

CHAPTER II

METHODOLOGY

2.1 Materials

Bisphenol-A (Commercial grade) was provided by courtesy of Siam Chemical Industry (Thailand). The paper 4A2162012-4, a Kimberly-Clark product supplied by courtesy of Kimberly-Clark Company (US), was used as received without any additional modification.

Formaldehyde aqueous solution (37%) (AR grade) and anhydrous diethylether (AR grade) were supplied by J.T. Baker Company. Paraformaldehyde (AR grade) was produced by Sigma Chemical Company. Aniline (99.5%) and 1,4-dioxane (AR grade) were purchased from Ajax Chemical Company. Sodium hydroxide (>99.0%) was purchased from Eka Nobel Company. Methylamine aqueous solution (40%) and sodium sulfate (anhydrous) were obtained from Fluka Chemika Company.

All chemicals were used without further purification.

2.2 Instruments and Equipment

2.2.1 Compression Molding Machine

The 30 ton Carver Compression Molder was used for paper reinforced composite with varied soaking time of the paper in molten benzoxazine resin.

The step curing process for this study is ; 120°C without pressure for various soaking times, 150°C with 2,500 psi pressure for 60 min, 175°C with 5,000 psi pressure for 60 min, and 190°C with 7,500 psi for 2 hours. The mold used in this work is a stainless steel mold coated with chromium and was cut into sheet sizes of 165mm×130mm×1.6mm.

2.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained on a FT-45A Bio-Rad Spectrometer with 64 scans at a resolution of 4 cm⁻¹. A frequency range of 4000-400 cm⁻¹ was observed using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D*, of 1×10⁹ cm. Hz^{1/2} W⁻¹.

2.2.3 Density Determination Kit

The density measurement was done with Sartorius YDK 01, YDK 01-0 D, the Density Determination Kit. The kit is composed of the 5 decimals balance equipped with beaker and sample holder and thermometer. The solid samples were immersed in the distilled water. The beaker which contained distilled water was kept constant at 23°C. Three bubble-free specimens were used for each test and the average specific gravity and density were reported.

2.2.4 Flexural Testing Machine

Flexural properties were performed on the Instron Universal Testing Machine, model 4206. In this work the instrument was used in three point loading fixture equipped with 5 kN load cell for flexural test. The support span was set to 25 mm while the crosshead speed was 0.8 mm/min. The

temperature and humidity were set at 23°C and 50% humidity, respectively. Six specimens were tested for each condition and the average value of flexural modulus, stress, and % strain at break were reported.

2.2.5 Dynamic Mechanical Spectrometer

Dynamic mechanical measurements were made with a Rheometric Dynamic Mechanical Spectrometer (RMS-800) equipped with 2000 g-cm force rebalance transducer. Dynamic mechanical mode was applied in this test. All tests were done in a rectangular torsion fixture. The sinusoidal strain of 0.1 % was applied after a strain sweep was performed to assure that the applied strain was in the linear viscoelastic region. The test frequency was controlled at 1 Hz, equivalent to 6.28 rad/sec.

2.2.6 Scanning Electron Microscope (SEM)

SEM digitized photographs were obtained from JEOL 5200 - 2AE (MP15152001), with a magnification range of 35-200,000 times. The surface and fiber/matrix interfacial pictures of benzoxazine paper composites were collected using a voltage of 10 kV and 100-200 times magnification.

2.3 Experimental Procedure

2.3.1 Monomer Preparation

Two benzoxazine monomers were synthesized for this study. Their chemical structures are shown in Figure 2.1.

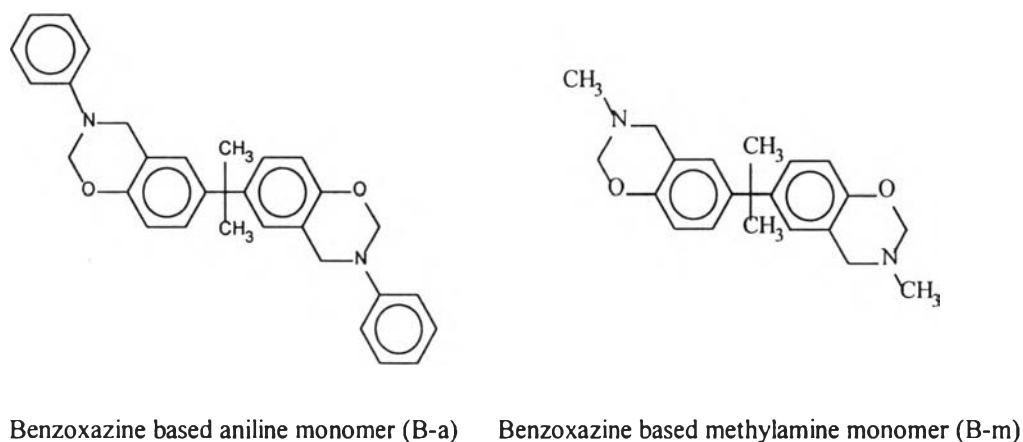
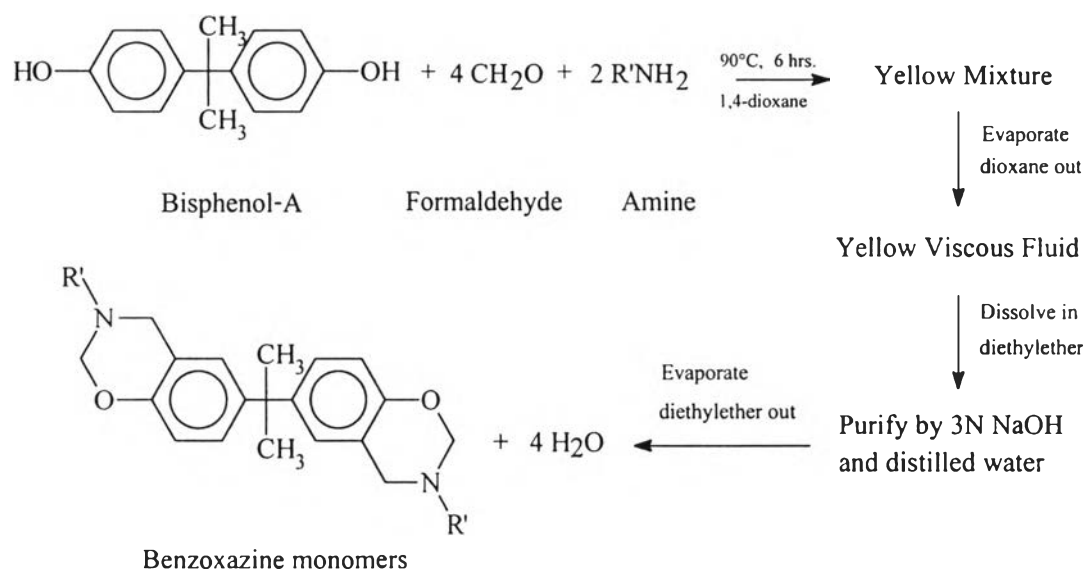


Figure 2.1 Chemical structure of B-a and B-m monomers.

The benzoxazine monomers, “B-a” and “B-m” were synthesized according to the following scheme :



Detailed descriptions of the syntheses and molecular characterizations of the benzoxazine monomers, B-a and B-m, were presented elsewhere (Ning and Ishida, 1994 and H. Ishida, U.S. Pat. No. 5,543,516, 1996, respectively).

2.3.2 Sample Preparation

B-a monomer, a yellow powder, and B-m monomer, a white powder were degassed in a vacuum oven at 100°C for 8 hours to eliminate residual solvent. The paper was dried in the vacuum oven at 110°C for 10 hours to reduce the moisture.

The paper was cut into the dimension of 125mm×150mm. In order to prepare the composite sheet the degassed monomer was spread on the mold, and a sheet of paper laid on top of the resin. Then, the benzoxazine resin and paper was spread on layer by layer until 8 layers of paper and resin were obtained. The material in the mold was then heated and compression molded. The curing steps were operated by varying the soaking time, which is the time for melting the resin to allow the paper to soak into the molten resin before compression molding at a higher temperature. The soaking temperature is 120°C and the curing conditions were varied as shown in Table 2.1

Table 2.1 Curing conditions utilized during the molding of specimens for physical and mechanical testing

Temperature (°C)	Time (min)	Pressure (psi)
120	0,30, 60, 90, 120*	-
150	60	2,500
175	60	5,000
190	120	7,500

* Soaking time : time for melting the resin and allow the paper to soak into the molten resin before compressing at higher temperature.

After the compression step was completed, the yellow-brown sheets of the B-m composites and red-brown sheets of the B-a composites were obtained. The sheets were then cut into the size of 75mm×25mm×1.6mm according to ASTM D570 for water absorption measurements. Specimens measuring 50mm×25mm×1.6mm, according to ASTM D790-92, were used for flexural testing.

2.3.3 Monomer Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

Samples were ground with oven dried KBr (spectroscopy grade) and subsequently pressed into pellets. A pure KBr pellet was used as background. The chamber was purged with dry N₂ for at least 5 min before data was collected.

2.3.4 Physical Characterization

Density Measurement

The density of the paper reinforced benzoxazine composites were measured by the water displacement method according to the ASTM D792-91 (Method A). The density of both benzoxazines, B-a and B-m, were also determined as references. Three specimens with the dimension of 20mm×20 mm×1.6mm were weighed on the upper pan of the sample holder, then tare the balance with the specimen on the upper pan, followed by removal of the

specimen from the upper pan and placing it on the lower sieve of the sample holder. The buoyancy, G , was then recorded, equivalent to $(M_a - M_f)$.

$$G = (M_a - M_f)$$

Where

G = buoyancy

M_a = weight of the specimen in air

M_f = weight of the specimen in distilled water

The specific gravity and density was calculated from the following equation :

$$\rho = \frac{M_a(\rho_f - 0.0012)}{0.99983(M_a - M_f)} + 0.0012 \quad (2.1)$$

Where

ρ = specific gravity of the specimen

ρ_f = specific gravity of distilled water at 23°C

The density of the specimen was calculated as defined in ASTM D792-91, with the following equation :

$$\text{Density (g / cm}^3\text{)} = \rho \times 0.9976 \quad (2.2)$$

The average value from three specimens was calculated.

Fiber Content (weight/weight) Calculation

The % fiber content was calculated from the completely cured benzoxazine paper composite with known weight of paper fiber and paper composites, according to the following equation :

$$\% \text{ fiber content (weight / weight)} = \frac{M_{\text{fiber}}}{M_{\text{composite}}} \times 100 \quad (2.3)$$

Where

M_{fiber} = Mass of the fiber in the composite

$M_{\text{composite}}$ = Mass of the composite

Water Absorption Measurement

Water absorption of the composites was carried out using three rectangular-shaped specimens having the dimensions of 75mm×25mm×1.6 mm, according to ASTM D570. All specimens were conditioned in an oven at 105°C for one hour, then cooled in a desiccator and immediately weighed to the accuracy of the analytical balance to 4 decimals. The specimens were then immersed in distilled water, and were weighed after a certain period of time.

The percentage of water absorbed was calculated from the following equation :

$$\text{Water absorption (\%)} = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100 \quad (2.4)$$

Where

wet weight = The weight of benzoxazine resin and composites
after immersion in distilled water

conditioned weight = The weight of composite after drying at 105°C
for 1 hour

The average value from three specimens were reported.

The % water absorption of fiber was calculated according to the
following equation :

$$\% \text{ water absorption of fiber} = \frac{\text{wet weight} - \text{conditioned weight}}{\text{fiber weight}} \times 100 \quad (2.5)$$

Where

wet weight = The weight of the composite after immersion in
distilled water for 30 days

conditioned weight = The weight of composite after drying in an oven
at 105°C for 1 hour

fiber weight = The weight of fiber after removing the resin
component by digestion method using a mixture
of sulfuric acid and hydrogen peroxide

2.3.5 Mechanical Characterization

Flexural Testing

The flexural properties (three point bending) of the B-a and B-m composites were measured according to ASTM D790-92. Six specimens with dimensions of 50mm×25mm×1.6mm were tested. The flexural modulus (E_f) and flexural strength (σ_f) were calculated from the following equations :

$$E_f = \frac{S^3}{4B \cdot W^2} m \quad (2.6)$$

$$\sigma_f = \frac{3P_c S}{2W \cdot B^2} \quad (2.7)$$

Where

S = length of the support span

B = specimen thickness

W = specimen width

m = slope of the tangent to the initial straight-line portion of the load-displacement curve

P_c = load at break of specimen

Dynamic Mechanical Measurement

Specimens with the dimension of 51mm×13mm×1.6mm were tested in temperature sweep mode. The average heating rate was approximately 2°C/min. Test data were collected at 2°C intervals from 25°C to a temperature above the glass transition temperature of the sample. The samples were

provided with a thermal soak time of 60 seconds for each step in the heating unit of the instrument before measurements was taken.

The storage modulus (G'), loss modulus (G''), and damping curve ($\tan\delta$) were determined. T_g was taken as the maximum point on the G'' curve in the temperature sweep tests.

2.3.6 Interfacial Characterization

The specimen which was flexed until breakage was used for the interfacial study. The fractured specimen was secured to a stub, then coated with gold for 4 min to obtain a thickness of approximately 300 Å. The fiber/matrix interface was then observed in a cross sectional view perpendicular to the fracture surface. The digitized pictures from the specimen at various magnification were taken with the SemAfore program. Then the saved digitized pictures were printed out directly from the computer.