

CHAPTER II

LITERATURE SURVEY

2.1 Benzoxazine

In recent years the benzoxazine-based family of phenolic resins has been developed and attracted significant attention. Polybenzoxazine has excellent properties commonly found in the traditional phenolic resins such as heat resistance, good electrical properties, and flame retardance. In addition, the molecular structure of benzoxazine compounds were designed with great flexibility and it can be synthesized from inexpensive raw materials, cured without strong acid or alkaline catalyst requirement and does not release by products during polymerization as common phenolic resins do (Ning and Ishida, 1994a & 1994b). The curing reaction of the benzoxazine precursor is autocatalytic (Rodrigues and Ishida, 1995). The phenol structures with free ortho position in the precursor have a catalytic effect and a suitable catalyst can decrease the induction time and increase the reaction rate.

Furthermore, polybenzoxazine has unique properties not found in the traditional phenolic resins. For example, the ring opening polymerization of benzoxazine occur with either near zero shrinkage or a slight expansion upon curing, polybenzoxazine exhibit excellent dimensional stability because of the ring opening mode of polymerization and behave low rate of water absorption and low electrical capacitance which are suitable for electrical applications (Ishida and Allen, 1996a).

Ishida and Allen (1996b) studied the copolymer based on benzoxazine and epoxy. They found that the crosslink density and mechanical properties of polybenzoxazine can be greatly improved by the addition of epoxy to the polybenzoxazine network.

Molecular modeling results show that the oxazine ring in a benzoxazine molecule assumes a distorted semi-chair structure in terms of minimum energy model (Wang and Ishida, 1999). The resulting ring strain makes it possible for this kind of molecule to undergo ring-opening polymerization under certain reaction conditions. Moreover, the strong basicity of the N and O atoms by Lewis definition makes the ring very likely to be opened via a cationic mechanism. With certain

cationic initiators, benzoxazine ring can be opened and polymerized at room temperature and the resin with high glass transition temperature and high char yield can be obtained. In contrast, an anionic initiator and a covalent initiator did not give polymer product.

Dunkers and Ishida (1999) investigated the effect of carboxylic acids as catalysts on the curing reaction. The results showed that polybenzoxazines cured with strong carboxylic acids were inferior to those cured with weak carboxylic acids. By using a weak carboxylic acid, the ring opening polymerization was likely to be an auto-accelerated reaction where amino methyl ester were initially produced and then electrophilic aromatic substitution occurs.

The thermal decomposition of polybenzoxazine dimers was studied by TGA-FTIR and GC-MS (Hemvichian, 2002). For the benzoxazine dimers, the cleavages of C-N and C-C bonds result in the evaporation of amines, leaving no char. The unblocked-ortho-position benzoxazine dimers degrade into volatile compounds, some of which can undergo crosslinking and aromatization processes and form char.

2.2 Polybenzoxazine Composites

Due to the excellent properties of the benzoxazine resin, it was investigated as a polymer matrix in various composite materials.

Shen and Ishida (1996a) produced the carbon fiber reinforced benzoxazine composite through a prepreg process and compression molding. The composites had low void content and gave high char yield, more than 87%. The good adhesion between fiber and matrix resulted the good balance between strength and toughness. The composite showed good mechanical properties compete with polyimide composite and bismaleimide composite. In the same year the carbon fiber reinforced polynaphthoxazine composite was made though the same process and the good results were also obtained (Shen and Ishida, 1996b).

Mechanical properties of CaCO₃-filled benzoxazine were studied in the 0-30%wt. filler contents (Suprapakorn, 1996). Tensile strength and flexural strength decreased while their modulus increased with filler content. Surface treatment of

CaCO₃ with stearic acid caused the reduction of composite strength. Dynamic mechanical measurement also supported the static mechanical testing.

A natural fiber polybenzoxazine composite was investigated by Goodwin (1997). Polybenzoxazine paper composites were prepared using 8 plies of paper by compression molding technique. These composites showed high modulus and T_g and have better mechanical properties than that of the pure polymer. The cellulose fibers in paper controlled the water absorption property of the composite.

The boron nitride-filled polybenzoxazine was prepared for electronic packaging application (Ishida and Rimdusit, 1998). This filled polymer exhibited a very high thermal conductivity because of highly thermally conductive filler with a matrix resin which has low melt viscosity and good adhesion to the filler. The molding compound exhibited high and stable mechanical strength up to 200°C and low water absorption.

The delamination toughness of carbon fiber/polybenzoxazine composites was improved by rubber modification (Jang and Yang, 2000). For improvement of mode II delamination toughness, amine-terminated butadiene acrylonitrile rubber (ATBN) was more effective than carboxyl-terminated butadiene acrylonitrile rubber (CTBN).

A novel polybenzoxazine-montmorillonite hybrid nanocomposite was successfully prepared by Agag and Takeichi (2000). In order to obtain maximum interfacial adhesion, organophilic montmorillonite (OMMT) was prepared using octyl, dodecyl or stearyl ammonium chloride. These nanocomposites have higher thermal stability than pristine polybenzoxazine. The storage moduli and the char yield increased with increase in the montmorillonite content. This kind of nanocomposites was then developed by melt method and solvent method (Takeichi, 2002). In melt method, which employs the blending of benzoxazine and OMMT above the melting point of benzoxazine without solvent, a complete exfoliation clay layers was achieved. In solvent method, where an organic solvent was used in blending, the intercalated or exfoliated composites were obtained depending on type of solvents.

Dansiri *et al.* (2002) prepared kenaf fiber-reinforced polybenzoxazine composites. Benzoxazines based on bisphenol-A/aniline and phenol/aniline were

used. Polybenzoxazine composites with 20% fiber content showed lower flexural and impact strengths, but higher flexural moduli compared with unsaturated polyester composites with the same fiber content.

2.3 Surface Modifications of Natural Fibers

For the reinforcing material, natural fibers are increasingly being used as reinforcement of polymer matrix composites, therefore there are many studies reporting their properties and surface modification.

Alkalization is one easy method usually used in number of papers. Valadez-Gonzalez *et al.* (1999) showed that the alkaline treatment had two effects on the natural fiber: (1) it increased the surface roughness resulting in a better mechanical interlocking and (2) it increased the amount of cellulose on the fiber surface, thus increasing the number of possible reaction sites. In 2001, Min Zhi Rong *et al.* investigated the effect of fiber treatment including alkalization, acetylation, cyanoethylation, the use of silane coupling agent, and heating on the mechanical properties of unidirectional sisal-reinforced epoxy composites was investigated. In general, fiber treatments can significantly improve adhesion between fiber and matrix and lead to ingress of the matrix resin into the fibers, obstructing pull-out of the cells. The better flexural modulus and flexural strength of the long hemp/kenaf fibers-polyester composites were obtained after treatment with a 0.06M NaOH solution (Aziz and Ansell, 2004). Moreover, SEM results showed that alkalization could eliminate surface impurities.

Modification of cellulose fibers by silane coupling agent is one popular method. Valadez-Gonzalez *et al.* (1999) studied the adsorption isotherm of a silane coupling agent on the henequen fiber. It was found that the formation of polysiloxanes inhibited the adsorption of the silane onto the fiber surface, and the efficiency of the silane treatment was increased by the alkaline treatment. The adsorption of several prehydrolyzed alkoxysilanes onto cellulose fibers was investigated by Abdelmouleh *et al.* in 2002. Silanes were adsorbed on fiber surface as a monolayer and multiple layers but can be extracted out by ethanol. A heat

treatment, above 100°C, produced condensation reactions resulting in covalent bonding between cellulose and silanes.

Abdelmouleh *et al.* (2004) characterized the silane-modified cellulose fiber by diffuse reflectance infrared spectroscopy and contact angle measurements. Contact angle measurements revealed that the hydrophilic character of the cellulose fibers strongly decreased after the silane treatment. Using the silane coupling agent improved the degree of fiber-matrix adhesion (Herrera-Franco and Valadez-Gonzalez, 2004). It was found that the mechanical properties, specifically, the tensile strength did not improve significantly when high concentration of silane was used.