CHAPTER III

APPARATUS AND EXPERIMENT METHODS

3.1 Apparatus

1. Differential Thermal Analysis ; Shimadzu Thermal Analysis Instrument DT-30

2. Gas Chromatography ; Shimadzu GC - 7AG

3. Infrared Spectrophotometer ; Perkin Elmer 1430

4. Nuclear Magnetic Resonance Spectrophotometer ; Bruker AFC 200

5. Infrared Lamp ; Fuji Electric Type ST3

6. Microwave ; Sunyo Microwave

7. Furnace ; Thermolyne Type 47900

8. pH-Meter ; Schott CG 825

9. High Quality Color Video Microscope System ; HI-SCOPE KH-2200

10. Mylar Film

11. Flat Sash Brush

12. Laminating Roller : roller size 3/4 x 6 inch

13. Drum : size 1 foot

14. Stainless steel Vernier Caliper : Mitutoyo

15. Deep Throat Dial Hand Gauge ; Schnelltaster 0-20 mm

16. Hand Operated Shear : Handop Jorg 40 Kg/mm^2

17. Heavy Duty Vertical Band Saw : Funo 1.5 KW

18. Light-duty Right-angle Grinder : McMASTER-CARR

19. Abrasive Disc : 50 grit

20. Photometric Bench 1.5 m

21. Incandescent Standard Lamp ; Toshiba SB21101C,
    95 - 5 VAC, 377 candela, 856 K

22. Illuminance Meter ; Minolta T-1, .01-99,000 Lux or
    .001-99,000 fcd, Accuracy 2%

23. Universal Testing Machine : Instron 4505

3.2 Chemicals

1.	Acetic acid	(Analar grade, Merck)
2.	Acetone	(Analar grade, Merck)
3.	Acetone	(Commercial grade)
4.	Anhydrous sodium sulphate	(Analar grade, BDH)
5.	Bisphenol A	(Analar grade, Fluka)
6.	Chloroform	(Analar grade, J.T.Baker)
7.	Cobalt octoate 1%	(Hoechst Thai Ltd.)
8.	Ethanol	(Analar grade, J.T.Baker)
9.	Fumaric acid	(Analar grade, Fluka)
10.	Hydrochloric acid	(Analar grade, Merck)
11.	Hydroquinone	(Analar grade, Merck)
12.	Maleic anhydride	(Siam Chemical Industry Co., Ltd.)
13.	Methanol	(Analar grade, J.T.Baker)
14.	Methyl ethyl ketone peroxide	(Hoechst Thai Ltd.)
15.	Methyl methacrylate	(Hoechst Thai Ltd.)
16.	Nitrogen gas	
17.	Phenolphthalein	(RPE reagent, carlo erba)
18.	Polyethylene glycol 1500	(Union Carbide Co., Ltd.)
19.	Poly(vinyl alcohol)	(Laboratory reagent, BDH)
20.	Propylene oxide	(Laboratory reagent, Aldrich)
21.	Silicone oil	
22.	Sodium hydroxide	(Analar grade, Merck and Eka Nobel)
23.	Styrene	(Siam Chemical Industry Co., Ltd.)

24. Toluene   (Analar grade, J.T.Baker and Merck)

25. Unsaturated polyester resin used in this study is identified as "ALPOLIT VUP 9026" supplied by Hoechst Thai Ltd.

3.3 Experimental Procedures

3.3.1 Synthesis of 2,2-Bis[4-(2-hydroxypropoxy)-phenyl]propane (39)

0.308 mole (12.3 g) of sodium hydroxide solution contained in a water solution (4.0% concentration) and 14.778 mole (266 ml) of distilled water were added to a 1000 ml three-necked rounded bottom flask equipped with mechanical stirrer, thermometer and a condenser. This flask was cooled with ice water to maintain the temperature of the solution at about 25°C during the reaction. 0.384 mole (27 ml) of propylene oxide and 0.154 mole (35.1 g) of bisphenol A were gradually added to the flask. The reaction was stirred for 12 hours. Then the solution was poured into a 1000 ml separatory funnel and 100 ml of toluene was added to the solution to extract the product from this mixture (5 times). The toluene layer was washed with 100 ml of distilled water (3 times), dried with small amount of anhydrous sodium sulphate, and then evaporated in a rotary evaporator. The yield of the recovered product was 70% (37.1 g).

3.3.2 Preparation of the Chemicals Used for Testing Acid Number of the Unsaturated Polyester Resins

3.3.2.1 Solvent

A mixture of toluene and methanol with

the ratio of 1 : 1 was used.

3.3.2.2 Phenolphthalein Indicator Solution

0.5 g of phenolphthalein was dissolved in 100 ml of a mixture of equal volumes of water and ethanol. A slight excess of 0.1 N NaOH solution (pink color) was added and then the solution was neutralize (colorless) with 0.1 N HCl.

3.3.2.3 0.1 mol/l (0.1 N) Ethyl Alcoholic Potassium Hydroxide Solution

7 g of potassium hydroxide was added to 5 ml of distilled water. Then the solution was diluted with ethanol to about 1000 ml and mixed well to dissolve any solid.

3.3.3 Synthesis of Self-emulsifiable Unsaturated Polyester Resin by Using Fumaric Acid (7)

The five-necked round bottom flask 500 ml equipped with mechanical stirrer, thermometer, a nitrogen gas inlet tube and a Dean-stark trap topped by a condenser was charged with 0.484 mole (166.4 g) of 2,2-bis[4-(2-hydroxypropoxy)phenyl]-propane, 0.452 mole (52.4 g) of fumaric acid, 55.3 g (25 parts by weight per 100 parts by weight of the sum of the polyester starting materials) of polyethylene glycol number 1500 and 0.2 g of hydroquinone. The mixture was heated under nitrogen atmosphere. During the reaction, the heating temperature was started at 160°C and gradually increasing to 210°C. The reaction was stopped when an acid number of the polyester was 25. The total reaction time was about 8-10 hours.

3.3.4   Synthesis   of   Self-emulsifiable   Unsaturated
        Polyester   Resin   by   Using   Maleic   Anhydride

The five-necked round bottom flask 500 ml equipped with mechanical stirrer, thermometer, a nitrogen gas inlet tube and a Dean-stark trap topped by a condenser was charged with 0.484 mole (166.4 g) of 2,2-bis[4-(2-hydroxypropoxy)phenyl]-propane, 0.450 mole (44.1 g) of maleic anhydride, 55.3 g (25 parts by weight per 100 parts by weight of the sum of the polyester starting materials) of polyethylene glycol number 1500 and 0.2 g of hydroquinone. The mixture was heated under nitrogen atmosphere. During the reaction, the heating temperature was started at 160°C and gradually increasing to 210°C. The reaction was stopped when an acid number of the polyester was 25. The total reaction time was about 8-10 hours.

3.3.5   Testing   Acid   Number   of   the   Unsaturated
        Polyester   Resin   (40)

Weigh about 1 g to 3 g of the sample was dissolved in about 10 ml of the mixed solvent. Then the solution was titrated with 0.1 mol/l (0.1 N) ethyl alcoholic potassium hydroxide solution using the mixed indicator until the colour of the solution turned from colorless to pink color. Put the mixed solvent and the reagent were in placed a separated erlenmeyer flask in the same manner as described above, and a blank test was carried out. Calculate the acid number by the following equation.

$$acid \quad number \quad = \quad \frac{(v_1 - v_2) \times 5.61}{m}$$

where v_1 = volume of 0.1 mol/l (0.1 N) ethyl alcoholic potassium
    hydroxide solution consumed in the titration, ml

   v_2 = volume of 0.1 mol/l (0.1 N) ethyl alcoholic potassium
    hydroxide solution consumed in the blank titration, ml

  m = mass of sample, g

3.3.6 Characterization of Monomer and Polymers

3.3.6.1 Infrared (IR) Measurement

   Infrared (IR) spectra of monomer and polymer were recorded on a Perkin-Elmer Infrared Spectrophotometer model 1430. The solid chemicals were examined by using KBr method. The viscous liquid monomer and polymer were recorded at neat samples by using a NaCl cell.

3.3.6.2 Nuclear Magnetic Resonance (NMR) Measurement

   The ^{1}H NMR of monomer and polymer were taken by using Bruker Nuclear Magnetic Resonance model AFC 200. The samples were dissolved in $CDCl_3$ to make the solution of 5% concentration.

3.3.6.3 Differential Thermal Analysis (DTA)

   DTA thermograms of monomer was obtained in static air atmosphere with chart speed of 2.5 mm/min, and the sensitivity range of $\pm$ 50 μv was selected. The weight of specimens used was milligram. The reliable melting temperature and decomposition temperature of monomer was obtained.

3.3.6.4 Gas Chromatography (GC) Measurement

   GC chromatogram of monomer was recorded

by using Shimadzu Gas Chromatography model GC - 7AG. The chromatography was obtained by using column OV-1 2% under nitrogen atmosphere with a flow rate about 45 ml/min and the column temperature was held isothermally at 160°C until the monomer was eluted, then programmed to 240°C at a rate of 8°C per minute. The weight of specimens used was milligram in 5 ml ethanol.

3.3.7 Preparation of an Oil-in-water Type Emulsion of the Unsaturated Polyester Resin as Film-forming Agents

The four-necked round bottom flask 500 ml equipped with mechanical stirrer, thermometer, and a condenser was charged with 54.1 g of an unsaturated polyester resin. This flask was heated at 90°C and then added 1.6 g (3% by weight of oil phase) of special surfactant. From that 127 ml of distilled water which preheated at 90°C was slowly added in a small portion to the flask to make 30% by weight of polyester emulsion, subsequently temperature of the mixture was allow to decrease to about 60°C and then added 0.1 g of poly(vinyl alcohol) predissolved in 15 ml of distilled water into the mixture and then cooled to room temperature.

3.3.8 Preparation of Sizing Agents

In this experiment, the main formulation of sizing agent was set at the same concentration of the basic materials in glass fiber manufacturing as constant parameters as shown in Table 3.1. Only the type of film-forming agent was changed from poly(vinyl acetate) emulsion to both polyester emulsion and the concentration of each polyester emulsion was varied, i.e.,

0.5, 2.5, 3.5 and 5.0% by weight of sizing agent. In some formulation, 5.0% poly(vinyl acetate) emulsion was mixed with polyester emulsion.

Table 3.1 The recipe of sizing agent in the experiment

Materials	% by weight
- Polyester emulsion (50 wt% polyester)	0 - 5.0
- Poly(vinyl acetate) emulsion (50 wt% PVAc)	0 , 5.0
- Coupling agent	0.30
- Antistatic agent	0.20
- Lubricant	0.15
- Acetic acid	-
- Deionized Water	-

The procedure of preparation sizing agent was done as follows :

1. Hydrolyze coupling agent with acetic acid in pH range 4.0-5.0.

2. Add polyester emulsion and mix thoroughly.

3. Add poly(vinyl acetate) and mix thoroughly.

4. Dissolve lubricant in hot deionized water and add to 2. Then mix thoroughly.

5. Predissolve an antistatic agent in deionized water and add to 2. Mix thoroughly.

6. Add deionized water to this system to adjust the level of sizing agent equal with 10 litres. Mix thoroughly.

7. Adjust pH of sizing agent to about 5.0-6.0 with acetic acid.

8. Test on chopped strand mat fiber.

3.3.9 Determination of Solid Content of Sizing Agents

1. Number two of the aluminum foil dishes. Weigh the first empty dish to the nearest 0.1 mg. Record this weight as "tare".

2. Shake the sample to assure uniformity. With a medicine dropper, add approximately 5 g of sample to the aluminum foil dish. Weigh the dish to the nearest 0.1 mg. Record this weight as "initial weight".

3. Place the dish under the infrared lamp. Turn the lamp on. Leave the dish under the infrared lamp for 15 minutes.

4. Remove the dish from under the infrared lamp with the crucible tong and place it directly into the desiccator for 10 minutes.

5. Remove the dish from the desiccator and weigh it. Record the weight as "final weight".

6. Calculate the solid content using the following formula :

$$S = \frac{F - T}{I} \times 100$$

where : S = percent solid content of the sample

F = final weight of the dried sample and dish, g

T = initial weight of the sample, g

I = tare weight of the dish, g

Note : All samples were performed in duplicate. The results from the two determinations were averaged to obtain the "Percent solid". The difference in the two determinations was less than 0.05%.

3.3.10 Determination of Moisture Content and Sizing Agent Content of Glass Fibers

1. Number four of the samples which were cut from wet cake. They were tied as knot and placed on the watch glass. Each sample was weighed approximately 4 - 6 g and recorded the weight as "initial weight".

2. Place the sample in microwave at 120°C about 40 minutes. Remove the sample from microwave and place it directly into the desiccator for 10 minutes.

3. Remove the sample from the desiccator and weigh it. Record the weight as "final weight 1".

4. Calculate the moisture content using the following formula :

$$M = \frac{I - F_1}{I} \times 100$$

where : M = percent moisture content of the sample

I = initial weight of the sample, g

F_1 = final weight 1 of the dried sample in microwave, g

5. Place the same sample in furnace at 625°C about 1 hour. Remove the sample from furnace and place it directly into the desiccator for 10 minutes.

6. Remove the sample from the desiccator and

weigh it. Record the weight as "final weight 2".

       7. Calculate the sizing agent content using the following formula :

$$S = \frac{F_1 - F_2}{F_2} \times 100$$

where : S = percent sizing agent content of the sample

      F_1 = final weight 1 of the dried sample in microwave, g

      F_2 = final weight 2 of the dried sample in furnace, g

Note : The results from the four determinations were averaged to obtain the "Percent moisture" and "Percent sizing".

3.3.11 Lamination of the Glass Fibers and the Unsaturated Polyester Resin, ALPOLIT VUP 9026

      In this experiment, the main formulation of the laminates was set as constant parameters as shown in Table 3.2. Styrene and methyl methacrylate were uesd as the crosslinking agent.

Table 3.2 The recipe of the laminates in the experiment

Materials	Weight (grams)
- Chopped strand glass fiber, 2 inch length	70
- ALPOLIT VUP 9026 Resin	140
- Cobalt octoate 1%	0.14
- Methyl ethyl ketone peroxide	0.14
- Styrene or Methyl methacrylate	7

The lamination was performed as follows:

1. Cut the glass fiber for laminating in a size of 2 inch length. Weigh the glass fiber approximately 70 g.

2. Prepare the area for lamination by cutting two pieces of mylar film in size of 14 x 14 inch. Attach one piece of mylar film on smooth polycarbonate sheet by using scotch tape. Draw a square line in size of 12 x 12 inch on the mylar film surface.

3. Weigh the ALPOLIT VUP 9026 resin approximately 140 g. Add cobalt octoate solution about 0.1% by weight of the resin and 5.0% styrene respectively. Mix thoroughly.

4. Add about 0.1% methyl ethyl ketone peroxide to the resin and mix thoroughly.

5. Pour the mixed resin onto the mylar film surface and brush around area in the square line with a flat sash brush. Distribute the chopped strand glass fiber uniformly in the square line. Pour the rest mixed resin onto the glass fiber.

6. Use the laminating roller to remove the air from wet fiberglass laminate and completely saturated between the glass fiber and the resin.

7. Cover the laminate by the other mylar film.

8. Use the drum to roll on the laminate to make the smooth surface and to remove all the air bubbles from the laminates.

9. Allow the resin to cure at room temperature for about 3 hours.

10. Clean the laminating roller immediately by using acetone.

11. After 3 hours, remove the mylar film and trim off the excess laminate with the hand operated shear.

12. Repeat this procedure with changing the crosslinking agent from styrene to methyl methacrylate.

3.3.12 Transparency Testing of the Laminates

The experiment described below was based on the test methods for light transmission in the following steps :

1. Cut the specimen for testing in a size of 4.8 mm width, 6.0 mm length and approximately 1.6 mm thickness by using the heavy operated shear.

2. Set the equipment for light transmission testing as in Figure 3.1.
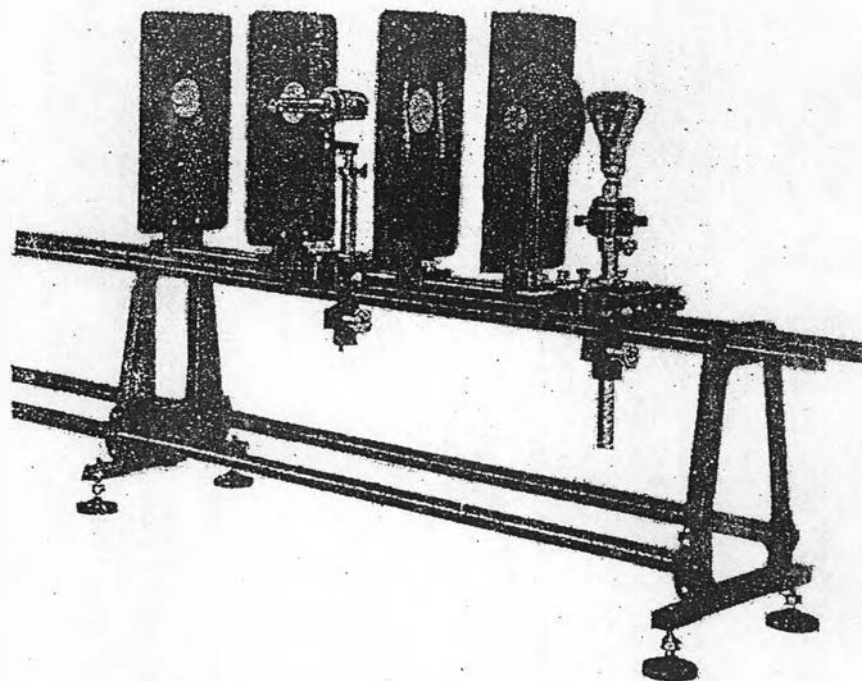
Figure 3.1 A setup of equipment for light transmission test.

3. Turn power switch of incandescent standard lamp to "on" and control voltage of this lamp at 95 volts

during this experiment.

   4. Select and set desired measuring unit of the illuminance meter in unit of Lux. Turn power switch to "on" and calibrate for zero level. Remove the cap on the light-recepter dome of the illuminance meter, record the data as "initial illuminance level".

   5. Insert the sample in sample slit. Record the data from the illuminance meter as "illuminance level of sample".

   6. Calculate the percent light transmission of sample using the following formula :

$$T = (S/L) \times 100$$

where : T = percent light transmission of sample

    S = illuminance level of sample, Lux

    L = initial illuminance level, Lux

Note : The results from the thirty determinations were averaged to obtain the "Percent light transmission".

3.3.13 Mechanical Properties Testing of the Laminates

   The experiment described below was based on the test methods of ASTM D790 (41) in the following steps :

   1. Cut the specimen for testing in a size of 2.5 mm width, 5.0 mm length, and approximately 1.6 mm thickness by using the heavy duty vertical band saw. Polish the cutting surface smoothly with an abrasive disc attached on a light-duty right-angle grinder.

   2. For a flexure test in a 3-point bending, the length of support span depends upon the thickness, in this

case the span length is 25 mm with support span-to-thickness ratios equal to 16 : 1 as shown in Figure 3.2. A test specimen was loaded via a 10 mm diameter of crosshead loading nose by using the rate of crosshead motion at 0.8 mm/min.

3. Calculate the flexural strength and flexural modulus by the following formulas :

$$S = \frac{3PL}{2bd^2}$$

$$Eb = \frac{L^3 m}{4bd^3}$$

where S = The strength of bending at midspan, MPa (N/mm^2)

Eb = The modulus of elasticity in bending, MPa (N/mm^2)

P = The load at the given point on the load-deflection curve, N

L = Support span, mm

b = The width of beam tested, mm

d = The depth of beam tested, mm

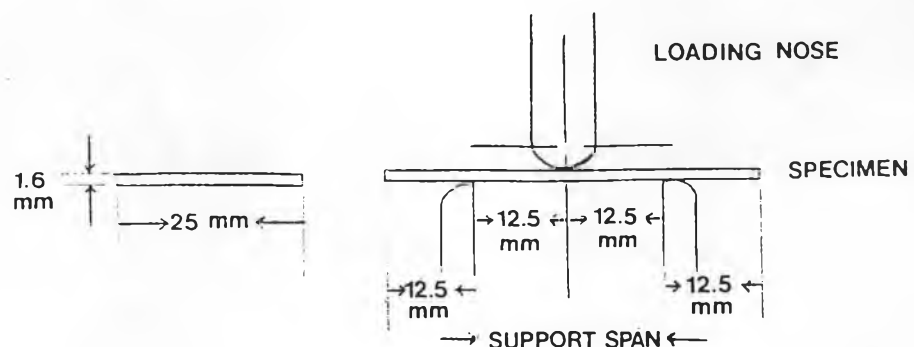m = The slope of the tangent to the initial straight-line portion of the load-deflection curve, N/m, of the deflection

Figure 3.2 A setup of load and 3 supportings for flexural test