

## CHAPTER III

### LITERATURE REVIEW

The following literatures reported the various environmental effects on the mechanical and thermal properties on fiber reinforced epoxy composites.

Clarke (1985) studied the aging in cured epoxy castings and its relevance to the fracture toughness testing. Epoxy resin employed was D.E.R. 383 liquid epoxy resin mixed with 4,4'-methylenedianiline (MDA), 99%. The mixture was poured into an aluminium sheet mould. Fracture toughness had a tendency to increase when the time interval after the preparation of casting increased. The fracture energy was found to increase by two folds after aging at 25°C, 50% RH for 150 days although normally physical aging had never been anticipated to increase the fracture energy. A possible explanation was attributed to the possibility of moisture absorption in the composites. Such absorption could be investigated simply by measuring the  $T_g$  and the fracture energy after physical aging. However, restoration of the original measured values, both the  $T_g$  and the  $G_{Ic}$ , was observed after four days of drying at 70°C under full vacuum. This indicated that plasticization by moisture absorption led to the changes in the  $T_g$  and in the  $G_{Ic}$ . Furthermore, different resin-hardener combinations responded differently to the presence of moisture.

Truong and Ennis (1991) determined the effect of physical aging on the fracture behavior, yield stress and Young's modulus of unmodified and rubber-modified epoxy resin at two aging temperatures and different displacement rates. The epoxy resin used was DGEBA cured with piperidine. The liquid rubber was carboxyl-terminated random copolymer of butadiene and acrylonitrile (CTBN). The samples were aged in a laboratory oven filled with nitrogen. The aging temperature was 60 or 80°C for periods up to 35 days. The results showed that yield stress increased during physical aging. This increase was roughly proportional to the endotherm peak of enthalpy

relaxation. Nevertheless, a significant increase in the modulus was observed in unmodified and modified epoxies with low rubber content of 5 phr aged at 60°C. Moreover, compressive yield stress was greater for the composites with low rubber content. Fracture toughness was found to decrease to 40-50% of the unaged ones for the unmodified and rubber modified epoxies during an aging period of 35 days. This meant that physical aging did not affect the fracture toughness for the system modified with rubber.

Won Ho Jo and Kyoung Jin Ko (1991) studied the effects of physical aging on the thermal and mechanical properties of an epoxy polymer with different amine/epoxy ratios. The epoxy resin and the curing agent utilized were DGEBA and ethylenediamine (EDA) respectively. Physical aging was simulated in the convection oven at the temperature of 20°C lower than the  $T_g$ 's for different periods of time. They found that the aged specimen exhibited a lower glassy state thermal expansion coefficient than the unaged one because the aged specimen had less free volume. In addition, the density of the aged specimen showed a higher value than that of the unaged ones since the aged epoxy had a smaller free volume than that of the unaged. The Young's modulus was found to increase as the density increased. This behavior showed that density was an important factor to the Young's modulus at glassy state. Summarily, the determining factor of glassy state modulus was the packing density, not the crosslink density or the average molecular weight between crosslinks ( $M_c$ ). The yield stress of an aged specimen appeared to be related to the packing density, like in the case of the Young's modulus. In the quenched state, the yield stress seemed to be more related to the crosslink density. Thus, in the lower free volume state, the major factor that determined the properties of epoxy was the packing density. However, in the state of adequate free volume, the major factor that determined the properties of cure epoxies was the crosslink density.

De Neve and Shanahan (1993) investigated the degradation of DGEBA crosslinked with dicyandiamide (DDA) and contained fillers under the combined effects of elevated temperature and humidity. The composites



were subjected to aging at 40, 50 and 70°C and 100% relative humidity. Viscoelastometric studies were performed after various periods of exposure. The absorption of water caused was found to decrease in the  $T_g$ , specifically 1% absorption of water led to a roughly 8°C reduction in the  $T_g$ . This behavior indicated the plasticization of polymer. There was also a reduction of the Young's modulus in the glassy and rubbery states after aging. The modulus in the rubbery state could be related to the average molecular weight between crosslink ( $M_c$ ). Its reduction disclosed an essential degree of molecular chain scission. Thus, it could be concluded that the hygrothermal aging of the epoxy resin guided both to plasticization of the polymer (a physical effect) and chain scission (a chemical effect) accompanied by degradation of the hardener.

Maddox and Gillham (1997) studied the rate and effects of isothermal aging of a fully cured epoxy-amine/glass fiber composite material. The thermoset system employed for this physical aging experiment was a miscible mixture of DGEBA and crystalline trimethylene glycol di-*p*-aminobenzoate (TMAB) as amine curing agent. This mixture was coated on a heat-cleaned glass fiber braid. Subsequently, data were collected through out a sequence of temperature scans and an isothermal aging temperature segment for an aging time of 600 min. This pattern was repeated for aging temperature ranging from -180 to 200°C. Maddox and Gillham found that the relative rigidity seemed to increase linearly with the log of aging time during isothermal aging. The slope of this curve represented the aging rate. Furthermore, it was discovered that the aging rate was raised when the aging temperature approached the  $T_g$  but it was zero when the aging temperature exceeded the  $T_g$ . From the effect of aging time, it was found that aging rate increased with the aging time. An investigation on the  $T_g$  of the aged composite revealed that the  $T_g$ 's did not appear to be affected by most aging temperature. They seemed to have been more influenced in the case of isothermal aging at the aging temperatures near the  $T_g$ 's. The majority of the isothermal aging effect could be almost totally eliminated by heating to a temperature above the aging temperature but below that of the  $T_g$ .

Siddaramaiah *et al.* (1999) studied the effect of aggressive environments on glass fiber reinforced epoxy composites that were made from diglycidyl ether of bisphenol A (DGEBA) and diethyl triamine (DETA) as hardener. The composites were exposed to different aggressive environments, for example, heat aging, humidity, lubricating oil and seawater. The mechanical properties tested were the tensile and the flexural properties. This research revealed a reduction in the mechanical properties of the composites treated with different chemical reagents. Debonding or deformation of bonds was believed to have taken place at the epoxy-glass fiber interface. The exposure of the specimens to distilled water and seawater showed a reduction in the mechanical properties as well. This was due to the moisture absorbing functional groups such as the residual epoxide and/or primary amines in amine network. For heat aging, a slight improvement and retained mechanical properties were remarked at the aging temperature of 70 and 100°C, respectively. However, much deterioration of the mechanical properties was observed in the case of 120°C heat aging. This was owing to the weakening interaction between the epoxy matrix and the glass fiber or a reduction in crosslink density of the composites. Furthermore, the  $T_g$ 's were raised after heat aging at 70 and 100°C because there was an increase in the crosslink density. However, the  $T_g$  was found to decrease at the 120°C heat aging. This was attributed to be due to the degradation of the epoxy matrix or weakening of the interaction between the epoxy matrix and the glass fiber.

Chen *et al.* (2001) explored the mechanical properties of epoxy resin utilized for reinforcement of bridges and buildings when the resin was contaminated with water in outdoor construction. The epoxy resin used was DGEBA with a mixture of polyoxipropyldiamine, cyclohexan-diamine, adipic acid dihydrazide and phenols as a hardener. The epoxy resin, the hardeners and water were mixed until a uniform solution was found. Then, the mixture was transferred to a spectroscopic cell that had been thermostated in advance. The thermostat was controlled manually to keep the cell at a given temperature. A test specimen was kept at 20°C for 7 days before testing. The mechanical properties examined were the ultimate tensile strength, the



flexural strength, the adhesive shear stress, the compression surrender strength, the impact strength and the hardness. This research showed that all of the aforementioned strength of the epoxy resin gradually diminished with an increase in the water content.

Lu *et al.* (2001) studied the effects of moisture on an epoxy molding compound. Mechanical properties, temperature transition and thermal degradation behavior were investigated. The resin used in this research was DGEBA that contained acid anhydride hardeners and a filler. Specimens were immersed in a water bath at 30°C. The tensile strength and the  $T_g$  were measured. The experimental results disclosed that the absorbed water plasticized the epoxy composite and acted as a crazing agent. Consequently, the tensile strength decreased with the time of immersion in water. The  $T_g$  was found to diminish at the early stage but it approached the equilibrium after several days. Moreover, the TGA results under an oxygen atmosphere indicated that a decomposition of the epoxy composite was composed of two independent steps. They consisted of a thermal degradation and a thermal oxidation.

Ivanova *et al.* (2001) studied the effect of hydration-dehydration cycling on the dynamic mechanical properties of a DGEBA cured with dicyandiamide, toughened with carboxyl-terminated butadiene acrylonitrile rubber. The composites were exposed to deionized water or 5% w/w NaCl solution in sealed jars maintained at constant temperature of 65°C in an electronically controlled oven. At chosen times, the entire sets of specimens were removed from the deionized water and then placed in an oven at 65°C with silica gel to allow desorption. The changes in the mechanical spectrum of the composites were detected. They found that water absorption at a weight fraction of up to 4.3% led to a reduction in the  $T_g$ . This was due to the plasticization of the polymer matrix. After dehydration, the  $T_g$  did not recover its original value owing to a residual amount of water trapped within the matrix.

Cascaval *et al.* (2002) characterized a semi-interpenetrating network synthesized from polyurethane (PU) and epoxy maleate of bisphenol A (EMBA). The influence of UV irradiation was investigated by an instrument equipped with a low pressure mercury lamp of  $30 \text{ W/m}^2$  in intensity, and 254 nm in wavelength at room temperature, in air. Their work indicated that the initial modulus of elasticity, the hardness and the resistance at break were much improved after the UV exposure. This was due to some additional crosslinks produced by UV radiation. Also, the variation of the mechanical properties with the thermal treatment could be observed. A decrease of the mechanical properties was found, they were probably induced by some degradation process.



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