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.

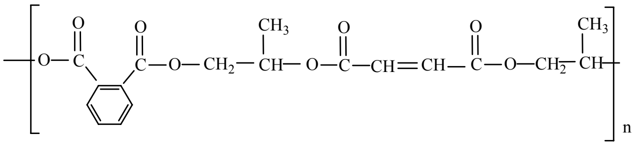
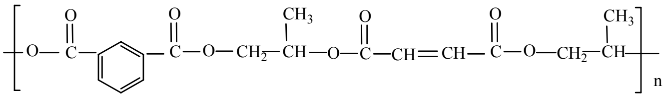
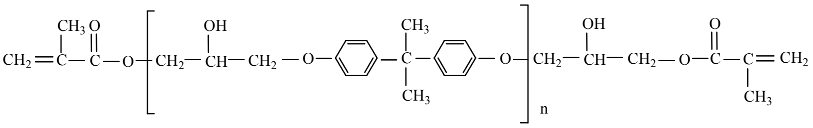
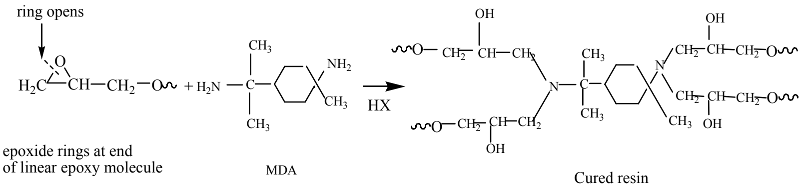
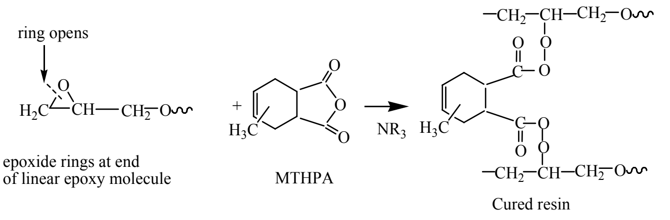
Item	Matrix system	Sample designation
Unsaturated polyester matrix system		
1.	Orthophthalic (TP910)	Ortho 30%
2.	Orthophthalic (TP910)	Ortho 60%
		
3.	Isophthalic (F046)	Iso 30%
4.	Isophthalic (F046)	Iso 60%
		
5.	Vinyl ester (Derakane 411)	Vinyl 30%
6.	Vinyl ester (Derakane 411)	Vinyl 60%
		
Epoxy 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 Titrato	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).

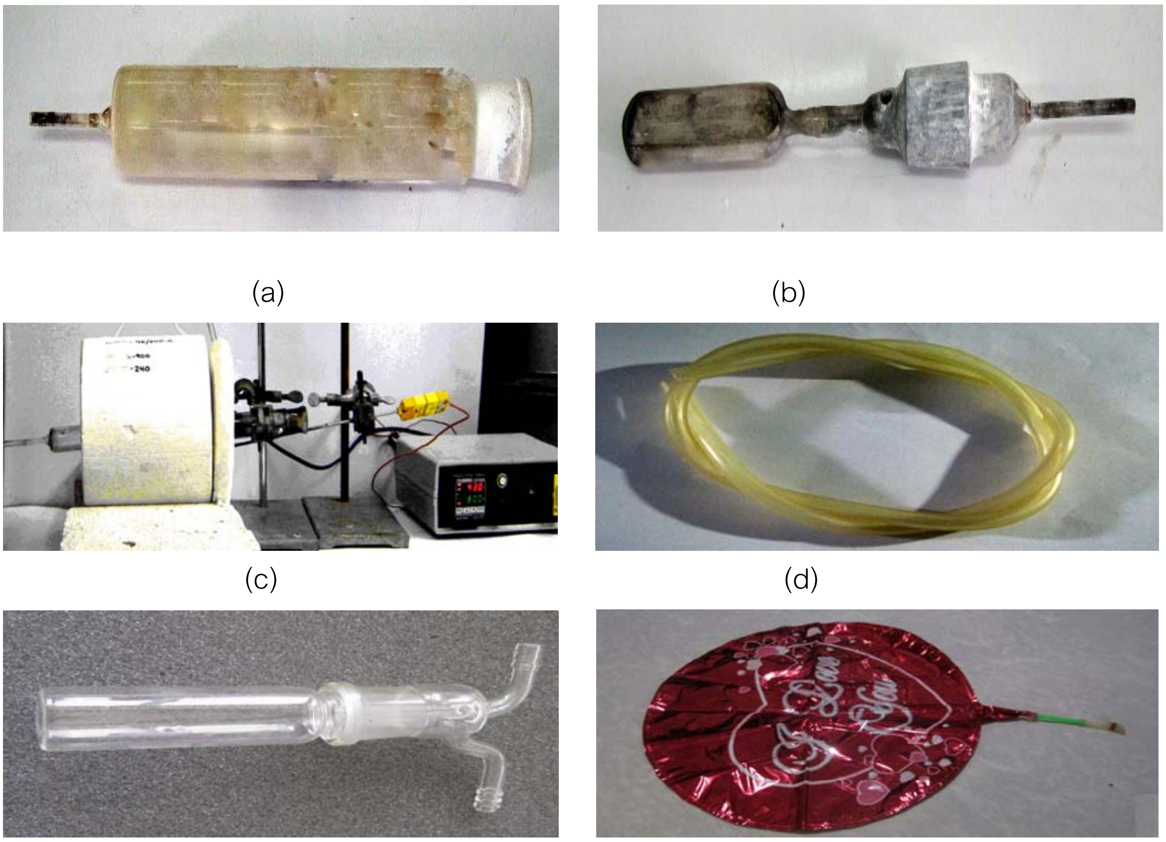
2. Quartz sample boat presented in Figure 3.1(b) was used for placing sample that will be pyrolyzed. It has 30 mm outside diameter and 300 mm long which can be placed the maximum weight of sample at 20 g per each run.

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

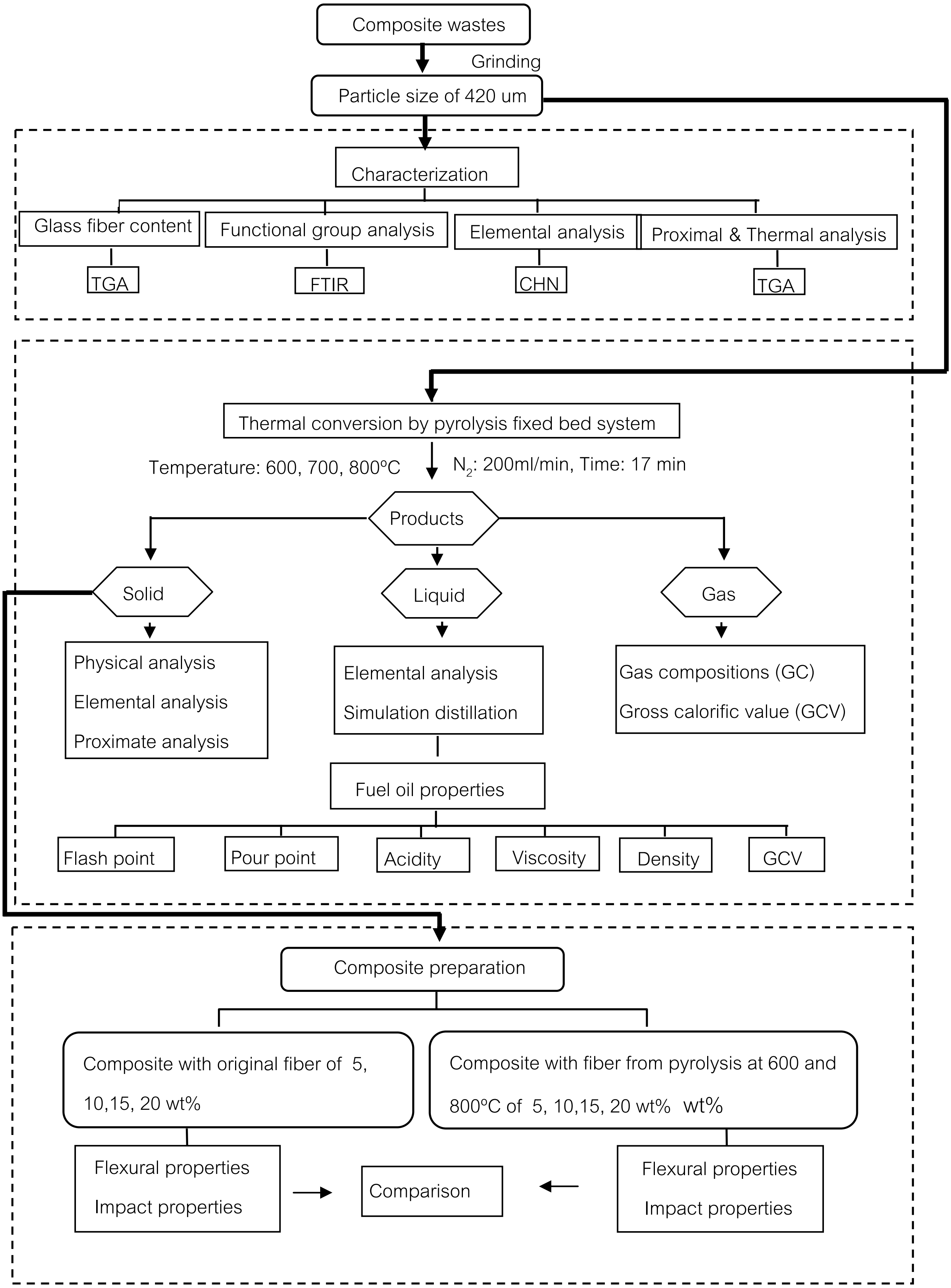


Figure 3.4 The flow chart of experimental procedure.

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.

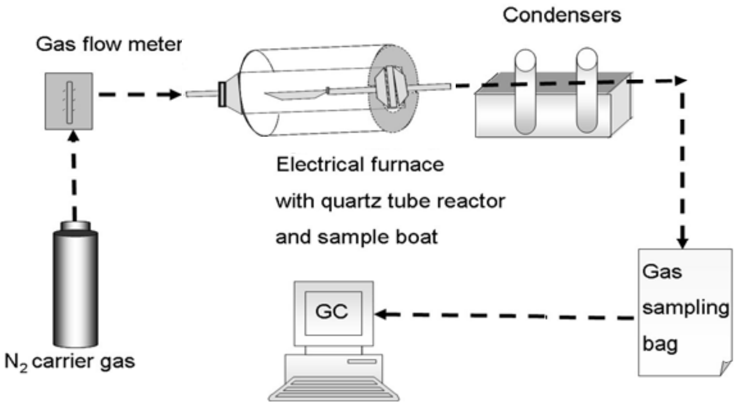


Figure 3.5 Schematic diagram of a horizontal fixed bed pyrolysis system.

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

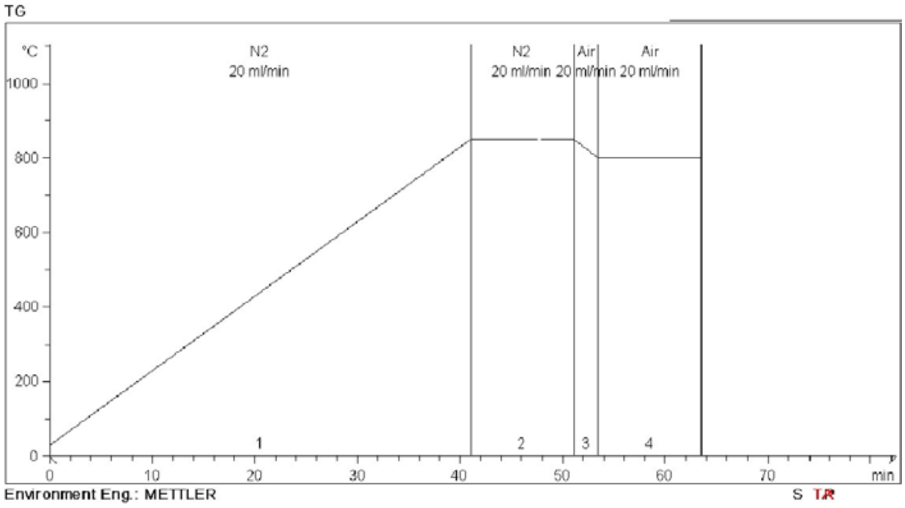


Figure 3.9 Temperature profile for proximate analysis of composite waste samples.

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 15ºC /min from an ambient to 900 ºC 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]:

$$\text{LHV (MJ/m}^3\text{)} = \frac{12.64 \times [\text{CO}] + 10.8 \times [\text{H}_2] + 35.72 \times [\text{CH}_4]}{\text{Total volume of gas (L/min)}} \tag{3.4}$$

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.