

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

The epoxy resin, bisphenol-A-(epichlorohydrin) (EPOTEC YD128), and the curing agent, cycloaliphatic amine (TH7301), were obtained from Aditya Birla Chemicals (Thailand) Ltd. Zinc oxide (nano-size and <1 micron) and copper oxide (nano-size and <5 micron) were supplied by Fluka. The hexagonal BN (PCTL30MHF) with an average particle size of 30 micron was supplied by Saint-Gobain Ceramics and Plastics, Inc., USA. Silane coupling agents,  $\gamma$ -glycidoxypropyltrimethoxy silane (GPS) and 3-aminopropyl triethoxy silane (APS) were supplied by Sigma-Aldrich (USA). Hexadecyl pyridinium chloride (HDPyCl, 98% purity), methyl methacrylate (MMA, 99% purity), styrene (99% purity), and potassium persulfate ( $K_2S_2O_8$ , 98% purity) were purchased from Fluka (Switzerland). Ethanol and sodium hydroxide were purchased from Merck (Germany). A series of cationic surfactants  $(C_nH_{2n+1})NH_3Br$  with  $n = 12, 14, 16,$  and  $18,$  were supplied by Fluka, and Sigma-Aldrich, Inc., Singapore. Methyl methacrylate and styrene were washed with 1% aq. NaOH to eliminate inhibitor prior to use. All other chemicals were used as received.

#### 3.2 Equipment

A JEOL scanning electron microscopy (SEM) model JSM-5200 (Japan) was used to study the fractured surface from flexural tests of epoxy composite filled with different fillers and to investigate the particle size of the fillers. The narrowest and longest dimensions of BN particles were measured using the Semafore program.

A Field Emission Scanning Electron Microscope (FE-SEM), Hitachi S-4800 (Japan), was used to study surface morphology of the untreated and admicellar-treated BN particles, as well as the fractured surface of the composites.

A Thermo Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectrometer was used to provide a chemical analysis of the components on the modified surface of BN particles.

A Brookfield viscometer (RVDVII) was used to measure the viscosity of the BN-epoxy mixture.

A Zetazier 3000HSA, Malvern instrument, was used to measure the zeta potential of BN powders as a function of pH.

A Drop Shape Analyzer (KRUSS, DSA 1 V 1.80, Germany) was used to measure the contact angles of water and epoxy resin on admicellar-treated, silane-treated, and cationic surfactant-modified BN surface.

A Quantachrome/Autosorb-1 Surface Area Analyzer was used to determine the surface area of the BN particles.

A SHIMADZU TOC-V csh organic carbon analyzer was used to determine the TOC values of the surfactant solutions.

A Hot Disk Thermal Analyzer (Hot Disk AB, Uppsala, Sweden) was used to measure the thermal conductivity of the composites.

An Instron series IX Automated Materials Testing System model 3366 was used to determine the flexural properties of the composites.

A Pendulum Impact Tester (Zwick, Germany) was used to determine the impact strength of the composites.

### **3.3 Methodology**

#### **3.3.1 Preparation of Metal Oxide-Filled Epoxy Composite**

The metal oxide was first dried in an oven at 100 °C for 2 h prior to processing. The desired amount of filler was gradually added into 60 mL of epoxy resin contained in a 250 mL plastic beaker. The loading of metal oxide powder was varied from 0.5%, 1.0% to 2.0 vol%. The mixture was then stirred by a mechanical stirrer

(A.L.C. International S.r.l. Class I) at the mixing speed of 80 rpm with the mixing time of 15 mins. Next, 36 mL of curing agent was added into the mixture which was then stirred until homogeneous. The mixture was then poured into a stainless steel mold 70 x 90 x 3 mm<sup>3</sup> in dimensions. The open mold was then placed in a vacuum oven at 50 °C for 10 min to evacuate the entrapped air. The mold was then closed by a 26x26 cm<sup>2</sup> metal plate and placed in the compression molding machine under 15 tons of loading for curing at 80 °C for 1 h.

### 3.3.2 Preparation of Admicellar-treated BN

Admicellar polymerization of each monomer (MMA and styrene) was carried out in two steps. First, 5 g of BN particles was added to 100 mL of an aqueous solution containing 1.0 mM HDPyCl surfactant, which is the concentration just above the CMC of the surfactant<sup>23</sup> to ensure maximum surfactant adsorption with minimum emulsion polymerization in the aqueous phase. Monomer was then added to give a surfactant:monomer molar ratio of 1:2.5, 1:5, 1:7.5, 1:10, 1:12.5, 1:15, and the initiator K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added to give a monomer:initiator ratio of 1:10. The mixture was shaken in a shaker bath at 30°C for 24 h to allow for the adsorption of surfactant onto the BN surface and the adsolubilization of the monomer into the surfactant bilayer. In the second step, the temperature was raised to 70°C to initiate the polymerization reaction which was allowed to take place for 24 h. At the end of the reaction time, the treated BN was washed several times with a mixture of 70/30 (v/v) water/ethanol at room temperature to remove remaining monomer and the upper-layer surfactant of the surfactant bilayer to expose the coated polymer on the BN surface. The sample was finally dried in the oven at 50°C for 24 h.

### 3.3.3 Preparation of Silane-Treated BN

The calculated amount of silane coupling agent was added into an aqueous solution at pH 4.5 to give a concentration of 0.025, 0.05, 0.075, 0.10, and 0.15 wt%, respectively. Then, 20 g of BN particles was treated in 100 mL of the prepared

silane solution for 2 h at room temperature. The BN particles were then filtered and dried in the oven at 50°C for 24 h.

### 3.3.4 Preparation of Surfactant-Modified BN

To prepare the surfactant-modified BN, a 1.5 mM surfactant solution was added to BN powder in a 250 mL Erlenmeyer flask using the ratio of 1 g BN to 10 mL solution. A rubber stopper was then put on the flask and a paraffin film was wrapped on to seal on top. This suspension was stirred at 80 °C for 5 h. All surfactant-modified BN particles were filtered and washed with deionized water to eliminate excess amount of surfactant. After filtration, the modified BN particles were dried at 50°C for 24 h until completely dried. The pH value of surfactant solutions was varied from 5.5, which was the initial value of the deionized water, to 6, 7, 8, 9, and 10, respectively, using 0.1 M NaOH.

### 3.3.5 Preparation of BN-Filled Epoxy Composite

The BN particles were first dried in a vacuum oven at 80°C for 24 h prior to processing. The calculated amount of BN was added gradually to 60 mL of epoxy resin contained in a 250 mL plastic beaker with continuous stirring. The mixture was then stirred by a mechanical stirrer (A.L.C. International S.r.l. Class I, Italy) at the desired speed, time and temperature. Next, 36 mL of curing agent was added into the mixture which was then stirred until homogeneous. The mixture was then poured into a stainless steel mold 70x90x3 mm<sup>3</sup> in dimension. The open mold was then placed in a vacuum oven at 50°C for 10 min to evacuate the entrapped air. The mold was then closed by a 26x26 cm<sup>2</sup> metal plate and placed in the compression molding machine under 15 tons of loading for curing at 80°C for 1 h.

### 3.3.6 Characterization of Filler and Composite

#### 3.3.6.1 *Particle size determination*

The particle dispersion of metal oxide in epoxy matrix was investigated. The epoxy filled metal oxide specimens were put in liquid nitrogen for a minute, then broken into a small piece and was placed on a stub and examined using JEOL scanning electron microscopy (SEM) model JSM-5200 (Japan).

To determine the particle size in the BN-epoxy mixture, after mixing at the desired conditions, BN particles in epoxy matrix were washed with ethanol to extract BN from the epoxy matrix and the extracted particles were then dried in a vacuum oven. The dried particles were then placed on a stub and examined using JEOL scanning electron microscopy (SEM) model JSM-5200 (Japan). The narrowest and longest dimensions of BN particles were measured using the Semafore program, and the average aspect ratio was calculated accordingly. A total of 120 particles were examined for each mixing condition and the average value was reported.

#### *3.3.6.2 Characterization of the fractured surface of the composite*

The Field Emission Scanning Electron Microscope (FE-SEM), Hitachi S-4800 (Japan), was used to study surface morphology of the fractured surface of the composites.

#### *3.3.6.3 Characterization of the admicellar-treated BN surface*

The untreated BN and admicellar-treated BN particles were prepared in the form of KBr pellets for the Fourier transform infrared (FTIR) measurements on a Nicolet 560 FTIR spectrometer (United States). Subtractive FTIR spectra of the treated samples were obtained using the untreated BN as the base line.

#### *3.3.6.4 Viscosity measurements*

The viscosity of the BN-epoxy mixture was measured by a Brookfield viscometer (RVDVII) with spindle No. 27 at  $25 \pm 1$  °C according to ASTM 2393-86.

#### *3.3.6.5 Determination of the Zeta Potential of BN*

The zeta potential of BN powders as function of pH was determined using Zetazier 3000HSA, Malvern instrument. The BN powders were homogeneously dispersed in distilled water by sonication method. The pH of the

aqueous BN suspension was adjusted using 0.1 M HCl and 0.1 M NaOH to cover the entire pH range under investigation (pH 2 to 10).

#### *3.3.6.6 Contact angle measurements*

The Drop Shape Analyzer (KRUSS, DSA 1 V 1.80, Germany) was used to measure the contact angles of water and epoxy resin on admicellar-treated, silane-treated, and surfactant-modified BN surface. BN particles, weighing 1.5 g, were compressed using a hydraulic pellet press at the pressure of 7 tons for 1 min to obtain a BN disc 1 cm in diameter and 3 mm in thickness. Either 20  $\mu$ L of water or epoxy resin droplet was placed onto the surface of the BN disc using 100  $\mu$ L micro-syringe and the contact angle of the droplet was measured every 5 sec for 60 sec. The test was performed at room temperature. Three readings were taken from each disc and each result was the average of the readings from two discs.

#### *3.3.6.7 Determination of the specific surface area of BN*

Nitrogen adsorption-desorption experiments were carried out on Quantachrome/Autosorb-1 Surface Area Analyzer. The specific surface area was calculated using the multi-point BET method. Three repeats were carried out for each sample.

#### *3.3.6.8 Determination of surfactant concentration*

Organic carbon contents of the surfactant solution before and after surfactant adsorption were examined using a SHIMADZU TOC-VCSH Organic Carbon Analyzer to obtain the TOC values. The amount of absorbed surfactant was then calculated from the TOC values.

#### *3.3.6.9 Determination of Thermal Conductivity of composite*

Thermal conductivity of the composites was measured using a Hot Disk Thermal Analyzer (Hot Disk AB, Uppsala, Sweden). A minimum of three individual measurements was performed for each specimen (20 x 20 x 3 mm<sup>3</sup>) with the sensor (3 mm diameter) placed between two similar slabs of material. The sensor supplied a heat-pulse of 0.03 W for 15-20 s to the sample and the associated change in temperature was recorded.

#### *3.3.6.10 Mechanical Property Testing*

Flexural testing was performed based on ASTM D 790-98 using the three-point bending tests. The testing was conducted by using Instron series IX Automated Materials Testing System model 3366 with load cell of 10 kN. The crosshead displacement rate was set at 5 mm/min. The specimens used for flexural testing were bars of rectangular cross section (flatwise) with a length of 60 mm and width of 14 mm. Three specimens were tested for each sample and the average value was reported

Impact strength was determined using a Pendulum Impact Tester (Zwick, Germany) and the testing method was in accordance with ASTM D-256. For each sample, five specimens measuring 63.5 x 12.7 x 3 mm<sup>3</sup> were tested and the average value was reported.