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.

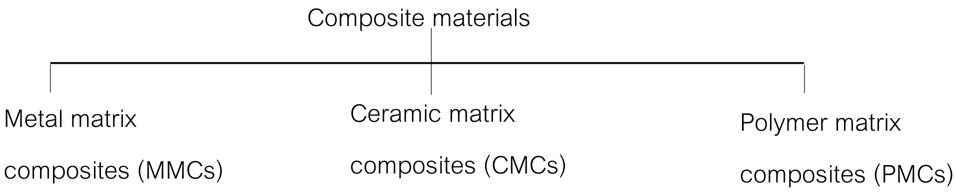


Figure 2.1 Classification of matrix composites [1].

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.

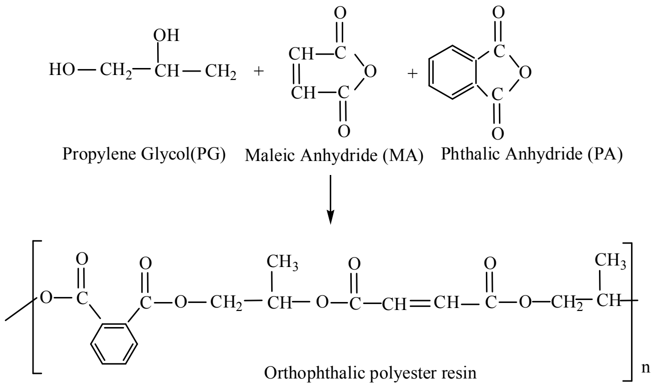


Figure 2.2 Synthesis of orthophthalic polyester resin [3].

- **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.

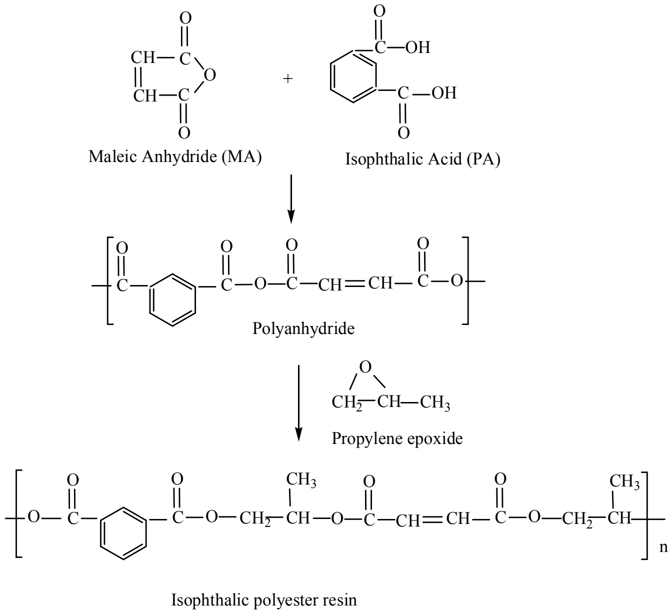


Figure 2.3 Synthesis of isophthalic polyester resin [3].

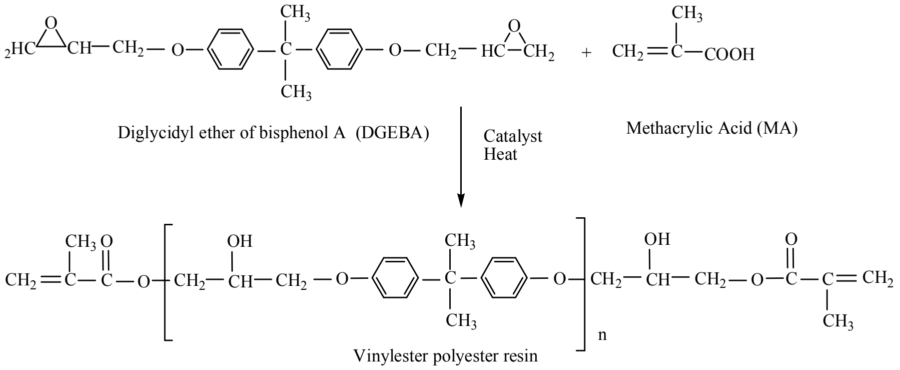


Figure 2.4 Synthesis of vinyl ester resin [3, 4]

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.

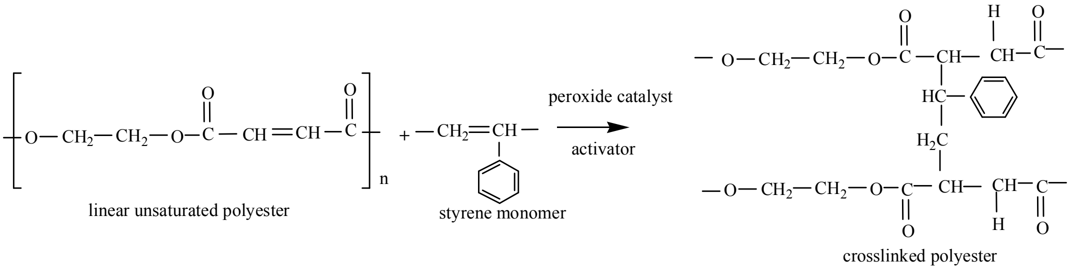
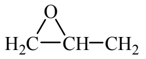


Figure 2.5 Chemical crosslinked reaction of unsaturated polyester resin [5].

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.

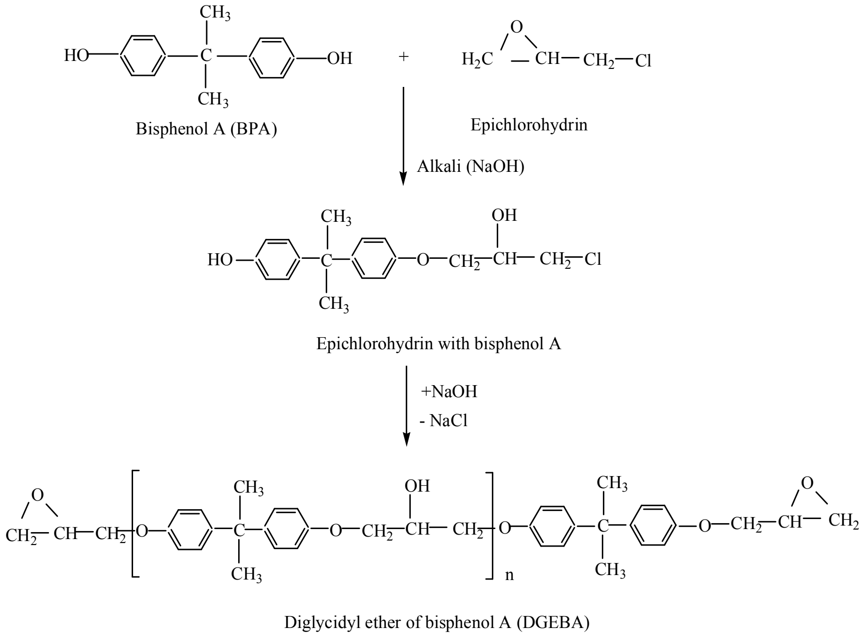


Figure 2.6 Synthesis of epoxy resin (diglycidyl ether bisphenol A;DGEPA) [6].

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.

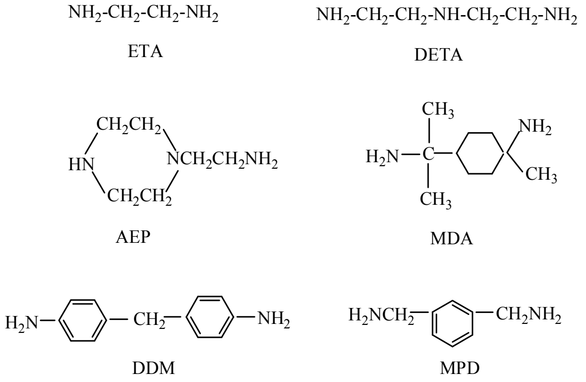


Figure 2.7 Chemical structure of amine curing agent [7].

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).

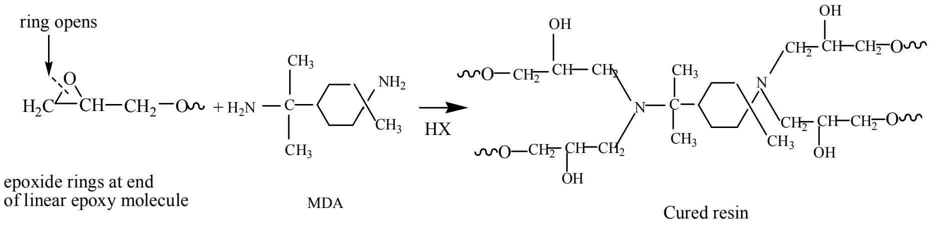


Figure 2.8 Chemical reaction of epoxy cure with MDA [7].

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.

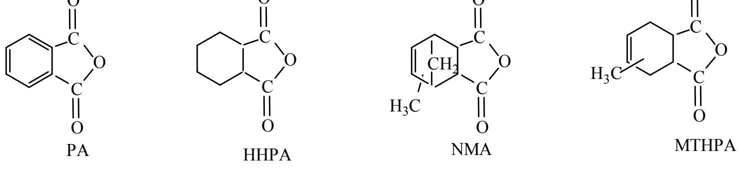


Figure 2.9 Chemical structure of anhydride curing agent [8].

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.

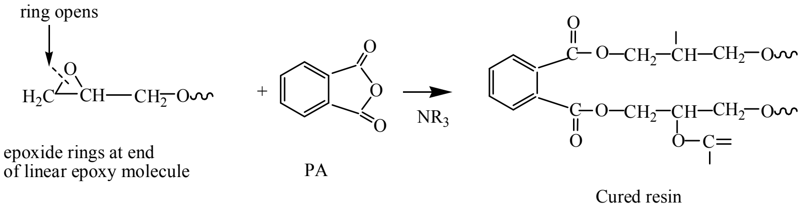


Figure 2.10 Chemical reaction of epoxy cured with PA [9].

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 1000ºC, 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 360ºC, 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

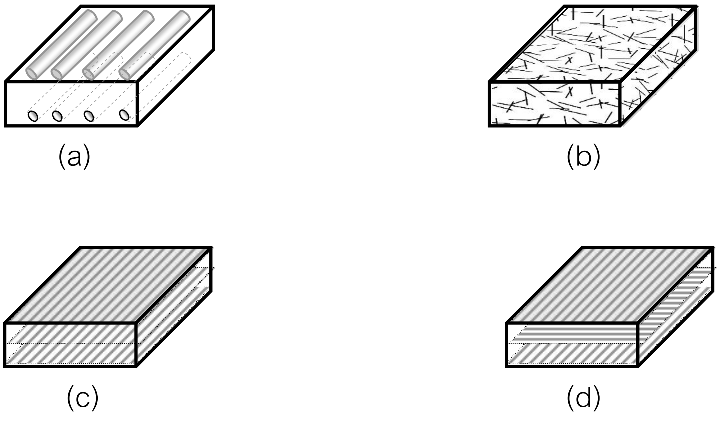
- **Carbon fibers** are manufactured from three precursors; polyacrylonitrile (PAN), pitch, and rayon. PAN, original precursor, are still popularly used as reinforcement for epoxy resins composite. They are the best reinforcement for advanced composite and engineering applications due to excellent properties 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.


(a) (b)

(c) (d)

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 70°C. 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, 600ºC, and 700 ºC 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 500ºC. 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 ºC 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 ºC 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 ºC 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 55ºC. 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]:

$$C + O_2 \rightarrow CO_2$$

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

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

$$CO_2 + C \leftrightarrow 2CO$$

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

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].