CHAPTER IV

EXPERIMENT

4.1 Materials

The materials used in this research are benzoxazine resin, phenolic novolac resin, and woodflour filler. Benzoxazine resin is based on bisphenol-A, aniline, and formaldehyde. Bisphenol-A (polycarbonate grade) was kindly supplied by Thai Polycarbonate. Para-formaldehyde (AR grade) and aniline (AR grade) were purchased from Merck and APS Finechem, respectively. Phenolic novolac resin is prepared by phenol and formaldehyde with acid catalyst (oxalic acid). Both reactants (AR grade) were purchased from Apec Chemical. Oxalic acid (AR grade) was obtained from Suksapanpanit. Woodflour filler (*hevea brasiliensis*) was obtained from Yu-nguan Industrial. All chemicals were used as received.

4.2 Benzoxazine Resin Preparation

Benzoxazine resin is synthesized using bisphenol-A, formaldehyde, and aniline at the stoichiometric mole ratio of 1:4:2. This resin was prepared based on a patented solventless method [H. Ishida, US Patent 5,543,516]. The preparation reaction is shown in Figure 4.1. The obtained benzoxazine monomer is clear-yellowish solid powder at room temperature. The product is then ground into fine powder and can be kept in a refrigerator for future-use.
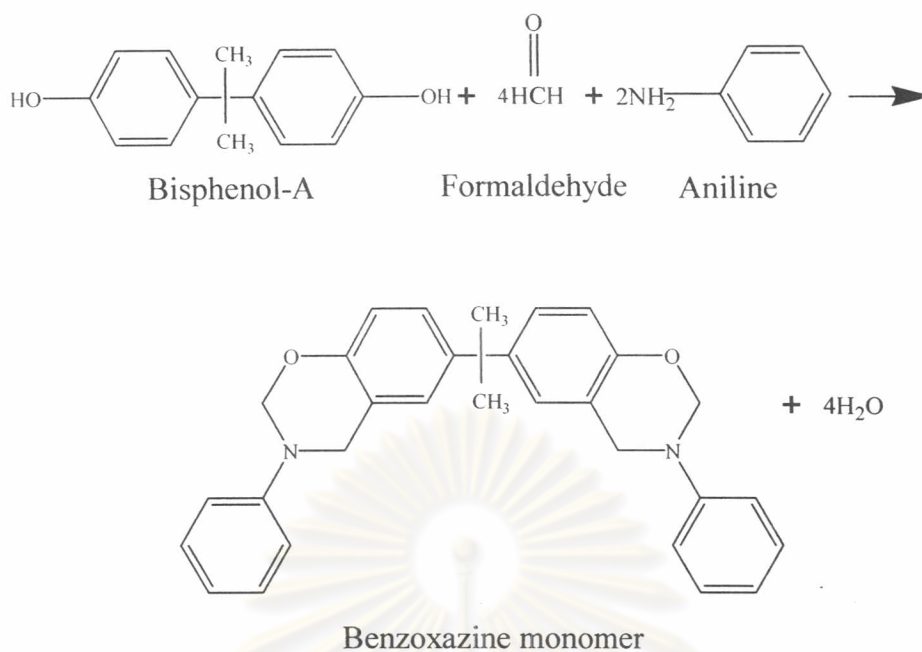
Figure 4.1: Preparation of bifunctional benzoxazine resin (BA-a).

4.3 Phenolic Novolac Resin Preparation

Phenolic novolac resin is based on phenol and formaldehyde. In the synthesis process, a phenol:formaldehyde mole ratio of 1.12:1 was used with oxalic acid as a catalyst [K. Sandler, 1994]. The preparation scheme of phenolic novolac resin is shown in Figure 4.2. The obtained product is yellow to orange solid at room temperature.
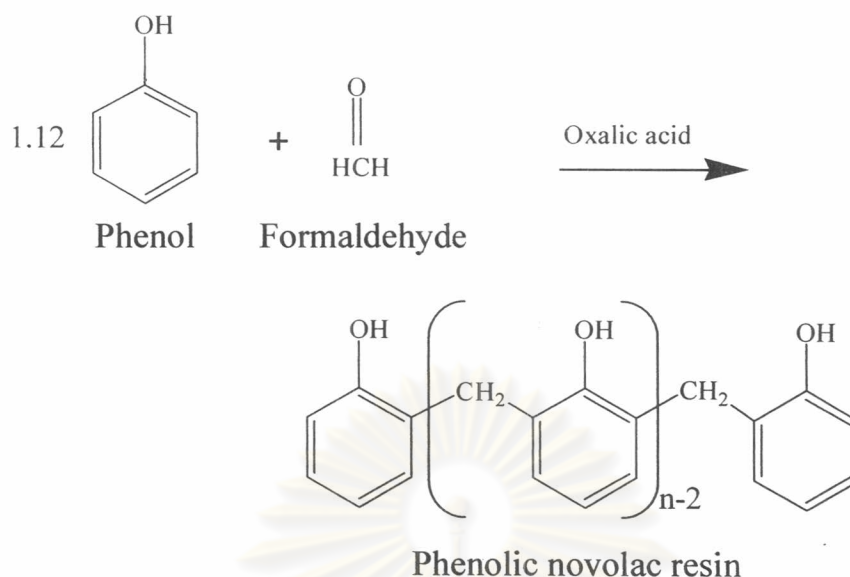
Figure 4.2: Preparation of phenolic novolac resin.

4.4 Benzoxazine/Phenolic Novolac Binary Mixture Preparation (BP Resins)

Binary mixtures of benzoxazine and phenolic novolac resins were obtained by melt-mixing the two monomer powders at desirable mass fraction at 80°C. The weight ratios of the benzoxazine (B) and phenolic novolac (P) binary mixtures at 90/10 (BP91), 80/20 (BP82), 70/30 (BP73), 50/50 (BP55), and 30/70 (BP37), were evaluated as potentially fire resistant matrices for wood composites.

4.5 Woodflour Preparation

Hevea brasiliensis woodflour was selected in this research. The woodflour particle size used was less than 150 μm. The woodflour was firstly dried at 110°C for 24 hours in a vacuum oven until a constant weight was achieved and was then kept in a desiccator at room temperature.

4.6 Processing Method of Wood Composites

The BP resin mixtures were compounded with woodflour using the fixed woodflour contents of 50% and 70% by weight. The compounding temperature is 80°C. Both the resin mixtures and the woodflour were mixed in an aluminium container for at least 15 minutes to ensure good wetting of the resin on the woodflour. The molding compound was placed in a preheated stainless steel mold and was compression-molded using a compression molder at 160°C and at a hydraulic pressure of 35 MPa for 120 minutes. The samples were then removed from the compression molder and cool down at room temperature. The diagram of wood composite preparation process is shown in Figure 4.3.
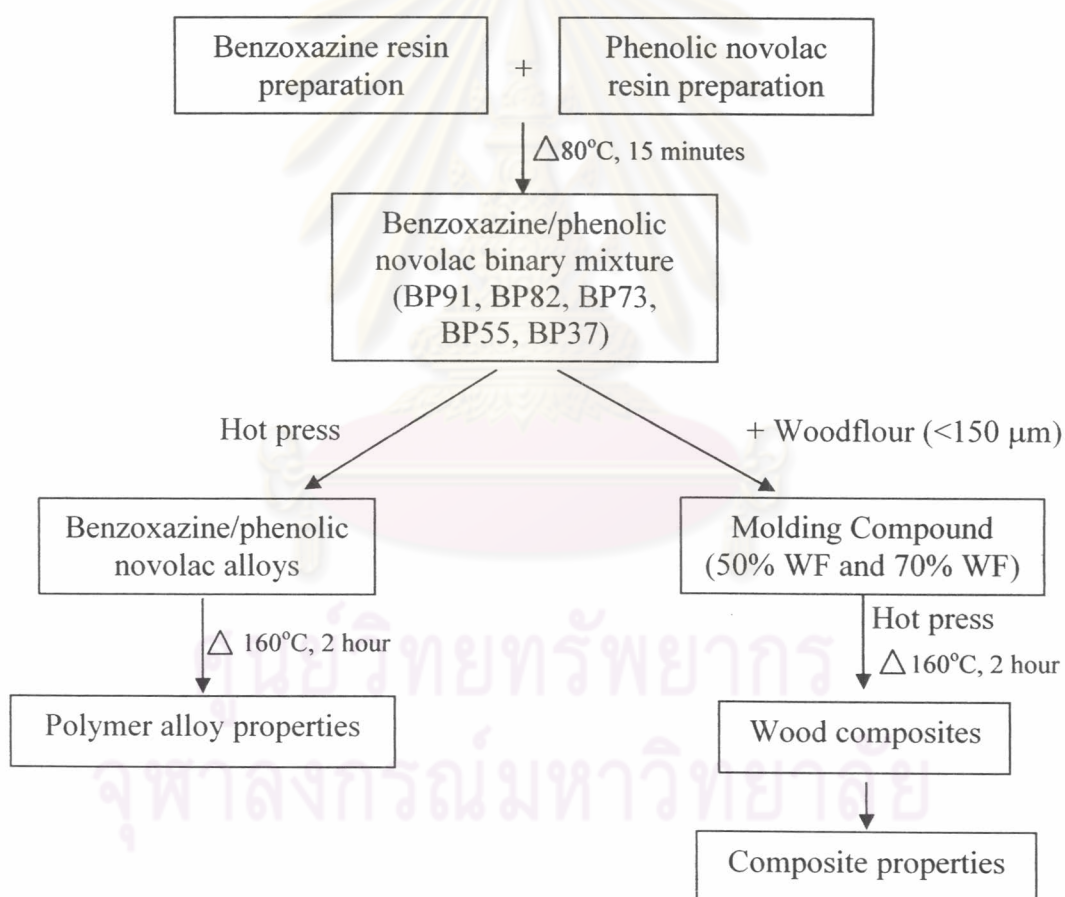

Figure 4.3: Wood composite process.

4.7 Processing Window Determination

Rheological properties of each alloy were examined using a Rheometer (Physica Parr) model MCR300 equipped with a parallel plate geometry under an oscillatory shear mode. The diameter of the upper plate is 25 mm. The measuring gap was set at 0.5 mm. The testing strain amplitude and the frequency were 1% and 1 rad/s. A sample mass of 2 g was used in each test. The testing temperature program was ramped from 60°C at a heating rate of 2°C/min to a temperature beyond the gel point of each resin and the dynamic viscosity was recorded.

4.8 Differential Scanning Calorimetry (DSC)

Curing temperature and curing time of the BP molding compounds were examined using a differential scanning calorimeter (model 2910) from TA Instuments in a temperature range of 30-300°C. A sample mass of 5-10 mg were placed in a non-hermetic aluminum pan with lid. The experiment was performed at a heating rate of 10°C/min under nitrogen purging. Baseline was tested at the first time for purging a contamination and calibrating the DSC. Then resins, alloys, or molding compounds were tested at the second time. Curing temperature, fully cured time, glass transition temperature were obtained.

4.9 Density Measurement

A density of each specimen was determined by a water displacement method according to ASTM D 792-91 (Method A). All specimens were prepared in a disk shape having 50.8 mm in diameter and 3.2 mm in thickness. The density was calculated by the following equation:

$$\rho = \left(\frac{A}{A - B} \right) \times \rho_o \tag{1}$$

where ρ = Density of the specimen (g/cm^3)

        A = Weight of the specimen in air (g)

        B = Weight of the specimen in liquid (g)

        ρ_o = Density of the liquid at the given temperature (g/cm^3)

The average value from at least three specimens was calculated.

4.10 Limiting Oxygen Index Determination

A minimum concentration of oxygen, expressed in volume percent, in a mixture of oxygen and nitrogen that initially shows flaming combustion of a material at room temperature was called a limiting oxygen index (LOI). LOI measurements were performed following ASTM D 2863-95. The tested specimen dimensions were about 7×70×3 mm^3. Three samples were required for calculating an average values. The calculation of the LOI of a material for each replicate follows equation (2) :

$$LOI \;=\; \frac{(100 \times O_2)}{(O_2 + N_2)} \tag{2}$$

where   LOI = Limiting oxygen index

        O_2 = Volumetric flow of oxygen (mm^3/s)

        N_2 = Volumetric flow of nitrogen (mm^3/s)

At least three types of samples with known LOI value were tested to calibrate a limiting oxygen index analyser.

4.11 Rate of Burning Evaluation

In this experiment, a bar of a specimen is supported horizontally at one end. The free end is exposed to a specified gas flame for 30 sec. An average burning rate is reported for each sample. The dimension of the specimen used was about 12×120×3 mm^3.

This test method was performed based on ASTM D 635-9. Three samples were required for calculating an average values. The burning rate is calculated from :

$$\text{Rate of burning (mm/min)} = \frac{75}{t - t_1} \qquad (3)$$

where t = Time period from start to time as flame has proceeded to the mark 100 mm

t_1 = Time period from start to time as flame has proceeded to the mark 25 mm

4.12 Heat of Combustion Determination

Calibration was operated at the first step before testing a sample for each day by using a benzoic. The tested composites were ground into solid powder. Heat of combustion (HOC) of the powder specimen was thus determined by combusting the powder sample with excess oxygen at a pressure of 2.97×10^6 N/m^2 in Bomb calorimeter (Leco AC-350). The mass of each sample was about 0.5 g. At least two samples of each composite specimen were required to perform the test to be save of the obtained result.

4.13 Thermogravimetric Analysis

Degradation temperature (T_d) and char yield of wood composites were studied using a thermogravimetric analyzer (model TGA/SDTA 851^e) from Mettler-Toledo (Thailand). Each sample was heated at a heating rate of 20°C/min from room temperature to 900°C under a nitrogen atmosphere. The initial mass of a tested sample was 15-20 mg. The degradation temperature at 5% weight loss and the char yield at 800°C were recorded for each specimen.

4.14 Dynamic Mechanical Analysis

A dynamic mechanical analyzer (D-29693) from GABO in a bending mode was used to identify glass transition temperature, storage modulus (G'), loss modulus (G'') or

loss tangent (tanδ) of samples. A dimension of each specimen was $7\times40\times3$ mm^3. Experiments were performed in a temperature sweep mode with a fixed frequency at 1 Hz and an average strain amplitude of 0.04%. Each specimens was tested using a heating rate of 2°C/min from 60°C to about 300°C.

4.15 Flexural Property Measurement

Flexural modulus and flexural strength of composite specimens were determined utilizing a Universal Testing Machine (model L2000R) from LLOYD Instrument. The test method used was a three-point bending mode with a support span of 48 mm. The crosshead speed was 1.2 mm/min. The dimension of the specimens was $25\times60\times3$ mm^3. The flexural properties were determined using ASTM D 790M-93 according to the following equations :

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

$$S = \frac{3PL}{2bd^2} \tag{5}$$

where E_B = Flexural modulus (MPa)

S = Flexural strength (MPa)

P = Load at a given point on the load-deflection curve (N)

L = Support span (mm)

b = Width of beam tested (mm)

d = Depth of beam tested (mm)

m = Slope of the tangent to the initial straight-line portion of the load-deflection curve (N/mm)

4.16 Water Absorption

A method was based on ASTM D 570-95. Each specimen was prepared in a disk shape with 51 mm in diameter and 3.2 mm in thickness. The water absorption of a specimen was calculated according to the following equation,

$$\text{Water absorption (\%)} = \frac{\text{wet weight} - \text{dried weight}}{\text{dried weight}} \times 100 \tag{6}$$

where   wet weight = Weight of specimen after water immersion at various time
       dried weight = Weight of dry specimen before water immersion at a certain period of time

4.17 Interfacial Bonding Examination

Interfacial bonding of a filled sample was investigated using a ISM-5400 scanning electron microscope at an acceleration voltage of 15 kV. Samples were coated with thin film of gold using a JEOL ion sputtering device (model JFC-1100E) for 4 min to obtain a thickness of approximately 30Å and the micrographs of the specimens fracture surface were taken. The obtained micrographs revealed the dispersion of woodflour particles and were used to evaluate qualitatively the interfacial interaction between the matrix resin and the woodflour filler.