

CHAPTER II

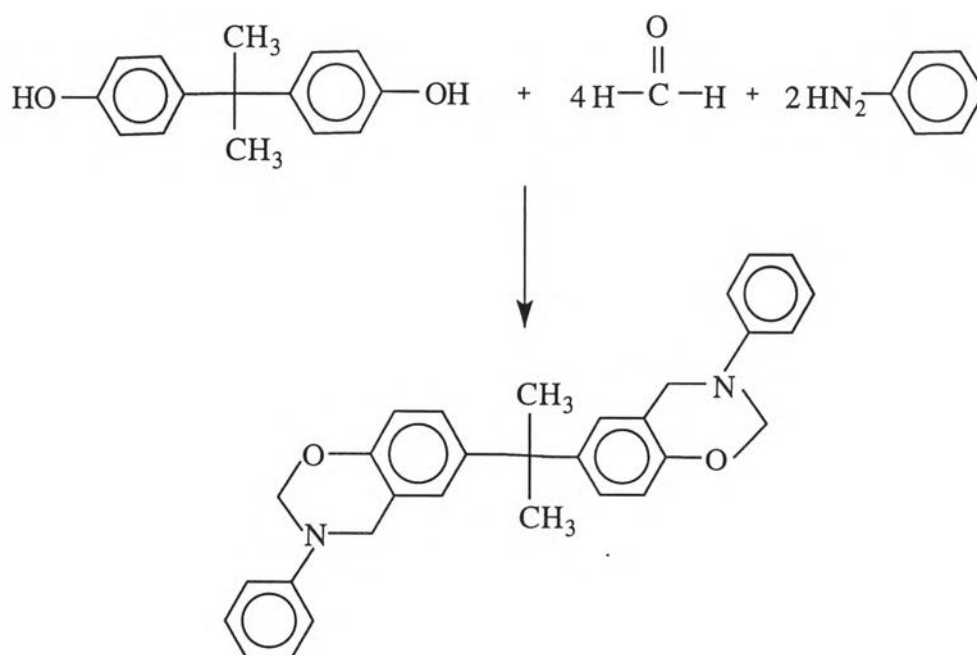
EXPERIMENTAL

2.1 Materials

Formaldehyde in 37 % aqueous solution was purchased from J.T.Baker. Dioxane and diethylether were bought from Ajax. Bisphenol-A, aniline and other chemicals were supplied by Aldrich. All chemicals were used as obtained.

2.2 Reaction Scheme

Synthesis of benzoxazine based on bisphenol-A and aniline (B-a) monomer is shown in the following scheme.



2.3 Synthesis Procedure

A mixture of 0.4 mol of formaldehyde (32.43 g) and 40 ml dioxane was added in a three-necked flask equipped with a thermometer and dropping funnel and cooled by an ice bath to keep the temperature below 10 °C. Aniline, 0.2 mol (18.6 g) in 10 ml dioxane, was slowly added through a dropping funnel. The mixture was stirred magnetically for 10 minutes before adding the solution of 0.1 mol bisphenol-A (22.8 g) in 50 ml dioxane. A condenser was then connected, the ice bath was replaced with a preheated oil bath, and the mixture solution was allowed to reflux for 6 hr.

After the reaction was complete, the solvent was removed by a rotary evaporator. The viscous fluid was purified by repeatedly washing with 3N NaOH solution to eliminate any phenolic structures. The reaction products were washed several times with water to eliminate any unreacted formaldehyde or aniline and dried over sodium sulfate. Evaporating the ether resulted in a viscous fluid at room temperature. The ether and unreacted amine were further removed in a vacuum oven for 4 hr.

2.4 Characterization

The composition and structures of as-synthesized and purified B-a were characterized by size exclusion chromatography (SEC) and Fourier transform infrared spectroscopy (FTIR).

The SEC chromatograms were obtained on a Waters 486 equipped with a Styrogel column of molecular weight ranging from 50-100,000 with

a flow rate of 1 ml/min and an ultraviolet absorption (UV) detector fixed at 254 nm.

FTIR spectra were obtained by Fourier transform infrared spectrometer (Bio-Rad Model 5A) with 4 cm^{-1} resolution. The frequency range was $4000\text{-}400\text{ cm}^{-1}$. The detector was a deuterated triglycinsulfate (DTGS) with the specific detectivity, D^* , of $1 \times 10^9\text{ cm.Hz}^{1/2}.\text{W}^{-1}$. The B-a was mixed with KBr powder and pressed into pellet.

2.5 Mechanical Testing

The mechanical test for adhesive in this work is single lap shear test according to the ASTM D1002. The equipment used is the Instron model 5583 with load cell 25 kN and crosshead speed of 1.3 mm/min for room temperature test and the Instron Series IX Automated Materials Testing System 1.07 with load cell 25 kN and crosshead speed 1.3 mm/min for 150 °C testing temperature.

Materials

1. Aluminum coupon 6063 (2.5 cm. x 11.5 x 0.3 cm)
2. Benzoxazine based on aniline (B-a)
3. Benzoxazine based on methylamine (B-m), obtained from the Department of Macromolecular Science, Case Western Reserve University
4. Amine -terminated butadiene/acrylonitrile (ATBN) (from 3M Company)
5. Gamma-aminopropyltriethoxysilane (γ -APS) (from Siam Chemical Company)

Procedure

The 6063 aluminum coupons were mechanically polished, soaked in acetone bath, washed in degreasing solution and rinsed with water. These aluminums were then treated with 0.1 % γ -APS (gamma-aminopropyltriethoxy-silane) to enhance surface adhesion for 30 min. After this, they were taken out and dried for half day. They were then heated at 110 °C for 15 min.

Polybenzoxazine was then spread onto one end of the aluminum coupon to cover an area of 1 sq.in. The adhesive was cured on compression molding machine. The curing temperature was increased stepwise from 125,150, to 175 °C with the curing time of 30 min at each step. Another aluminum coupon was then placed on the first one over the area covered by the adhesive when the adhesive was sufficiently viscous. Then the coupons were compressed with very slight pressure and the adhesive was further cured at 190 °C for 30 min and another 1 hr at 200 °C.

To improve the strength of the polybenzoxazine adhesives, the amine terminated butadiene acrylonitrile (ATBN) was mixed with the adhesives at 2, 5, 10, 15, 20 % by weight. The specimens were prepared as mentioned above except that the curing temperatures in this case were 125, 150, and 165 °C for 30 min, and 185 °C for 1 hr.

To study the elevated temperature adhesive strength, the B-m specimens were prepared without adding ATBN. The curing conditions were the same as described above.

2.6 Corrosion Investigation

The corrosion inhibition on copper was investigated. Copper plates (2.5 x 5 x 0.3 cm) were mechanically polished with sand paper #2400 and diamond paste 1 micron, washed with acetone in ultrasonic bath, rinsed with dilute hydrochloric acid and distilled water, and dried with a stream of air. B-a was dissolved in chloroform, solution cast onto metal substrates and air dried. Film thickness was calculated based on the concentration of the solution, density of the B-a, and the area of metal surface. In this study, 200 nm thick films were used. The coated metals were exposed to water vapour in a beaker filled with distilled water and kept in an oven at 80 °C. The spectrum was taken every 24 hours. Surface reflection spectra were obtained by subtracting the spectrum of a clean copper plate from that with B-a film. The reflection-absorption attachment (Harrick Scientific) was mounted on a Bomem Michelson MB Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector with a specific detectivity, D^* , of $1 \times 10^{10} \text{ cm Hz}^{1/2} \text{ W}^{1/2}$. Spectra were collected with 400 scans at 4 cm^{-1} resolution. The angle of incidence used was 75° .