CHAPTER IV

EXPERIMENTAL

4.1 Raw Materials

Bisphenol-A, polycarbonate grade, was contributed by Thai Polycarbonate Co.,Ltd, Para-formaldehyde ($\geq$99% purity) was purchased from Merck & Co.Inc, Aniline (99% purity) was used from Fluka Chemicals Co.Ltd and Novolac Epoxy was supplied by **Thai Organic Chemicals Co., Ltd (Epoxy Division)**.

4.2 Preparation of Aniline-based Benzoxazine Monomer

A 0.01 mol (2.28 g) of bisphenol-A was placed in an aluminum pan and 0.04 mol (1.20 g) of paraformaldehyde and 0.02 mol (1.87 g) of aniline were added to the pan. The temperature was raised to 80-90°C and the heating continued for about 30-40 min. Mixing until the mixture became homogeneous and turned light yellow. The temperature was then raised to 110-120°C for removal of water for 20-30 min. The whole mixture became a transparent yellow color. It was then slowly cooled to room temperature.

4.3 Samples Preparation

4.3.1 Polybenzoxazine and epoxy resins

The copolymers between benzoxazine and epoxy resins based on novolac epoxy were synthesized with different composition ratio of 100/0, 80/20, 60/40 and 40/60. Novolac epoxy and benzoxazine were thoroughly mixed at 85°C. After 30 min, the mixture was poured into a mold. The resin-filled mold was initially heated at 50°C for 30 min in order to remove any air trapped during the mold-filling process. Then the material was subjected to a curing schedule of 1 hour at each of 150°C, 170°C, 190°C, and 200°C. After completing the curing process, the

molded specimen was slowly cooled to room temperature. No catalyst was used in these experiments.

4.3.2. Fabrication of composites

The composite material is prepared by hand lay-up technique using 80 g/cm^2 E-glass fabric. Fabric pieces of size 20 x 12.5 cm weighing 50 g is heated to 150°C in a hot air oven for 2 h to remove moisture and then cooled to 30°C. Preweighed mixture of benzoxazine and novolac epoxy prepolymer resin with a various component (%wt) is applied over a fabric sheet using rubber roller. The fabric pieces coated are kept at 70°C for 5 min. The prepreg material is kept one over the other in the releasing agent coated mould and a compression pressure of 60 kg/cm^2 is applied for a period of 3 hours, step cured at 170°C for 1 hour, 190°C for 1 hour and 200oC for 1 hour, respectively. The mould is taken out and cools down at 30°C for 1 hour. Then, the composites are removed from the mould.

4.4   Samples Characterization

4.4.1   Chemorheology of Aniline-based benzoxazine resin and novolac epoxy copolymers.

Rheological and gelation behaviors of each resin and resin mixture were investigated using a rheometer (Haake Rheo Stress 600, Thermo Electron Corp.) equipped with disposable parallel plate geometry. The measuring gap was set at 0.5 mm. The processing window was performed under and oscillatory shear mode at a frequency of 1 rad/s (0.159 Hz). The testing temperature was ramped at a heating rate of 2°C/min to a temperature beyond its gel point. A frequency sweep in the range of 10-100 rad/s was performed isothermally as a function of time at 150, 170, 190, 200°C. The gel point is obtained from the point where the loss tangents of different frequencies, i.e. 1.6, 2.8, 5.0, 9.0, and 15.9 Hz, intersect each other.

4.4.2 Differential Scanning Calorimetry (DSC)

Curing behaviors of each resin and its copolymers with epoxy were studied using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. Each specimen with a mass in a range of 3-5 mg was sealed in an aluminum pan with lid. The heating rate used was 10°C/min and the sample temperature was scanned from room temperature to 300°C under nitrogen purging. The purge nitrogen gas flow rate was maintained to be constant at 50 ml/min.

The degree of conversion (α) of a sample was determined according to the following relationship:

$$\alpha = 1 - \left(\frac{H_{rxn}}{H_o} \right) \qquad (4.1)$$

Where :

H_{rxn} = the heat of reaction of the partially cured specimen as determined from the DSC experiment, mW/mg.

H_o = the heat of reaction of the uncured resin, mW/mg.

4.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structure of each sample was analyzed by a Fourier transform infrared spectroscopy (FTIR). The FTIR measurement was carried out on a Spectrum GX FTIR spectrometer from Perkin Elmer instrument with an ATR accessory. All spectra were taken as a function of time with 32 scans at a resolution of 4 cm^{-1} and spectra range of 4000-650 cm^{-1}.

4.4.4 Density Measurement

The densities of benzoxazine resins copolymer with novolac epoxy were determined by water displacement method according to ASTM D 792-00 (Method A). The dimension of each rectangular shape specimen is 10 X 50 X 2 mm^{3}. All measurements were performed at room temperature.

The density of the specimen was calculated by a following equation:

$$\rho = \left[\frac{A}{A-B}\right] \times \rho_o \qquad (4.2)$$

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 measurement was run 5 times for each specimen and the average value of the sample volume was obtained.

4.4.5   Dynamic Mechanical Analysis (DMA)

A dynamic mechanical analyzer (NATZSH, model DMA242) was used to obtain a storage modulus (E') and loss modulus (E") of the polymeric specimens. The specimen, with a dimension of 10 X 50 X 2 mm^3, was tested using a 3 point bending mode at the frequency of 1 Hz and heating rate of 2°C/min from room temperature to the temperature beyond the glass transition temperatures (T_g) of each specimen. The glass transition temperature was taken as the maximum point on the loss modulus or loss tangent curves.

4.4.6   Thermomechanical Analysis (TMA)

The coefficient of thermal expansion (CTE) was measured with a Perkin Elmer Instrument Technology SII Diamond thermal mechanical analyzer (TMA). The thickness of specimens was set about 2mm. During the TMA measurement, the specimen was heated from room temperature to the temperature beyond the glass transition temperature at a heating rate of 10°C/min. Generally thermal expansion of a material increases with an increase in its temperature and the CTEs were calculated from the slope of the thermogram. An abrupt

change in slope of the expansion curve indicates a transition of the material from glassy to rubber state.

Coefficient of thermal expansion (CTE) of a specimen was calculated by a following relationship:

$$\varepsilon_l(T,\alpha) = \frac{(l - l_o)}{l} = \gamma^{CTE}(\alpha)\Delta T \qquad (4.3)$$

Where

ε_l	=	the thermal linear strain.
l	=	the final specimen length.
l_o	=	the initial specimen length.
$\gamma^{CTE}(\alpha)$ =		the coefficient of thermal expansion.
ΔT	=	the temperature variation.

4.4.7 Thermogravimetric Analysis (TGA)

Degradation temperature (T) and char yield of all polybenzoxazines and benzoxazine alloys at various mass fractions of epoxy resin were studied using a perkin Elmer Instrument Technology SII Diamond TG/DTA thermogravimetric analyzer. A heating rate of 20°C/min from room temperature to 900°C under nitrogen atmosphere was used to acquire TGA thermograms. The pure nitrogen gas flow rate was maintained at 100 ml/min. The sample mass used was measured to be approximately 10-15 mg. Weight loss of the sample was measured as a function of temperature. The degradation temperature (T_d) of polybenzoxazines and benzoxazine-epoxy copolymers was reported at their 5% weight loss. Char yield of the above specimens were also reported at 800°C.

4.4.8 Universal Testing Machine (Flexural Mode)

The flexural strength, flexural strain and the corresponding modulus of polymers or polymer alloy were determined using a universal testing machine (model 5567) from instron Co.,Ltd. The test method was a three-point loading with the supporting span of 32 mm and tested at a crosshead speed 0.85 mm/min. A dimension of a specimen is 25 X 50 X 2 mm.

Flexural properties were determined based on ASTM D7902-03. The flexural strength, flexural strain and the modulus were calculated by the following equations:

$$E_b = \frac{L^3 m}{4bd^3}$$ (4.4)

$$S = \frac{3PL}{2bd^2}$$ (4.5)

Where
E_b	=	Flexural modulus, GPa.
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.

4.4.9   Water absorption

To determine the total water absorbed when substantially saturated, the conditioned specimens were placed in a container of distilled water maintained at a temperature of 22-24°C, and shall rest on edge and be entirely immersed. At the end of 24 hours, the specimens were removed from the water one at a time, all surface water wiped off with a dry cloth, and weighed to the nearest 0.001 g immediately, the specimen shall then be considered substantially saturated. The difference between the substantially saturated weight and the dry weight shall be considered as the water absorbed when substantially saturated. When materials are known or suspected to contain any appreciable amount of water-soluble ingredients, the specimens, after immersion, shall be weighed, and then reconditioned for the same time and temperature as used in the original drying period. They shall then be cooled in desiccators and immediately reweighed. If the reconditioned weight is lower than the conditioned weight, the difference shall

be considered as water-soluble matter lost during the immersion test. For such materials, the water-absorption value shall be taken as the sum of the increase in weight on immersion and of the weight of the water-soluble matter. Percentage increase in weight during immersion, calculated to the nearest 0.01 % as follows:

$$\text{Increase in weight, \%} = \frac{\text{Wet weight} - \text{Conditions weight}}{\text{Conditioned weight}} \times 100 \qquad (4.6)$$

4.4.10 Hardness Measurement (Shore D)

The Shore hardness is a measure of the resistance of a material to the penetration of a needle under a defined spring force. It is determined as a number from 0 to 100 on the scales A or D. The higher the number is the higher the hardness. The Shore A is used for flexible typed specimen and the Shore D is for a rigid type. In this research, the Shore D scale was used to determine a hardness value of those specimens because of a relatively rigid nature of all polybenzoxazines and epoxy copolymers. A dimension of each specimen was 25 X 50 x 2 mm and the specimen was determined following ASTM D2240 using a Bareiss hardness tester, Germany, at room temperature. The measurement was evaluated 5 times at different position of each specimen and the average hardness value of the sample was obtained.

4.4.11 Scanning Electron Microscope (SEM)

SEM was used to investigate the surface structures as well as the cross-sections of particles. For particle surface analysis, particles were adhered to the plate. For cross-section analysis, particles were potted in epoxy resin and microtomed until a smooth cross-section was obtained.