CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

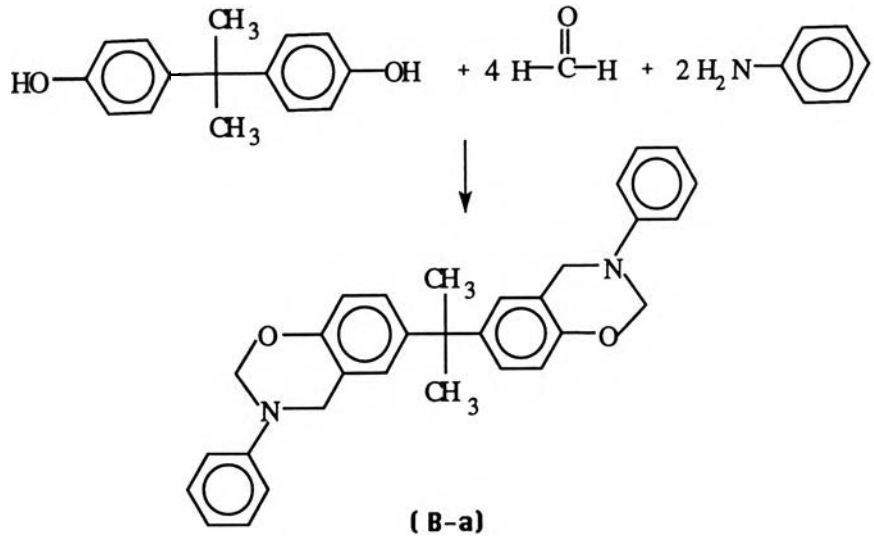
Bisphenol-A and paraformaldehyde were purchased from Aldrich Chemical company. Aniline was produced by Ajex Chemical. All chemicals were used without further purification.

Calcium carbonate used was an Omya product obtained from Surint Omya Chemicals (Thailand) company. There were 2 types of calcium carbonate whose surface is either untreated or treated with stearic acid. The average particle size of the treated calcium carbonate was 5 mm, whereas the mean particle sizes of the untreated grade were determined to be 1, 5, and 20 mm.

Phenol-formaldehyde oligomer of novolac type was provided by courtesy of Polymer Engineering company.

2.2 Benzoxazine Synthesis

Benzoxazine based on bisphenol-A and aniline, abbreviated as B-a, was synthesized through the Mannich reaction according to scheme I:



Scheme I Synthesis of B-a

A detailed description of the synthesis procedures and molecular characterization was presented elsewhere (X.Ning et al., 1994).

2.3 Sample Preparation

Calcium carbonate (0 - 30 wt.%) was dispersed in B-a by mechanically stirring at 110 °C for 15 min. Then the mixture was precured in an oven at 125 °C for 30 min followed by 150 °C for 30 min. After that, the precured sample was compressed in a frame plate at 175 °C for 30 min, 190 °C for 30 min, and finally at 200 °C for 1 hr. The sample was cut in appropriate sizes as described in the following section for mechanical property measurements.

Benzoxazine (B-a) and phenolic oligomers were melted in vacuum oven for 0.5 hr. at 100°C and for 0.5 hr. at 170°C, respectively, to eliminate the bubbles. This sample was then placed between parallel plates for viscosity measurements.

2.4 Measurements

The statically mechanical properties of the cured B-a resin filled with calcium carbonate were measured by the following methods;

2.4.1 Flexural Testing

The flexural properties were measured by an Instron Universal Testing Machine (Model 4206) according to the ASTM D790-91 test procedure. Eight specimens with the dimension of 50 x 25 x 1.7 mm were tested for each composition. The sample were flexed until breakage occurred at a rate of 0.8 mm/min in a three point loading with a 25 mm support span. The flexural modulus (E_f) and flexural strength (σ_f) were calculated from the following equations:

$$E_f = \frac{S^3}{4B \cdot W^2} m$$

$$\sigma_f = \frac{3P_c \cdot S}{2W \cdot B^2}$$

where S is the length of the support span, B is the specimen thickness, W is the specimen width, m is the slope of the tangent to the initial straight-line portion of the load-time curve, and P_c is the load at break of specimen.

2.4.2 Tensile Testing

Tensile properties were measured by an Instron Univeral Testing Machine (Model 4206) according to the ASTM 638-91 test

procedure at a crosshead speed of 3 mm/min. At least 7 dumbell specimens with the dimension of 150 x 10 x 1.7 mm were tested for each composition. The tensile modulus (E_t) and tensile strength (σ_t) were calculated from the following equations:

$$E_t = \frac{P/A}{\Delta L/L_0}$$

$$\sigma_t = \frac{P_C}{A}$$

where $P/\Delta L/L_o$ is a slope of the tangent to the initial straight-line portion of the load-displacement curve, and A is the cross-sectional area of the dumbell specimen.

2.4.3 Izod Impact Testing

Izod impact strength values were estimated on V-notched samples on a Zwick Instrument according to the ASTM D 256-90b test procedure. The size of test specimens was 3.5 x 12.7 x 62 mm. Each sample was machined across its thinnest dimension (3.5 mm) to produce a V-notch with a 45 degree angle.

2.4.4 Dynamic Mechanical Measurement

Dynamic mechanical spectra were obtained on a Rheometric Dynamic Mechanical Spectrometer (RMS-800) equipped with a 2000 g-cm force rebalance transducer. Specimens with the dimension of approximately 42 x 12 x 1.7 mm were tested in a rectangular torsion fixture. A maximum strain of 0.13% was applied sinusoidally after a strain sweep performed to

assure that the applied strain was within the linear viscoelastic limit. The test frequency was 1 Hz (6.28 rad/sec) for temperature sweep tests. A frequency range between 0.628-62.8 rad/sec was applied to the temperature/frequency sweep tests to obtain the activation enthalpy of the glass transitions. Measurements were made at 2 ℃ intervals as the samples were heated at a rate of approximatly 2 ℃/min from 28 ℃ to above the glass transition of the material. Samples were provided with a thermal soak time of 45 seconds for each step in temperature.

2.4.5 Shear Viscosity Measurement

Measurement for steady shear viscosity were conducted on a Rheometric Dynamic Mechanical Spectrometer (RMS-800) using a 25 mm parallel plate fixture. The gap between plates was set at 1.0 mm. The plates were preheated to the desired temperature for 15 min before the gap was adjusted to zero for reference. The measurements were recorded in a shear rate from 0.1 to 100 sec^{-1} and a strain of 0.12%. The experiments were carried out from 80 to 150℃ for benzoxazine and from 110 to 170℃ for phenol-formaldehyde oligomer at 10℃ interval.