

CHAPTER III EXPERIMENTAL

3.1 Materials

Sisal fibers with diameters ranging from 100 to 300 μm and 100 cm length were obtained from a local source. Bisphenol-A-type epoxy resin, methyl tetrahydrophthalic anhydride, methyl hexahydrophthalic anhydride, hexahydrophthalic anhydride and N,N-dimethylbenzylamine were supplied by Thai Epoxy and Allied Products Co., Ltd.

γ -Glycidoxypropyltrimethoxysilane (98%), γ -aminopropyltrimethoxysilane (>97%) and ethylenediamine (>99%) were purchased from Aldrich Company. Paraformaldehyde (>95%), phenol (>99.5%) and sodium hydroxide were purchased from Merck Company. Diethylether (99.5%), methanol (99.8%) and dichloromethane (99.8%) were purchased from Labscan Company. All chemicals were used without further purification.

3.2 Equipment

3.2.1 Nuclear Magnetic Resonance Spectrometer (NMR)

NMR spectra were collected from a Mercury NMR spectrometer (Bruker) with a proton frequency at 400 MHz. Deuterated chloroform was used as a solvent.

3.2.2 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectra were obtained from a Nexus 670 spectrometer (Nicolet) with 32 scans at a resolution of 4 cm^{-1} and a frequency range of 4000-400 cm^{-1} .

3.2.3 Thermogravimetric Analysis (TGA)

TGA was performed by High Resolution TG-DTA Pyris Diamond (Perkin Elmer) with a heating rate of 10°C/min using a nitrogen purge with a purge rate of 200 ml/min.

3.2.4 Differential Scanning Calorimetry (DSC)

DSC analysis was performed by differential scanning calorimeter 822e (Mettler Toledo) at a heating rate of 10°C/min with nitrogen purge with a purge rate of 60 ml/min.

3.2.5 Scanning Electron Microscope (SEM)

Morphology of the fibers and the composite samples was studied by a Scanning Electron Microscope JEOL, model JSM 2590 (Jeol Ltd., Tokyo, Japan).

3.2.6 Contact Angle Instrument

Contact angle was measured by DSA10 contact angle measuring instrument, model DSA10-MK2 TIC (KRUSS, Germany)

3.2.7 Compression Molding Machine

Composite samples are prepared by compression press, model V50H-18-CX (Wabash).

3.2.8 Instron Universal Testing Machine

Tensile and flexural tests of the composite samples were carried out by an Instron Universal Testing Machine model 4206.

3.2.9 Zwick Pendulum Impact Tester

Impact tests of the composite samples were performed by a Zwick Pendulum Impact Tester model 5113.

3.2.10 Lloyd Universal Testing Machine

Tensile tests of single sisal fibers were carried out using Lloyd universal testing machine, LRX. A gage length of 50 mm was employed with a crosshead speed of 10 mm/min

3.3 Methodology

3.3.1 Monomer Preparation

The benzoxazine monomer synthesized in this work has chemical structure as shown in Figure 3.1. The molar ratio of phenol:p-formaldehyde:ethylenediamine was 2:4:1.

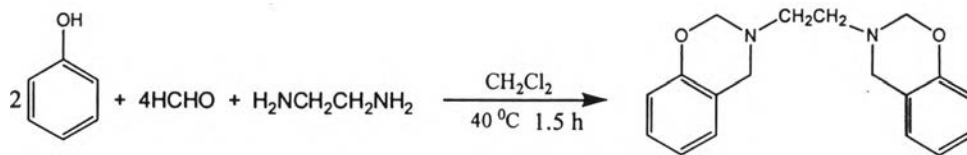


Figure 3.1 Synthesis reaction of the diamine-based benzoxazine.

3.3.1.1 Melt method

Phenol, paraformaldehyde and ethylenediamine were added to a round bottom flask without solvent. The mixture was then heated and stirred at reaction temperatures (Table 4.1). (The reference for this method is: H. Ishida, U.S. Pat. 5,543,516, Aug. 6 (1996))

3.3.1.2 Solvent method

Both ethylenediamine and paraformaldehyde were dissolved separately in dichloromethane (or chloroform or toluene) using 50% concentration of the reactant and cooled in an ice bath. Ethylenediamine solution was then added dropwise into the formaldehyde solution which was stirred for 30 minutes. After that, 50% phenol dichloromethane solution was added dropwise into the reaction flask and left for 30 minutes. Then the solution was refluxed for a fixed time (Table 4.1). After this, the solvent was evaporated by a rotary evaporator and the crude product was redissolved in diethylether. The crude reaction products were then washed by 2N NaOH aqueous solution three times and finally, diethylether was evaporated by a rotary evaporator. The monomer was obtained as a white powdery solid. The monomer was characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

NMR spectra were obtained on a Merqury 400 spectrometer (Bruker). FTIR spectra were obtained on a Nexus 670 spectrometer (Nicolet) with 32 scans at a resolution of 4 cm^{-1} and a frequency range of 4000-400 cm^{-1} . TGA was performed by High Resolution TG-DTA Pyris Diamond (Perkin Elmer) with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ using a nitrogen purge with a purge rate of 200 mL/min. DSC analysis was performed by differential scanning calorimeter 822e (Mettler Toledo) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ with nitrogen purge with a purge rate of 60 mL/min.

3.3.2 Fiber Surface Treatments

3.3.2.1 *Alkalization*

NaOH solution was prepared with concentrations of 2, 4, and 6 percent by weight (wt%). Fibers were placed in the NaOH solutions at room temperature for 1, 5, and 24 h. The treated fibers were rinsed several times by distilled water until neutral. Then fibers were dried in an oven for 2 h at 110°C.

3.3.2.2 *Silanization*

γ -Aminopropyltrimethoxysilane aqueous solution was prepared with concentrations of 0.1, and 0.5 percent by volume (vol%) and γ -glycidoxypropyltrimethoxy silane with concentrations of 0.1, and 0.5 vol% were prepared and adjusted to pH 5.5 by hydrochloric acid. The fibers were soaked in the silane solutions for 2 h. The obtained fibers were dried in an oven for 2 h at 110°C.

3.3.3 Fiber Characterization

Scanning electron microscopy (SEM) (JEOL, JSM 5200, 20 kv) was used to study surface morphology of the treated fiber. The fiber sample was coated by gold for 4 min before being analyzed. The FTIR using attenuated total reflection mode (ATR) with a ZnSe plate was used to analyze the chemical groups present on the fiber surface. TGA of sisal fibers was performed at a heating rate of 10°C/min using a nitrogen purge with a purge rate of 200 mL/min.

For contact angle measurement (KRÜSS contact angle measurement instrument, DSA 10-Mk2), the fibers were cut into short segments 3 mm in length and 60 mg of the cut fibers were pressed by hydraulic press of 8 tons for 5 minutes to form a disc of 13 mm diameter and 0.45 mm thick. The dynamic contact angles of a water droplet placed on the surface of the disc were measured at every 0.1 second for 2 seconds. The curve of contact angle versus time was recorded for later analysis.

Tensile tests of single sisal fibers were carried out using Lloyd universal testing machine, LRX. A gage length of 50 mm was employed with a crosshead speed of 10 mm/min in accordance with ASTM C1557-03. Twenty single

fibers of 15 cm were tested. The cross-sectional area of fibers was determined by SEM.

3.3.4 Preparation of Composites

Sisal fibers were cut into 15 cm length and dried in an oven at 60°C overnight to remove the moisture. Benzoxazine and epoxy resin were mixed together, with 25, 50, 75, and 100 wt% of epoxy without any hardeners or catalysts, then melted and degassed in a vacuum oven at 120°C for 1 hour to remove any remaining volatiles. For epoxy composites, the epoxy resin, anhydride hardener and tertiaryamine catalyst were mixed at ratio of 100:90:0.1. The composite was prepared by a Wabash compression press. In the compression molding process, the mold, measured 17 cm x 13 cm, was first coated with a silicone mold release agent and preheated to 140°C. The molten monomer was poured into the preheated mold to fill up to 50% of the mold. Sisal fiber weighing, 5, 10, and 15 vol% of the composite was laid unidirectionally in the mold. After that, the remaining 50% of the resin required to fill the mold was poured onto the laid fibers. The mold was then closed and the composite was cured according to the temperature program shown in Table 1. The thickness of the composite was 3 mm.

Table 3.1 Temperature program for compression molding process

Temperature (°C)	Time (min)	Pressure (10 tons)
140	30	-
160	30	-
180	60	+

- not be compressed

+ compressed by 10 tons

3.3.5 Mechanical Testing

Tensile and flexural tests of the composite samples were carried out on an Instron universal testing machine (Instron 4206) according to ASTM D638-96 and D790-96a, respectively. Tensile tests were conducted using dumbbell shape

specimens with 140 mm in length, a crosshead speed of 5 mm min⁻¹ and a gauge length of 50 mm. For flexural tests, five rectangular test specimens of each sample measuring 62x12.7x3 mm were used at a crosshead speed of 1.28 mm min⁻¹ in a three-point loading, fitted with a 100 kN load cell. Impact tests were performed on a pendulum impact tester (Zwick 5113) in accordance with ASTM D256-97. Five rectangular test specimens with dimensions of 62x12.7x3 mm were used. All reported values are the average of the five tests.