# CHAPTER III

# EXPERIMENTAL

## 3.1 Chemical and Material

The type and source of chemicals and materials used in the experiments are shown in Table 3.1.

Experimental work was based on the use of a modified isophthalic polyester resin catalyzed with t-butyl perbenzoate (TBPB), 1,1-di-t-(butyl peroxy) cyclohexane (DTBC), to enable molding to take place at 150°C, and with benzoyl peroxide (BPO) to enable molding to take place at 120°C. The resin used was an unsaturated polyester resin (ALPOLITE UP 746) with medium reactivity. It could form sheets at high temperature and provide higher mechanical strength and heat resistant than the general purpose grade. The basic components of resin were isophthalic acid and neopentylglycol, dissolved in 42% of styrene. Some important properties of the resin are shown in Table 3.2 (18).

The filler used in the experiments was the coated fine particle calcium carbonate ($CaCO_3$) powder, treated with

stearic acid to increase compatibility with the resin. Some specifications of this filler are shown in Table 3.3 (19).

Thickener used in the experiments was magnesium oxide, light grade with the average particle size of about 2 micrometers. The magnesium oxide helps in dispersion of resinous paste.

Releasing agent used in the experiments was zinc stearate, because it can melt under the processing temperature of 150°C.

Glass fiber used in the research work was the chopped strand mat which was suitable for preparing an SMC. The length of fiber is about 25-30 mm. The weight of fiber is approximately 450 $g/m^2$. The fiber dispersed anisotropically in the sheet, therefore, there was no effect of fiber direction on mechanical property, as it dispersed in all directions.

Table 3.1

Material and source of supply used in the SMC compounding.

| Material | Chemical name | Trade name | Source of supply |
|---|---|---|---|
| Resin | Unsaturated polyester resin | Alpolite UP 746 | Hoechst Thai Co.,LTD. |
| Catalyst | Benzoyl peroxide | Benzoyl peroxide | Metha Group Co.,LTD. |
| | t-butyl perbenzoate | PERBUTYL-Z | Siam Chemical Industry CO.,LTD. |
| | 1,1-di-(t-butyl peroxy) cyclohexane | LUPEROX 331M50 | Penwalt Co.,LTD. |
| | parabenzoquinone | parabenzoquinone | Siam Chemical Industry Co.,LTD. |
| Filler | Calcium carbonate | Sila Flex | Silathip Salaburi Co.,LTD. |
| Thickener | Magnesium oxide | Magnesium oxide | SCS Xenon Co.,LTD. |
| Mold release | Zinc stearate | Zinc stearate | Gentra International Co.,LTD. |
| Wax | Mold Release Wax | High temperature wax | Phol Dhanya Co.,LTD. |
| Reinforcing | Glass fiber | Emulsion Mat 700 | Nanthavichitr Co.,LTD. |
| Film | Polyethylene film | - | - |

Table 3.2

Some physical properties of the resin, Alpolite UP 746.

| Property | Test standard | Value | Unit |
|---|---|---|---|
| Styrene content | DIN 16945 | 42 ± 2 | % |
| Viscosity at 20°C | DIN 53402 | 1,500 ± 150 | mPa-s (cp) |
| Viscosity at 23 °C | DIN 53402 | 1,250 ± 150 | mPa-s (cp) |
| Density at 20°C | DIN 51757 | 1.04 - 1.06 | $g/cm^3$ |
| Refractive index at 20°C | DIN 53491 | 1.53 - 1.55 | - |
| Storage stability under UV light at 15-25°C | | at least 6 months | |
| Machanical data of the non-reinforced polymerised resin | | | |
| Property | Test standard | Value | Unit |
| Flexural strength | DIN 53452 | 115 | $N/mm^2$ |
| Flexural modulus | DIN 53457 | 3600 | $N/mm^2$ |
| Tensile strength | DIN 53455 | 60 | $N/mm^2$ |
| Elongation | DIN 53455 | 3.8 | % |
| Impact strength | DIN 53453 | 15 | $kJ/m^2$ |
| Mechanical data of the glass fiber reinforced, polymerised resin | | | |
| Property | Test standard | Value | Unit |
| Glass fiber mat content | DIN 52330 | 30-35 | % by wt |
| Flexural strength | DIN 53452 | 200 | $N/mm^2$ |
| Flexural modulus | DIN 53457 | 10300 | $N/mm^2$ |
| Tensile strength | DIN 53455 | 120 | $N/mm^2$ |
| Elongation | DIN 53455 | 3.6 | % |
| Impact strength | DIN 53453 | 160 | $kJ/m^2$ |

Table 3.3

Some physical properties of the treated $CaCO_3$,

Sila Flex 3 CG special grade.

| Property | Unit |
|---|---|
| Average particle size | 2.0 micrometers |
| Oil absorption (DOP) | 21.0 g/100 g |
| Moisture content | 0.2 % |
| Specific Gravity | 2.7 |
| Brightness | 97.0 % |
| Stearic acid treated on the surface | 1.0 % |

## 3.2 Machine and Equipment

The machine and equipment used in this experiment were as follows :

a. Compression Molding Machine : Hydraulic press type, was constructed for this experiment, the details of which are shown in Table 3.4.

Table 3.4

The detail of compression molding machine used in the experiments.

| Description | Unit |
|---|---|
| Capacity | 65 ton |
| Table size | 30 x 45 cm |
| Stroke | 38 cm |
| Travelling Speed | 75 mm/min |
| Shut Height | 100 mm |
| Heater, automatic control | 6000 watt |
| Motor | 15 Hp |

b. Mold : The mold used in the experiment was made with the following dimension: 152.4 mm width; 254 mm length; and 4 mm thickness, installed with a heating device and a temperature controlling system with a maximum temperature at 300°C.

c. Mixer : KIKA Lab., RN 28 W, Janke & Kunkel.

d. Viscometer : Digital Brookfield Viscometer, rotating viscometer type, model HBTDV-II.

e. Infrared Spectrometer : Nicolet 205, FTIR.

f. Universal Testing Machine : Instron UTM, model 4206.

g. Scaning Electron Microscope : Model JSM.T20, JEOL Co., Japan.

h. Shore Durometers, Type A : The Shore Instrument & MFG. Co., New York.

i. Colorimeter : Micromatch 600, Instrumental Colour Systems Limited, United Kingdom.

j. Thermocouple and Digital Thermometer : DIGICON model DP-50.

k. Temperature-Controlled Silicone Oil Bath with Thermostat.

l. Thermometer.

m. Balances.

n. Vernier.

o. Stop Watch.

p. Paint Cans, Capacity of 1/4-pt., (Apporximately 5.00 cm in diameter and 6.00 cm depth).

## 3.3 Formulation for SMC

In this experiment, the main formulation was set at the concentrations of the basic materials in the SMC as constant parameters as shown in Table 3.5. Only the concentrations of each catalyst were varies either from 1 to 3 phr or the suitable quantities.

Table 3.5

The recipe of SMC in the experiment.

| Material | Concentration (phr) |
|---|---|
| Unsaturated polyester resin | 100 |
| Calcium carbonate | 40 |
| Magnesium oxide | 3 |
| Zinc stearate | 2 |
| Catalyst formulation | varies |
| Glass fiber content | 30 % by wt. |

## 3.4 Mixing Procedure and Preparation for the SMC

There were 3 steps for an SMC preparation. The first step was to prepare a paste mixing component, the second one was to prepare the SMC sheet and the last was to bring the SMC sheet to be processed in the mold. The detail of these 3 steps are shown as follows:

### 3.4.1 Paste Mixing Method

1. Weighted the Polyester resin (UP746) in a mixing container connected with a stirring rod.

2. Added the catalyst and then started to mix the mixture. Stirred for 3 to 5 minutes until they were well dispersed.

3. Added the filler ($CaCO_3$) in the mixing container and followed by mixing for about 7-10 minutes until they were well dispersed.

4. Added zinc stearate in the mixing container and mixed for about 5 minutes until zinc stearate was well dispersed.

5. Added the thickener, magnesium oxide, in the mixing container and mixed for about 5-7 minutes until magnesium oxide was well dispersed.

6. Measured and controlled the viscosity of the resin mix by a Brookfield viscometer.

### 3.4.2 SMC Sheet Preparation

1. Cut the glass fiber into a size of 6 x 10 inch and weighted six layers of the cut glass fibers in one measurement.

2. Weighted the resin paste previously mixed, in a ratio of 70 to 30 of the cut glass fibers (by weight).

3. Poured the resin paste onto a polyethylene (PE) film and then layered it with the chopped strand glass fiber mat.

4. Covered the chopped strand glass fiber mat with another piece of PE film and then kneaded the surface to eliminate entrapped airs with a roller. The glass fiber could impregnate or be wet out with the resin paste into a sheet, just similar to a sandwich form, by the mixture being placed between two layers of PE film.

5. Stored the SMC Sheet at room temperature (29°C), so as to age the SMC sheet for 3 days to 45 days in order to study the effect of shelf life of the SMC on machanical properties.

### 3.4.3 Molding Procedure

1. Set the mold temperature approximately at 150°C (149°C-153°C) and the pressure at 6900 kPa (1000 psig).

2. Cleaned the mold surface with a paint brush and treated the surface by waxing with a mold release (TR-104, High Temperature grade).

3. Cut the SMC sheet into a mold size of 6 x 10 inch, and removed the PE film from both sides of the

sheet.

4. Placed the SMC sheet in the mold and closed the mold. The curing times were set at 1 minute or 2 minutes, then opened the mold.

5. Removed the molded parts from the mold. For a typical cycle time, the molding process usually requires the followings:

| | |
|---|---|
| Loaded SMC sheet | 5 sec |
| Closed mold | 5 sec |
| Cure time | 60 sec , 120 sec |
| Opened mold | 7 sec |
| Part removal | 7 sec |
| Total time | 84 sec , 144 sec |

## 3.5 Effect of the Catalysts on Hardening Characteristics of the Resin

The different type and concentration of catalysts used in the experiment are shown in Table 3.6.

Table 3.6

Type and concentration of the catalysts on effect to hardening characteristics of the resin.

| Type | Catalyst | Concentration (phr) |
|---|---|---|
| 1 | t-butyl perbenzoate (TBPB) | 1, 2, 3 |
| 2 | 1,1-di-(t-butyl peroxy)-cyclohexane (DTBC) | 1, 2, 3 |
| 3 | benzoyl peroxide (BPO) | 0.05, 0.5, 1, 2 |
| 4 | TBPB : parabenzoquinone (PBQ) | 2.0 : 0.025 |
| | | 2.0 : 0.05 |
| 5 | TBPB : DTBC | 0.5 : 0.5 |
| | | 0.5 : 1.5 |
| | | 1.0 : 1.0 |
| | | 1.5 : 0.5 |
| 6 | TBPB : BPO | 2.0 : 0.05 |

Procedure :

1. Prepared the instrument for the experiment as shown in Figure 3.1. Set the temperature of an oil bath at 150 $\pm$ 1°C.

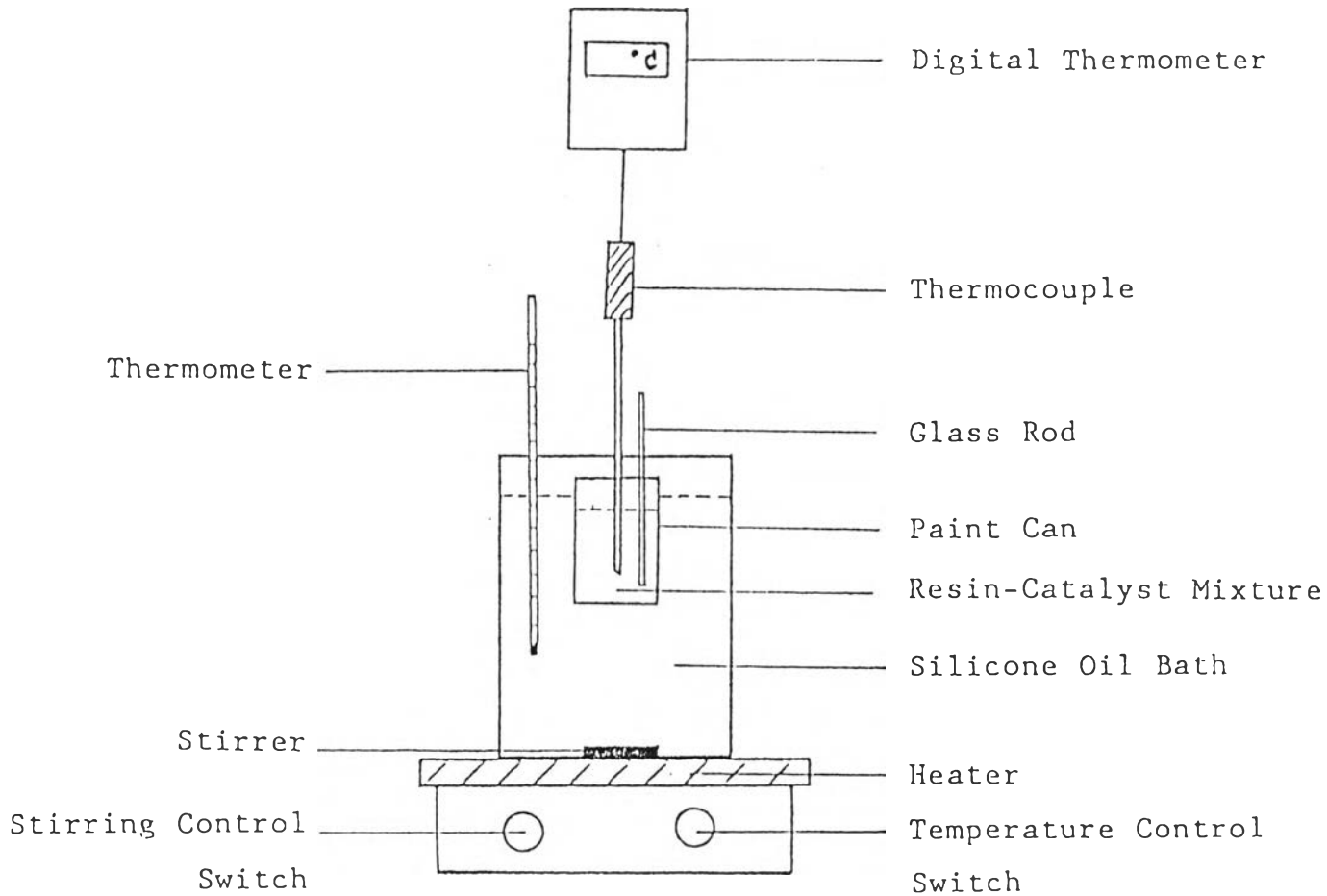



Figure 3.1 A setup of the study of the effect of catalyst on hardening characteristics of the resin.

2. Weighted 50 g of the resin on a weighing balance to the nearest 0.1 g and placed it in the sample container, a paint can of 1/4-pt capacity.

3. Added a specific amount of the catalyst, then stirred with a glass rod to make the mixture a homogeneous solution; avoiding air entrapment by slow agitation.

4. Fixed the containers firmly in the oil bath maintained at 150 $\pm$ 1°C so that the surface of the sample was at about 1 cm below the level of the surface of oil. Started the stop watch, and inserted the thermocouple in the middle of the solution.

5. Continued recording the times and temperatures until the temperature started to drop.

## 3.6 Effect of the Catalysts on Cure Reaction of the Resin

1. Mixed the resin with different types and concentrations of the catalyst, stirred until a homogeneous paste was obtained and left the mixture for 3 minutes for removing air bubbles.

2. Placed a few drops of the resin mix in a liquid cell of the FTIR spectrometer and recorded the spectra from the near IR region at 2000 $cm^{-1}$ to 400 $cm^{-1}$.

3. Cure the thin film of the resin mix in an oven at 150°C with different curing times at 1 minute and 2 minutes.

4. Prepared a specimen by grinding the film of the resin-catalyst mixture and mixing with the dried analytical KBr and pressed into a thin film which was then placed in a cell of the spectrometer. Recorded the spectra again, as in 2, from the near IR region at 2000 $cm^{-1}$ to 400 $cm^{-1}$.

5. Compared the spectra of the resin mix before and after curing; also studied the effect of different curing times.

## 3.7 Effect of the Catalysts on Viscosity Behavior of the Resin Paste

### 3.7.1 Sample Preparation

It was found that the addition of 3 phr of magnesium oxide gave too high the paste viscosity. Although it took longer time for the resin mix to become thick, it was nevertheless more convenient to handle the thinner mixture and studies of the effect of the catalysts were consequently much easier. Therefore, the concentration of 1.2 phr magnesium oxide was used instead as shown in Table 3.7.

Table 3.7

Formulation of the resin mix for the study of the effect of catalysts on viscosity behavior of the paste.

| Material | Concentration (phr) |
|---|---|
| Unsaturated polyester resin | 100 |
| Calcium carbonate | 40 |
| Magnesium oxide | 1.2 |
| Zinc stearate | 2 |
| Catalyst concentration : | |
| TBPB | 1, 2, 3 |
| DTBC | 1, 2, 3 |
| BPO | 0.5, 1 |

Procedure were as follows :

1. Prepared the resin paste according to the formulation shown in Table 3.7. Poured the paste into a plastic container, as a sample holder, of 70 mm in diameter and 90 mm in height. The level of the paste should be higher than the mark on the plunger.

2. Put the plunger of the viscometer into the resin paste in such a way that the plunger was in the

paste with the mark on the shaft of the plunger just at the top level of the paste. Let the set stand still for about five minutes at a controlled temperature of 26 $\pm$ 1°C.

3. Adjusted and set the velocity-plunger assembly to obtain an appropriate and accurate reading within the range of the viscometer, i.e., the readings were higher than scale 10 on the dial, and reset zero.

4. Let the motor run for three minutes and took the value of the reading in centipoise (mPa-s) by direct reading of the number displayed on the viscometer at the end of the third minute.

5. Measured the paste viscosity every 30 minutes for five consecutive hours and measured further the viscosity of the paste every day until the paste viscosity was higher than 64 x$10^6$ centipoises (mPa-s), the maximum reading of the viscometer.

6. Determined the relationship between time and viscosity of the paste.

## 3.8 Effect of the Catalysts on Storage Life of the SMC

### 3.8.1 Effect of Temperature on Storage Life of the SMC

1. Prepared the resin paste according to the formulation shown in Table 3.5 as that used for making two sheets of the SMC, in the absence of the catalysts.

2. Kept one sheet of the material at 28°C (ambient temperature) and kept the another sheet of material at 40°C for 1, 3, 8, 15, 22, 29, 36 and 45 days. Measured the surface hardness of the SMC accordingly by using the Shore A durometer.

3. Compared the relationship between the storage time and the surface hardness of the SMC at the both of the temperature.

### 3.8.2 Effect of Type and Concentration of the Catalysts on Storage Life of the SMC

1. Prepared the resin paste according to the formulation shown in Table 3.5 as that used for making four sheet of the SMC, in the presence of the catalysts as shown in the Table 3.8.

2. Kept one sheet of the materials at 28°C (ambient temperature) for 1, 3, 8, 15, 22, 29, 36 and 45 days. Measured the surface hardness of the SMC accordingly by using the Shore A durometer.

3. Determined the relationship between the

storage time and the surface hardness of the SMC.

Table 3.8

Type and concentration of the catalysts used in the study of the effect of catalysts on storage life of the SMC.

| Type | Catalyst | Concentration (phr) |
|---|---|---|
| 1 | t-butyl perbenzoate (TBPB) | 0.5, 1, 2, 3 |
| 2 | 1,1-di-(t-butyl peroxy)-cyclohexane (DTBC) | 0.5, 1, 2, 3 |
| 3 | benzoyl peroxide (BPO) | 0.05, 0.1, 1 |

## 3.9 Effect of the Catalysts on Mechanical Properties of the SMC

The experiments described below was based on the test methods of ASTM D790M (20).

### 3.9.1 Sample preparation

The samples used in the testings for mechanical properties of the SMC were prepared by following the recipe in Table 3.5 in which the type, and concentration of the catalysts were studied in terms of the

effect of the catalysts on curing time in conjuction with mechanical properties. Therefore, a full spectrum of parameters could be categorized as the following :-

1. Storage life of the SMC at 3, 17, 30, and 45 days.

2. Type and concentration of the catalysts as shown in Table 3.9.

3. Curing time in the mold of the SMC at 1, 2, and 3 minutes.

Table 3.9

Type and concentration of the catalysts used in the study of the effect of catalysts on mechanical strength of the SMC.

| Type | Catalyst | Concentration (phr) |
|---|---|---|
| 1 | t-butyl perbenzoate (TBPB) | 0.5, 1, 2, 3 |
| 2 | 1,1-di-(t-butyl peroxy)-cyclohexane (DTBC) | 0.5, 1, 2, 3 |
| 3 | benzoyl peroxide (BPO) | 0.1, 0.5, 0.75, 1 |
| 4 | TBPB : PBQ | 2 : 0.025 |
| 5 | DTBC : PBQ | 2 : 0.025 |
| 6 | Dual Catalyst ; TBPB : DTBC | 0.5 : 0.5 |
| | | 0.5 : 1.5 |
| | | 1.0 : 1.0 |
| | | 1.5 : 0.5 |

### 3.9.2 Testing Procedure

1. Cut the specimen for testing in a size of 10 mm width, 80 mm length, and approximately 4 mm thickness. Polished the cutting surface smoothly with a sand paper.

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 64 mm with support span-to-thickness ratios equal to 16 : 1 as shown in Figure 3.2. A test specimen was loaded via a 6 mm diameter of crosshead loading nose by using the rate of crosshead motion at 1.7 mm/min.

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

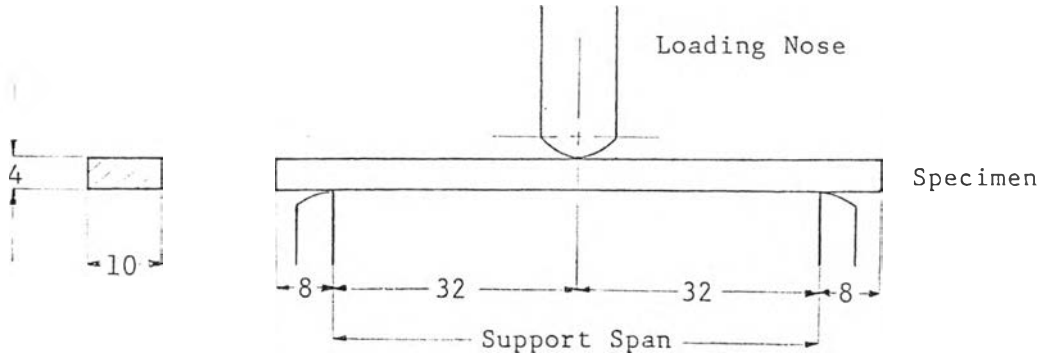
$$S = \frac{3PL}{2bd^2}$$

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

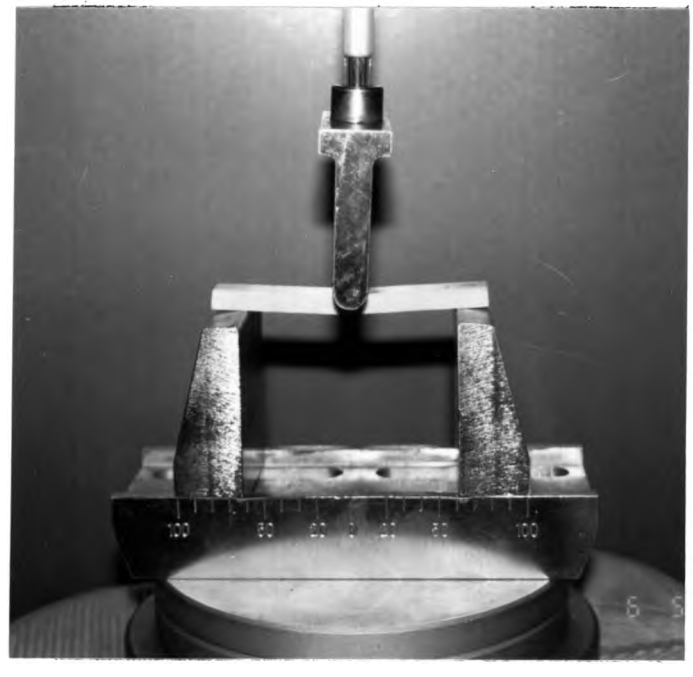
when S = The strength of bending at mid span, MPa ($N/mm^2$),

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

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




(a)



(b)

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

(a) Specimen geometry and loading, all dimensions are in mm.

(b) Flexural test setup.

L = Support span, mm,

b = The width of beam tested, mm,

d = The depth of beam tested, mm,

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

## 3.10 Effect of the Catalysts on Micromechanical Properties of the SMC

The characteristic of the interface between glass fiber and resin matrix was assessed by scanning electron microscopy (SEM).

1. Used the samples that were tested in the previous section.

2. Cut the samples cross-sectionally into a small specimen of 1 cm x 1 cm.

3. Coated the surface of specimen with gold by ion sputtering method in the Edward sputter coating device, model SCD-040, Balzers Union at an excitation voltage of 15 KV.

4. Scanned the sample and took the electron micrographs of the specimen at a 500-1000 time enlargement.