

## Chapter 3

### Materials and Methods

The materials used in the preparation of resin coated sand mixes were sand, phenolic resin as a binder, curing agent, and additive. These materials were mixed in sand mixer, which was specially designed and constructed for lab scale use.

#### 3.1. Materials

Phenolic novolac type resins from both Thai and imported producers were used, these were identified as FD-1 and PSM-6412, respectively. The curing agent used was hexamine which is a water soluble white powder. Calcium stearate which is also white powder but insoluble in water, was used as an additive. All materials were supplied by International Casting Co., Ltd. The specifications of resins (obtained from the manufacturer) are shown in Table 3.1.

Table 3.1. Specified properties of the resins used in this experiment

Properties	Thai resin (FD-1)	Imported resin (PSM6412)
Color	yellow	brown
Appearance	Granular (diameter $\approx$ 5 mm)	Granular (diameter $\approx$ 3-5 mm)
Softening point ( $^{\circ}$ C)	97	84
*Gelation time (second at 150 $^{\circ}$ C)	44	61
*Flow (mm at 125 $^{\circ}$ C)	37	48

Remark: \* Including Hexamethylenetetramine (hexamine) 15 %

The color and appearance are shown in Figure 3.1 and 3.2, respectively.

The softening point, gelation time, and flow of resin are important parameters affecting the performance of shell molds and cores. These parameters are defined as follows:

-The softening point is the temperature at which resin starts to soften. It can be observed that at the softening temperature resin particles can coalesce or change in form as well as start to flow.

-The gelation time is the time taken from the addition of the curing agent until a liquid resin changes to a gel. As shown in Table 3.1, gelation time for both Thai and imported resins are measured at 150°C, in accordance with JIS K 6909.

-Flow length of resin was determined on a heated glass plate, in accordance with JIS K 6909. The resin is compressed to tablet formation. The tablet is placed in an oven at 125°C. The plate is kept in the oven for about 3 minutes in the horizontal position. After this time, gently incline the glass plate to 30° and continue the heating for 20 minutes. The length of the flow produced is measured.

The flow length is a function of both the curing rate and the melt viscosity. If curing rate and melt viscosity are high, the flow length will be reduced. The short flow resins have a tendency to harden before they have time to form a strong bond between sand grains. The long flow resins produce higher tensile strength bonds but may contribute to peelback in the shell molds and cores. The medium flow resins have a wide range of application and are a good compromise between strength and peelback tendency. Peelback is a problem which occurs during molding when part of the partially cured mold falls away.

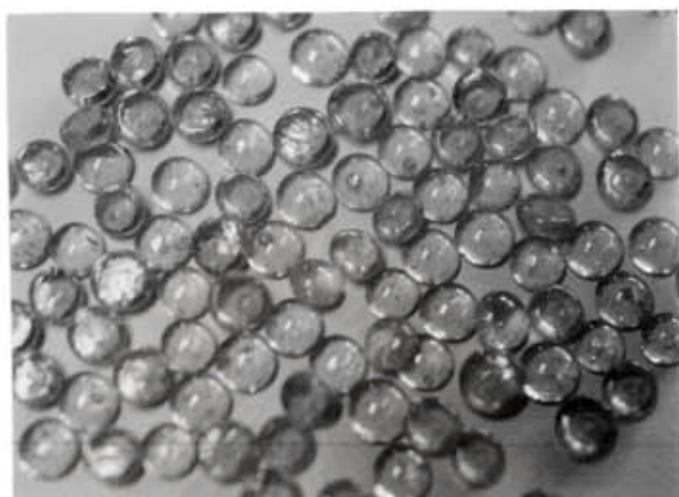


Figure 3.1 Optical microscopic examination (7.5x) of the shapes of Thai resin



Figure 3.2 Optical microscopic examination (7.5x) of the shapes of imported resin

Three types of silica sand were used in this study. These include Australian sand, Rayong (local) sand, and reclaimed sand. The reclaimed sand is in fact a mix of Australian sand and Rayong sand that has been through a reclamation process. The chemical compositions of the sands were analysed by X-ray Fluorescence Spectrometer (Fison, ARL-8410), and the physical properties of sand was determined in accordance with Mold & Core Test Handbook (American Foundrymen's Society, 1989) e.g. specific gravity, AFS grain fineness number, acid demand value, surface area, and coefficient of angularity. In addition, the sand particle morphology was examined using optical microscope.

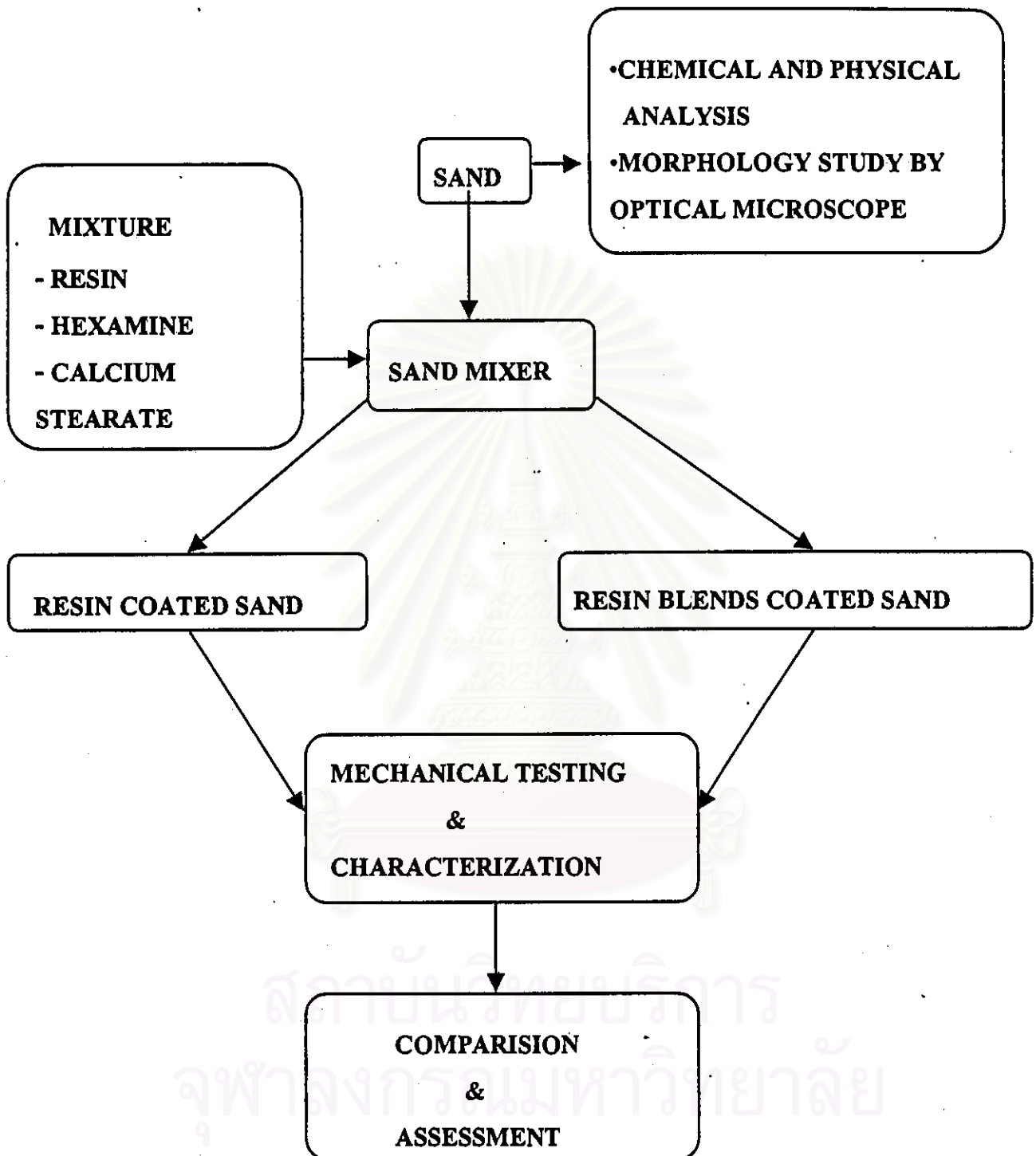
### **3.2. Sample Preparation**

Flow chart of the experimental approaches used in this study is shown in Figure 3.3.

#### **3.2.1. Sand Mixer**

The sand mixer was used to mix materials of sand, resin, curing agent and additive for producing resin coated sand. The function of a "sand mixer" is to distribute the bonding media around the sand grains (Parkes, 1970). The small scale sand mixer used in this study is shown in Figure 3.4. This mixer was required to produce small sized mixes suitable for research. The criteria considered in design and construction of this mixer were simplicity, low cost, efficiency, and reproducibility of mixes.

The sand mixer basically consists of four major components: 1) impeller, 2) motor, 3) chamber, and 4) air pressure pump, as illustrated in Figure 3.5.



**FIGURE 3.3** Flow chart of experimental approach

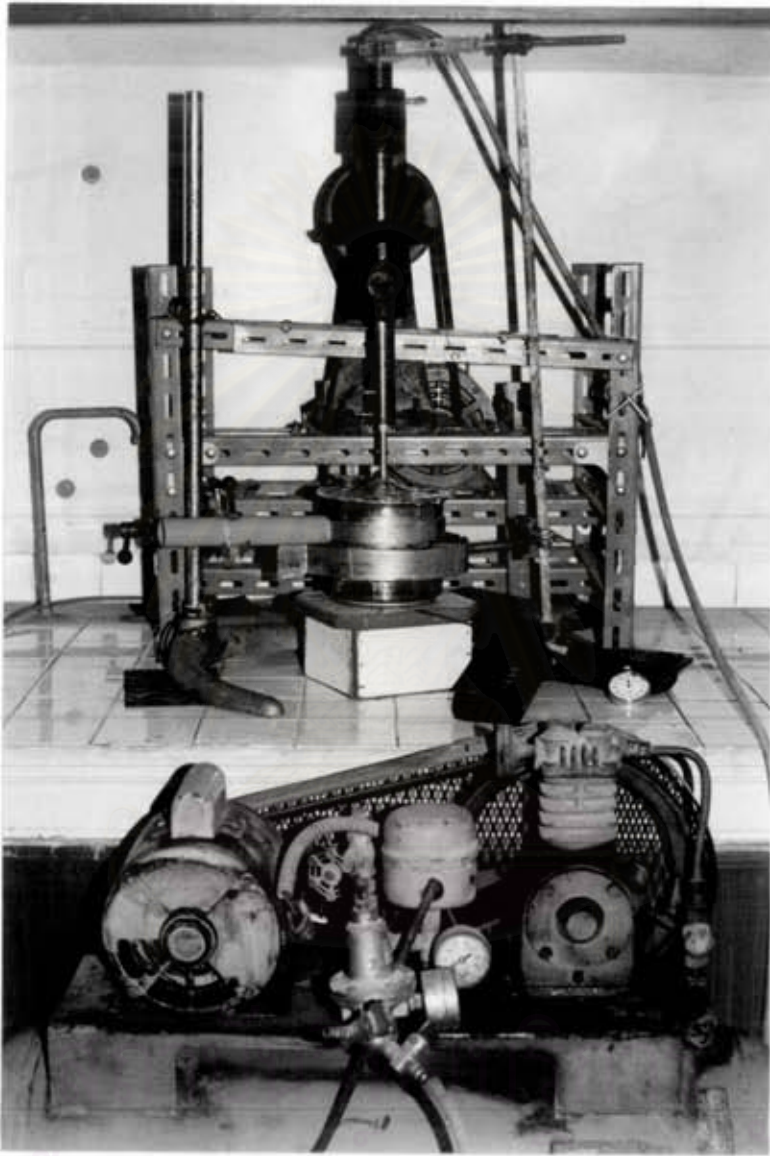


Figure 3.4 Small scale sand mixture



Figure 3.5 Four-blade paddles in axial turbine (scale 1:2)

An impeller has four-blade paddles set at  $45^\circ$  in axial turbine shape that are attached to a rotating shaft. This impeller has two vertical scrapers to help ensure stir the mix that climbs over the blade. An overall stirring or churning action should give rise to uniform mixing. The impeller has two vertical scrapers to help ensure stir the mix that climbs over the blade. The central shaft is hollow with an air inlet at the top and air outlet at the bottom of the shaft. As shown in Figure 3.5, a few small holes of about 2 mm in diameter (air outlet) locate at the end of the shaft. Air travels through the hollow shaft and is blown into the mixture to ensure air distribution. This air also carries out the water evaporates off and serves to cool and reduce the temperature of the coated sands so that resin is harden.

With regard to a motor of the mixer, it should be noted that this type of mixer should use a high power/torque motor. Since the resin melts partially during mixing and the mass in the mixer becomes very sticky, this increases the resistance to the moving action of the impeller. Moreover, when hexamine is added into the mixture, the resin is partially cured causing an increase in viscosity. Thus, the mixer needs to be able to overcome these effects and hence provide high quality consistent mixes in reasonably short mix times (Dietsche, 1998).

This mixer was designed to mix batches of approximately 300 g capacity. The diameters of the chamber and impeller were about 14 cm and 13.6 cm, respectively. The air pressure used was  $1 \text{ kg/cm}^2$ . The impeller was driven by a 1 hp motor and had a speed of 250 rpm.



### 3.2.2 Resin Coated Sand Procedure

A foundry plant, in Thailand, uses various formulas depending upon types of metals and casting product required, as shown in Table 3.2.

Table 3.2 A summarized various formulas for resin coated sand

Resin content, %	Type of resin	Type of sand	Applications
1.7	Thai resin	Australian sand	Core
2.1	Thai resin	Australian sand	Core
2.4	Thai resin	Australian sand	Core
3.2	Thai resin	Reclaimed sand	Mold for aluminum casting
2.7	Import resin	Reclaimed sand	Mold for iron casting
4.3	Import resin	Rayong sand	Mold for iron casting

These formulas used hexamine of 15% and 17% by weight for imported resin and Thai resin, respectively. In the case of Thai resin formula, calcium stearate of 0.125% by weight of sand was added, whereas calcium stearate of 0.2% by weight was used for imported resin. Each formula contained approximately 3% water by weight. In general, hexamine was added with water as a solution. Resin coated sand or sand-binder composite was produced as follows:

- 1) Weigh sand of 300 g in an alumina crucible was heated in the furnace at the temperature of 300°C for 30 minutes.
- 2) Heated sand was transferred into the mixer chamber and then stirred in the mixer until the temperature of sand was approximately 125-135°C.

- 3) Resin was added and mixed with the sand for 60 seconds.
- 4) The hexamine solution was added and the mixing action continued for 110 seconds when Thai resin was used and for 130 seconds in the case of imported resin. After the addition of hexamine solution, air was blown rapidly (in order to protect the agglomeration of mixture) into mixture to reduce the temperature and accelerate the water evaporation until the sand was dried. The air pressure used was  $1 \text{ kg/cm}^2$  at room temperature.
- 5) Calcium stearate was added immediately and mixed for 30 seconds.
- 6) The coated sand was discharged (measured sand temperature was about  $75^\circ\text{C}$ ) and screened size to achieve a complete of agglomerates coated sand to give free flowing sand.

### 3.2.3 Resin Blends Coated Sand

Apart from single resin formulations, blends of both Thai and imported resins were produced to prepare resin coated sands following the procedure detailed in previous section.

In the case of resin blends, two specific formulas with the resin content of 2.7% and 4.3% by weight were prepared (see Table 3.2). Thai resin and imported resin were blended with Thai resin content varying from 20, 40, 60, 80 and 100 by weight percent. The sands used were reclaimed and Rayong sand. Hexamine and calcium stearate used were 16% by weight of resin and 0.16% by weight of sand, respectively. Water of 3% by weight of sand was added.

### **3.3. Mechanical Testing**

#### **3.3.1. Specimen Preparation for Bend test**

The bend test specimens were prepared by specimen forming equipment, as shown in Figure 3.6. This equipment consists of the hopper, curing block, and thermostat. This block is a split pattern (75 x 150 mm size) having five cavities for five specimens preparation. A specimen has a square cross section 10 x 10 mm and length 60 mm. The specimen was made by feeding the resin coated sand into the hopper. Sand was then placed into the cavity pattern of the curing block whose temperature was set at  $250 \pm 10^\circ\text{C}$ . Sand was cured in the cavities for 90 seconds. The excess was removed from the pattern. When the specimens were completely cured, they were taken from the pattern and then cooled to room temperature before testing.



Figure 3.6 A specimen forming equipment for bend test

### 3.3.2 Bend Test

Bend testing was performed in accordance with ASTM D 790, using a bend tester with 100 Kgf load capacity and loading speed of 5 mm/min. Figure 3.7 illustrates a three point bending test set-up used in this study. The span for bend test is 50 mm. In this test, the specimen was symmetrically placed on two supports and the force was applied at midspan until fracture. The force applied to the specimen was recorded. The mean value of bending strength and standard deviation were calculated from five repeat tests. This was applied as a procedure for reproducibility tests. The dimension of specimens was also measured prior to testing. If the break or crack occurred outside the central region of the specimen, the measurement was discarded and retest was made. Note that the central region of the specimen was specified by dividing the specimen (before test) into three equal lengths.

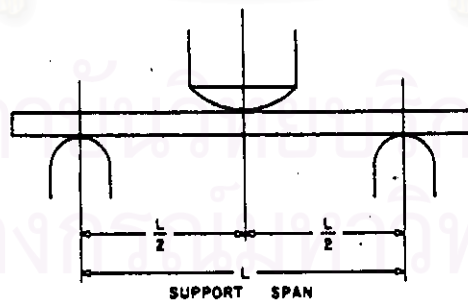


Figure 3.7 The three-point loading system

### **3.4 Characterization Techniques**

#### **3.4.1 Microscopy**

Morphologies of and fracture surface of resin-bonded sand were determined using a scanning electron microscope (JEOL/JSM-6301F). The fracture surfaces were obtained after bending test. The specimen was (lightly) coated with gold for enhanced surface conductivity to avoid charging in the electron beam. Fractured specimens were sputter coated with gold using a Fine coater (JEOL/JFC-1200) at 15 mA for 180 seconds.

#### **3.4.2 Melting Point Apparatus**

Melting point of resin was measured by Mettler (FP 90) apparatus. The sample put into a capillary tube was heated from 40°C to 110°C at the heating rates of 2°C /min, in accordance with DIN 16916 part 2. Results were analyzed using the software provided in the apparatus.

#### **3.4.3. Differential Scanning Calorimetry (DSC)**

Thermal behavior of the as-received resin was investigated by DSC. In DSC, the characteristic thermal transitions (i.e., the glass transition temperature,  $T_g$ ) of the resin sample was determined. Sample was scanned on a Perkin-Elmer DSC 7. Approximately 7-8 mg of powdered resin was put in a small aluminum pan and heated from 30 to 250°C at the heating rates of 10°C/min under nitrogen atmosphere. Resulting thermogram was collected continuously and analyzed using the software provided in the instrument.

#### **3.4.4. Thermogravimetric analysis (TGA)**

TGA studies was carried out on as-received resin to obtain information on the weight loss and on the thermal stability as a function of increasing temperature over a period of time. This was achieved by using TGA (Perkin-Elmer TGA 7). Approximately 5 mg of sample was heated from 50 to 800°C at heating rates of 20°C/min in a nitrogen atmosphere. Data was recorded as a thermogram of weight versus temperature and analysed by software provided in the instrument.

#### **3.4.5. Gel Permeation Chromatography (GPC)**

Molecular weight is an extremely important characteristic because it relates directly to a chemical structure of resin. The GPC technique is used to determine the molecular weight distribution, number-average and weight-average molecular weight of resin. This information can be used to compare the characteristics and properties of Thai resin with imported resin.

Size exclusion chromatography used in investigation was the GPC model Waters 150 CV was equipped with the styragel Mixed B columns and two detectors (i.e., a refractive index detector and a viscometer). The molecular weight resolving range of the columns is between  $5 \times 10^2$  and  $1 \times 10^7$ . The columns were calibrated with polystyrene standards. Resin samples were dissolved in tetrahydrofuran (THF) solvent. The concentration of resin in THF was  $\approx 0.3\%$  w/v. THF was used as an eluent at a flow rate 1.0 ml/min, at 30°C.

### 3.4.6 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR can be used to identify resin isomers. Since hydrogen atoms of the methylene bridges are in different environments, depending on whether the methylene is ortho or para to the phenolic hydroxyl groups. Based on the use of  $^{13}\text{C}$ -NMR relative peak intensity ratios for different characteristic chemical groups contribute to novolac resin isomers. The  $^{13}\text{C}$  nuclei range is much greater at least 200 ppm, which is the greater resolution of peaks and finer discrimination of structural features of polymer chains. While the total range of proton chemical shifts in organic compounds is on the order of 10 ppm. This is the principal reason for the great interest in the study of polymers by  $^{13}\text{C}$ -NMR. Thus, NMR peaks obtained can be identified as the *o,o'*, *o,p'*, and *p,p'* isomers. Chemical structures of these three isomers are shown in Figure 3.8. The area under the peaks can be measured by integration. The overall results provide information of a ratio of the three isomers. Structure and property comparison can then be made between Thai and imported resins.

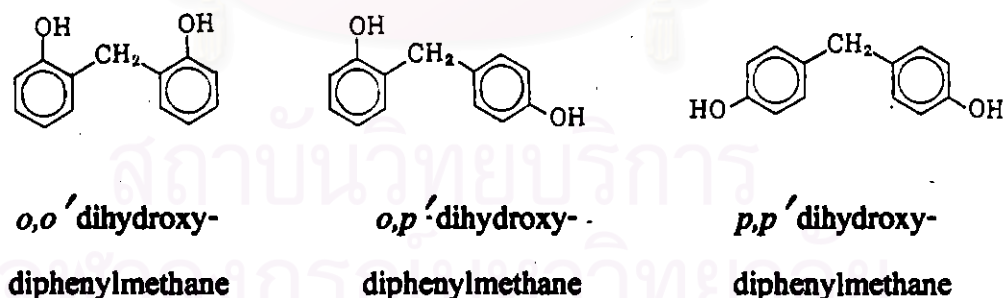


Figure 3.8 Chemical structures of three isomer of dihydroxydiphenylmethane



As an example, Figure 3.9 shows three peaks resulting from a test of a crude dihydroxydiphenylmethane using proton magnetic resonance. The integral curve gives a ratio of the three isomers of this resin 18:52:30 which is a normal ratio for an acid-catalyst novolac (Keutgen, 1969)

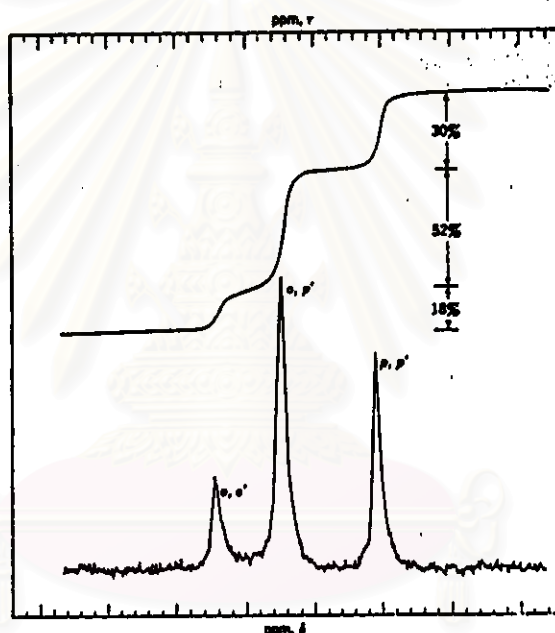


Figure 3.9 Portion of proton magnetic resonance spectrum of crude dihydroxydiphenylmethane

The  $^{13}\text{C}$ -NMR spectrum of the liquid resins was obtained on a Bruker DPX-300 FT-NMR spectrometer with frequency of 300 MHz. Samples were dissolved in deuterated methyl alcohol (MeOD).

### 3.4.7 Stick Point (Fusion Point or Melting point)

These terms are used interchangeably and refer to heat sensitivity of the resin coated sands. Stick point indicates the lowest temperature at which the resin becomes soft enough to adhere to itself or other surfaces.

An equipment for stick point determination has fifteen thermometers. A temperature gradient is established so that the thermometer at left end ( $110^{\circ}\text{C}$ ) is hotter than the right end ( $70^{\circ}\text{C}$ ), see Figure 3.10. In this test, resin coated sand was applied to the test base with a size of 45 mm wide x 450 mm long. The sample was allowed to dwell for 60 sec and then the air pressure  $1 \text{ kg/cm}^2$  was blown on test base. At the point where the sand resists blowing off, the temperature at this point was recorded from thermometer as "stick point".

### 3.4.8 Thermal expansion coefficient

The thermal expansion coefficient of the sand was measured by means of a Adamel Lhomargy DI-24 Dilatometer in which the heating rate of  $10^{\circ}\text{C}$  per minute was used.

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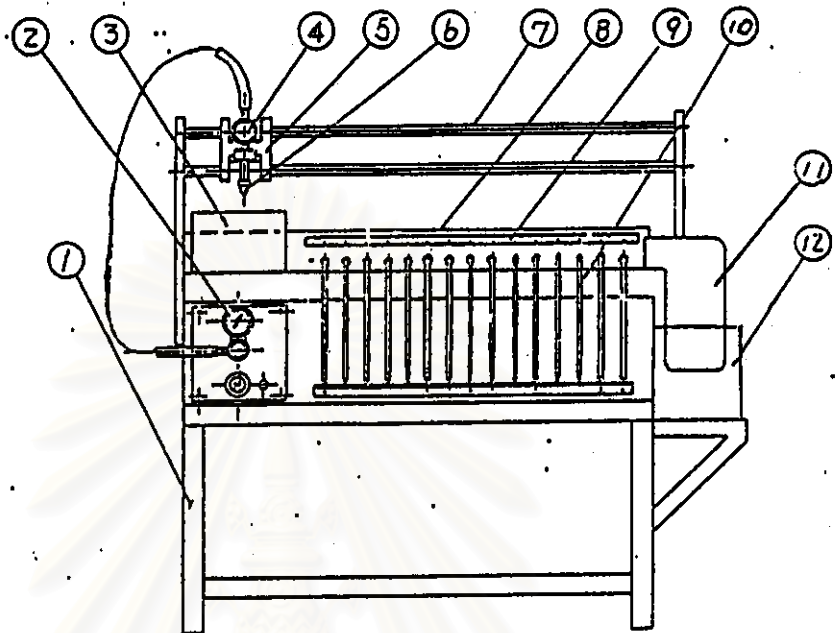


Figure 3.10 A equipment for stick point determination

- |                 |                 |
|-----------------|-----------------|
| 1. Frame        | 7. Guide rail   |
| 2. Regulator    | 8. Test base    |
| 3. Heater       | 9. Scales       |
| 4. Stop valve   | 10. Thermometer |
| 5. Sliding head | 11. Fin         |
| 6. Nozzle       | 12. Water bath  |