

CHAPTER III

LITERATURE REVIEWS

Polybenzoxazine is a newly invented thermosetting polymer family with interesting properties as high performance, cost competitive matrix for composite materials [X. Ning and H. Ishida, 1994]. The developed benzoxazine resins offered greater molecular design flexibility than conventional phenolic resins. They do not release any by-product during curing reactions and there were no solvent other than for the solvency which the reactants may had for each other. In addition, the polybenzoxazine was found to exhibit excellent mechanical and thermal properties with good handling capability for material processing and composite manufacturing, e.g. having the glass transition temperature above 190°C, a tensile modulus of 3.2 GPa, and tensile strength of 58 MPa which were higher value when compared to epoxy (165°C, 2.7 GPa and 59 MPa) and phenolic resin (121°C, 3.8 GPa and 48 MPa, respectively).

Beside the inherent molecular design flexibility of a benzoxazine resin, the resin has reported to offer an outstanding capability to be alloyed with various existing resin systems such as phenolic novolac resin, urethane, and epoxy resin. S. Rimdusit and H. Ishida (2000) investigated ternary systems of benzoxazine, epoxy and phenolic resins. In this resin hybrid systems, benzoxazine resin was reported to impart thermally curable, low water uptake, high char yield, and excellent mechanical strength to the material while epoxy was used mainly to reduce the melting point and the viscosity of the ternary mixture. Finally, phenolic novolac functioned as a curing accelerator to the ternary systems. The results indicated that a glass transition temperature of the ternary system as high as 180°C can be achieved based on the three species of the starting monomers used. The fully cured polymer mixtures show relatively high degradation temperature, reported at 5% weight loss, i.e. up to 370°C. The char yield of the ternary systems increase significantly compared with the pure epoxy. This is due to the fact that both the

polybenzoxazine and the phenolic novolac are known to render higher char yield compared to the epoxy resin.

Phenolic resin is one of the well-known resins that are widely used for fire resistant purposes. Thermal stability and flammability of phenolic novolac resin cured with formaldehyde and hexamethylenetetramine (HMTA), were studied by R. Antony and C.K.S. Pillai (1994). Using thermogravimetric analysis (TGA) and limiting oxygen index analysis, respectively. The TGA thermograms (in nitrogen) of phenolic novolac showed very high char residue up to 62% at 600°C. Moreover, the LOI value of the phenolic novolac is 35 which is considered as a highly fire resistant, self-extinguishable system. These indicated that phenolic novolac can be used satisfactorily for high char yield and high flame resistant applications.

As a consequence, phenolic resin has been blended with other thermosetting resin in order to improve the fire resistant characteristics of the base polymer. H.T. Chiu *et al.* (2000) studied thermal degradation and fire retardant behaviors of an interpenetrating network (IPN) of unsaturated polyester (UP) resin and a resole type of phenolic resin. Thermogravimetric analysis (TGA) was also used to monitor the degree of thermal decomposition of the UP/phenolic IPN structure and the change of the limiting oxygen index (LOI) was used to describe the variation of the combustion behaviors. The results by TGA showed the first stage of thermal decomposition shifted to the higher temperature for the UP/phenol IPN structure when compared with the neat UP. The char residue of the UP/phenolic alloys was found to be remarkably increased as the content of the phenolic resin increased. In addition, the LOI value of the alloys increased as the content of the phenolic resin increased. The LOI values of the systems rose from 20.3 in the neat UP to 26.5 in the neat phenolic resin. The phenolic resin was thus the effective resin system to improve fire resistant behaviors of the base UP resin.

Recently, the polymer alloys between benzoxazine (B) and phenolic resins of both the novolac (N) and the resole (R) types have been investigated [N. Jalongwongsha, 2003]. The experimental resoles revealed that fire resistant properties gave high values.

Glass transition temperature (T_g) can be raised to 178°C in the BR73. Char yield increased when resole increased from 30.71% in the polybenzoxazine to 58.63% in the pure resole BR19. Limiting oxygen index (LOI) increased with increasing resole content (from 26.8 in the polybenzoxazine and 30.9 in the BR55). Burning rate decreased from 25.08 mm/min in the polybenzoxazine to 5.19 mm/min in the BR55). While T_g of novolac type decreased when novolac increased. Char yield increased from 30.71% in the polybenzoxazine to 46.48 in the BN19. The LOI of the BN systems increases to 29.4 in the BN55. The rate of burning decreased from 25.08 mm/min in the polybenzoxazine to 5.46 mm/min in the BN55 system. The results indicated that the resole was slightly higher fire resistant ability than the novolac. However the resole had higher viscosity than the novolac, it was hard to processing. Although the novolac type gave lower flame retardation, it can improve fire resistant and also it can be decreased the curing temperature of the benzoxazine resin.

One major shortcoming of utilizing thermoplastics as a matrix for wood composites is a relatively low mechanical properties due to the poor compatibility between the hydrophilic woodflour filler and the rather hydrophobic thermoplastics matrices. S.I. Farid *et al.* (2002) investigated tensile and flexural properties of the woodflour-reinforced low density polyethylene composite. The experiments indicated that though the tensile strength, tensile modulus, flexural strength, and flexural modulus of the LDPE composite at 50% by weight of woodflour content were expectedly higher than those of the unfilled polymer, i.e. high as 12.6 MPa, 1.5 GPa, 19 MPa, and 1.05 GPa respectively, the values are significantly lower than those of the natural wood (i.e. flexural strength of 66 MPa). Furthermore, the results were somewhat scattered largely because of the less homogeneity of the filled systems. However, these results showed thermoplastic wood composites had low mechanical properties which was no suitable for using as matrix of composite system.

Thermosetting wood composites were reported to help solve the poor mechanical properties of conventional thermoplastic wood composites. J. L. Odell investigated mechanical properties of jute-filled polyester with 30% by weight jute. Tensile strengths

of composite were range of 26-45 MPa for transverse and longitudinal. While tensile modulus were range of 1.8-3.6 GPa. In addition, flexural strength and modulus were range of 46-61 MPa and 2.2-3.0 GPa. The results implied that composite made of matrix as thermosetting type improved the mechanical properties.

Thermosetting wood composites not only provide enhanced mechanical properties comparing to thermoplastic wood composites, but they also can help improve thermal properties of the composite. N.E. Marcovich *et al.* (2001) evaluated thermal degradation of composites made from an unsaturated polyester/styrene thermoset with woodflour filler. The degradation of the woodflours, the matrix, and the resulting composites was estimated by thermogravimetric analysis (TGA) in nitrogen environment. Thermogravimetry was shown to be sensitive enough to detect differences between the composites with different woodflour contents. The thermal degradation (at 10% weight loss) and the char yield (at 500°C) of the untreated woodflour were 248°C and 20.5% respectively, while those values of the matrix were 360°C and 4.5%. While, the composites made of the untreated woodflour at 40% by weight of the filler gave the expected intermediate degradation temperature and char yield to be 280°C and 20% respectively.

Polybenzoxazine wood composites have been recently investigated by C. Jubsilp (2000). The author investigated the effect of woodflour loading on thermal, mechanical and physical properties. The results indicated that the benzoxazine resin can be added up to 75% by weight of woodflour due to the low melt viscosity of the benzoxazine resin. For mechanical property, the flexural modulus value was 7.0 GPa in 75% by weight of woodflour. Glass-transition temperature (T_g) increased with increasing woodflour content up to 220°C in 75% by weight woodflour content. For water uptake, 75% by weight of woodflour-filled polybenzoxazine had low water absorption value, for example, the value was 6% at 24 hour time period. From above results, the benzoxazine resin was to suit for making as matrix of the wood-substituted composites.