic polyester, and (c) vinyl ester composite.

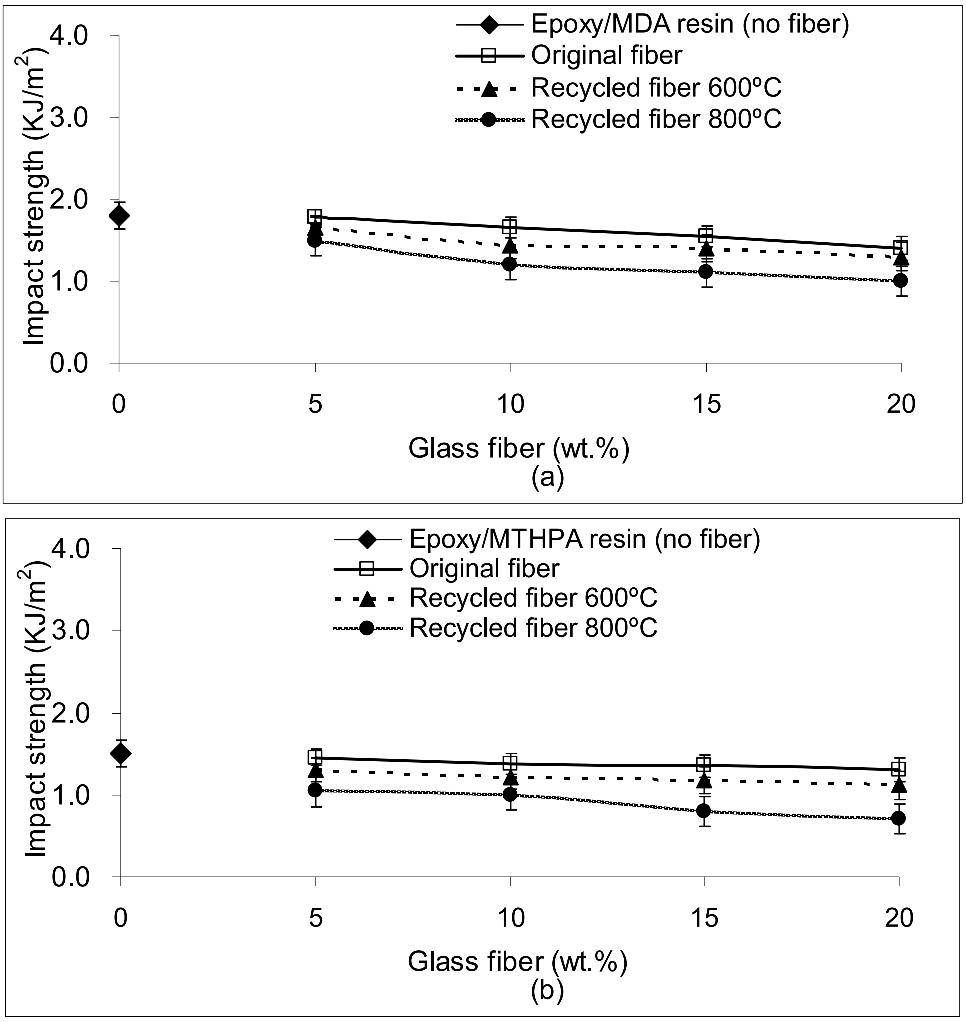


Figure 4.43 Impact strength of epoxy resin and BMC composites in relation to weight fraction of glass fiber (a) epoxy cured with amine (MDA), (b) epoxy cured with anhydride (MTHPA).

Comparing between two types of recycled glass fiber, both BMC composite systems containing recycled glass fiber at 600°C exhibited better impact strength than their counterparts. This is because recycled glass fiber at 800 °C showed poorer interfacial bonding between matrix and glass fiber as evidenced by the presence of many holes as previously presented by SEM micrographs in Figures 4.37 and 4.38.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

The results of the research from the investigation of thermal behavior and thermochemical conversion by pyrolysis of 30 and 60 wt% glass fiber reinforced orthophthalic, isophthalic unsaturated polyester, vinyl ester, and epoxy cured with amine and anhydride at the temperature of 600, 700, and 800ºC in order to study effect of the pyrolysis temperature and difference of resin matrix such as chemical structure of unsaturated polyester matrix and curing agent of epoxy matrix on the product yield and characteristic of solid, liquid, and gaseous products are summarized into three sections as follows:

5.1.1 The Characteristic of Composite Waste Samples

- The characteristic of each composite wastes such as functional group, chemical composition depended on type of matrix resin which generated from the vibration of carbonyl ester group, aromatic ring, and unsaturated alkene in main chain. Whereas the spectra of epoxy depended on its curing agent. The elemental composition results showed that the amount of carbon, hydrogen, and nitrogen was related to glass fiber content. The increase in glass fiber content resulted in the decrease in carbon, hydrogen, and nitrogen.
- The thermal behavior of composite wastes greatly depended on chemical structure of resin matrix and glass fiber content. Vinyl ester show higher activation energy of decomposition greater than that of isophthalic and orthophthalic polyesters. This is due to the effect of bisphenol A in main chain and methacrylate steric pendant group at the end of vinyl ester backbone which exhibit good thermal stability.

Anhydride (MTHPA) cured epoxy displayed better thermal stability than that of amine cured epoxy due to the presence of benzene ring in anhydride structure. In addition, the presence of higher glass fiber content in composite resulted in lower activation energy. This is because glass fiber content inhibited curing process which led to decrease in degree of cured resin matrix thus lower thermal stability.

5.1.2 Thermal Conversion by Pyrolysis Process

- The product yields are significantly affected by reaction temperature, glass fiber content in composite feedstock, and resin matrix. It was found that the pyrolysis of all composite waste at temperature of 600ºC gave maximum solid and liquid yields. The reaction temperature of 800ºC is the promising condition to produce gaseous products. The liquid and gaseous products generated from pyrolysis of 30 wt% glass fiber composite waste are higher than those of 60 wt% glass fiber composite waste around 30 %) under the same resin and pyrolysis conditions. Orthophthalic polyester matrix composite shows the highest liquid yield due to the effect of phthalic anhydride original monomer. Whereas epoxy cured with amine (MDA) at room temperature can be degraded to form higher liquid product than that of epoxy cured with anhydride (MTHPA) at 150ºC.
- The reaction temperature, resin matrix type, and glass fiber content in composite feedstock do not have prominent effects on characteristic of solid, liquid, and gas in each resin system due to the similar of functional group in polymer matrix which can be degraded and similarly formed liquid and gaseous products.
- Liquid obtained from pyrolysis process of unsaturated polyester and epoxy reinforced with 30 wt% glass fiber at temperature of 600ºC can not be directly used as fuel product due to high composition of oxygenated

compound which can cause to corrosion problem and flash point is lower than conventional fuel product. On the contrary, such oils have the gross calorific value within the range of standard oil and high fraction of gases/naphtha which can be utilzed as gasoline products.

- The gaseous products evolved largely consisted of CO_2, CO, and some amount CH_4 and H_2. The gross calorific value of gas generated from pyrolysis of unsaturated polyester (12-14 MJ/m^3) is lower than that of epoxy composite (17-21 MJ/m^3) due to the larger volume fraction of CH_4 in the later matrix.

5.1.3 Characteristic of Composites Prepared from Original Glass Fiber and Recycled Glass Fiber from Pyrolysis Process.

- Flexural strength of unsaturated polyester resin depended of their chemical structure. The vinyl ester resin had higher flexural strength than isophthalic and orthophthalic polyester resin approximately 9 and 27%, respectively due to the presence of bisphenol A in a main chain and methacrylate at the end of vinyl ester backbone. Similarly, anhydride (MTHPA) cured epoxy resin had higher flexural strength than of amine cured around 20% because of the effect of benzene ring in anhydride structure.
- Flexural strength of both BMC composites with original glass was increased 2-5 %,upon increasing the fiber content 5-10 wt% and tended to decrease 1-2 wt% when original glass fiber was increased to 15-20 wt% . This is due to the agglomeration of original glass fiber .
- In addition flexural strength of both BMC composite containing with recycled glass fiber at 800ºC were clearly lower than that of the BMC composite containing original glass fiber (10- 15%) and recycled fiber 600 ºC (3-7%) with it was increased to 20 wt% because of the presence of fiber pulled out in resin matrix

- The flexural modulus of all BMC composite showed slightly increased, upon increasing of glass content from 5-20 % which depended resin matrix.
- The impact properties vinyl ester resin was greater than isophthalic and orthophthalic polyester approximately 7 and 25 %, respectively due to the effect rigidity structure . Where as cycloaliphatic amine structure of MDA curing agent contributed to better toughness of epoxy approximately 20%
- The addition of 5 wt% glass fiber had no influence on the impact strength of BMC composite. Further loading the glass fiber resulted in the decrease in the impact strength, owing to the agglomeration of glass fiber loading.

Conclusively, the impact properties and flexural properties of composite prepared from recycled fiber obtained from pyrolysis process showed that the recycled glass fiber obtained from pyrolysis of all composite waste at 600°C can be recycled to used as reinforcement up to 5 and 10 wt%, to improve impact strength and flexural strength of resin matrix. While the composite prepared from recycled glass fiber at 800°C showed lower mechanical properties than that of 600°C. because SEM image showed many holes in matrix. This results suggested that the fiber was pulled out during applied load. Indicating of the poor interfacial between fiber and matrix.

5.2 Recommendation

There were some problem that found in this research, which can be mention for further good studied as summarized:

- The pyrolysis system should be continuous process connected with the good flow out of evolution gases to gas analyzer. Because the generated gas during process consisted of the large a mount of oxygenated oxygen. It may cause to explode if the evolution gas are more increased in the system.

- In the step of sample feed should be applied to atomatic controlled feed with the good distribution in to the reactor. This is because of the resin matrix is thermosetting plastic that degrade and cover at the top surface if it is the batch process resulted in the evolution gas can not flow out
- The solid residues which mainly contained with glass fiber should be removed the remained resin or some carbon by oxidizing under room temperature.
- For future study, should study to sample size in order to achieve the large size that can be studied, in fact that the composite waste generated in the manufacturing process or unusable products are in the large size which it can reduce the step of preparation sample and may easier to process.

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PUBLICATIONS:

International Journal

- K. Saetiaw, D. Atong, V. Sricharoenchaikul, and D. Aht-ong, 2011. "Fuel Gases from Gasification Process of Glass Fiber /Epoxy Composite Waste", Materials Science Forum, 695, (2011): 5-8. International presentation.
- K. Saetiaw, D. Atong, V. Sricharoenchaikul, and D. Aht-ong, 2010. "Thermal Decomposition and Kinetic Study on Different Types of Glass Fiber/Unsaturated Polyester Pipe Waste", Materials Science Forum, 654-656, (2010): 2652-2655.

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