

CHAPTER II

LITERATURE SURVEY

Many reports have studied polybenzoxazines. Holly and Cope (1944) first synthesized oxazine-based phenolic resins by ring-opening polymerization of the aromatic oxazines through Mannich reactions from phenols, formaldehyde, and amines. During the 1950s and 1960s, Burke *et al.* synthesized many benzoxazines and naphthoxazines. Heat-cured polymers derived from benzoxazines were first achieved by Schreiber (1973). Riess *et al.* (1985) investigated the polymerization of monofunctional benzoxazines with and without phenol as an initiator, resulting in linear polymers having molar masses less than 4000. Ning and Ishida (1994a, 1994b) synthesized bifunctional benzoxazine precursors. These polyfunctional benzoxazines were found to exhibit excellent mechanical and thermal properties with good handling capability for material processing and composite manufacturing. Furthermore, they offered greater flexibility than conventional phenolic resins in terms of molecular design. They do not release by-products during curing reactions and there are no strong acid or alkaline catalyst requirements. Ishida and Rodriguez (1995a, 1995b) studied the curing kinetics of benzoxazine precursors based on bisphenol-A and aniline by differential scanning calorimetry (DSC). The curing of benzoxazine precursors was an autocatalysed reaction until vitrification was reached, when diffusion began to control the curing process afterwards. They also studied the effect of potential catalysts on the curing reaction of a new benzoxazine-based phenolic resin. They showed that the curing of benzoxazine precursors with suitable catalysts can effectively decrease the induction time for curing and increase the

reaction rate. Dunkers and Ishida (1995a, 1995b) reported on vibrational assignments of 3-alkyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazines through model compounds. They also reported on vibrational assignments of N,N-bis(3,5-dimethyl-2-hydroxybenzyl)methylamine resulting from ring opening polymerization of benzoxazine monomers.

Ishida and Allen (1996a) showed that the ring opening polymerization of polybenzoxazines occurs with either near-zero shrinkage or even a slight expansion upon cure. Dynamic mechanical analysis revealed that these candidates for composite applications possess high moduli and glass transition temperatures, but low crosslink densities. Furthermore, these materials have a low rate of water absorption, low water saturation levels and are suitable for electrical applications. Liu and Ishida (1996) reported on synthesis methods, reaction conditions, side reactions, characterization, physical and mechanical properties of benzoxazine monomers and polymers. Shen and Ishida (1996c) synthesized polyfunctional naphthoxazines and characterized the products using NMR. It was shown that polynaphthoxazine could exceed epoxies and compete with bismaleimides in terms of mechanical and thermal properties. Ishida and Allen (1996b) compared the mechanical properties of copolymers based on benzoxazine and epoxy resins. The addition of epoxy resin to a polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and improves its mechanical properties. Copolymerization leads to a significant increase in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer with only a minimal loss of stiffness. Shen and Ishida (1996a, 1996b) developed and characterized high-performance carbon fiber reinforced benzoxazine composites. The composites showed good mechanical properties, could exceed bismaleimide composites and compete with polyimide composites in term of mechanical and thermal

properties, while exhibiting easier processability than polyimides. Moreover, a polynaphthoxazine composite with 60% by volume of carbon fiber was also successfully developed in order to attain a high-temperature resistant composite with good performance as well as processability. Dunkers *et al.* (1996) studied the X-ray crystal structure and hydrogen-bonding characteristics of N,N-bis(3,5-dimethyl-2-hydroxybenzyl)methylamine as a model dimer for benzoxazine-based phenolic resins. Ishida and Low (1997) studied the volumetric expansion of benzoxazine-based phenolic resin on curing. It was shown that the volumetric expansion of the benzoxazine resin is mostly due to the consequence of molecular packing influenced by inter- and intramolecular hydrogen bonding.

Ishida and Krus (1998) synthesized and characterized structurally uniform model oligomers of polybenzoxazine. The synthesis was made possible by modifying many of the synthetic methods used for similar phenol-formaldehyde model oligomers. Suprapakorn *et al.* (1998) studied the effect of Calcium carbonate (CaCO_3) on the static and dynamic mechanical properties of polybenzoxazine based on bisphenol-A and aniline. They found that tensile and flexural strength decreased while the modulus increased with filler content. Dynamic mechanical spectroscopy studies showed a higher loss modulus and a lower activation enthalpy of the specimen fabricated with surface treated CaCO_3 than those of the untreated one. Low and Ishida (1998) studied the thermal decomposition of polybenzoxazines based on bisphenol A and various aliphatic amines under a nitrogen environment. It was proposed that the Mannich base in polybenzoxazines plays a significant role in the thermal degradation of polybenzoxazines. Furthermore, they synthesized a silane coupling agent with a benzoxazine functional group. A series of nonpolar solvents resulted in a high yield of high-purity benzoxazine. The effectiveness of the silane coupling agent was evaluated by measuring the

interlaminar short-beam shear strength of silane-treated glass fiber-reinforced polybenzoxazine composites. Wirasate *et al.* (1998) reported the effect of temperature on hydrogen bonding of polybenzoxazines. It was found that temperature influences statistically distributed hydrogen bonding but has little effect on conformationally preferred hydrogen bonding below the glass transition temperature. The breakup of statistically distributed hydrogen bonding is influenced by the β -transition. Russell *et al.* (1998a, 1998b) studied the characterization and curing of a phenyl benzoxazine using ^{15}N solid-state NMR. The results showed that the polymerization progressed at a much higher rate at 200°C as opposed to 150°C, as expected. Moreover, they also studied the characterization and curing of a phenyl benzoxazine using ^{13}C solid-state NMR. The results from the cure studies indicate that the reaction kinetics are significantly different for the two cure temperatures of 150 and 200°C. Schnell *et al.* (1998) investigated hydrogen bonding in benzoxazine dimers by fast magic-angle spinning and double-quantum ^1H NMR spectroscopy. Ishida and Rimdusit (1998) investigated the thermal conductivity of boron nitride-filled polybenzoxazine and found that it exhibited a very high conductivity value at its maximum filler loading of 78.5% by volume. Kim *et al.* (1999) reported on the molecular characterization of the polymerization of acetylene-functional benzoxazine resins. Acetylene-functional benzoxazines polymerized in air resulted in higher char yield and thermal stability than when polymerized under an inert atmosphere. Dunkers and Ishida (1999) studied the reaction of benzoxazine-based phenolic resins with strong and weak carboxylic acids and catalysts using FTIR, NMR, and dielectric analysis.

There are many reports detailing studies of the modification of natural fiber surfaces to improve the compatibility of fiber with polymer matrix. Mukherjea *et al.* (1983) studied jute fiber composites with polyesteramide

polyol as the interfacial agent between fiber surface and resin. The strength of the polyester resin composite hardly changed while the strength of the composite prepared from epoxy resin significantly increased. Roe and Ansell (1985) reported on the mechanical properties of jute reinforced polyester composites. They showed that these properties all follow the rule of mixtures relationship. Composites with optimum properties were made with a jute fiber volume fraction of about 0.6. Zadorecki and Flodin (1985) studied the surface modification of cellulose fibers from pulp by using three types of triazines coupling agent consisting of octyl amino, methacrylate, and diallyamino in the molecular structures. It was observed that the last two coupling agents, which contain double bonds and can connect with the resin by covalent bonds, developed optimum strength values while the first one, which could not connect to polyester resin by covalent bonds, had reduced strength when compared to unmodified fiber. Zadorecki and Flodin (1986) studied the effects of improved interfacial adhesion on the environmental aging behavior of cellulose-polyester composites. They found that the fiber treatments did not induce any reduction in moisture content of the fibers at saturation. Whitening of the specimens were caused by the presence of debonding cracks in those specimens based on the untreated fibers or on fibers treated but not covalently bonded to the matrix. Zadorecki *et al.* (1986) studied the mechanical properties of cellulose fiber-reinforced polyester composites. It was concluded that cellulose-based composites have lower elongation at break, higher elastic modulus, and lower or equal tensile strength compared to the non-reinforced polyester sample. An indirect method for the determination of the elastic modulus of short-cellulose fibers using a micromechanical approach was proposed. The order of stiffness of different cellulose fibers can be estimated by measuring the bulk modulus of unbonded fiber systems. Stafford *et al.* (1987) studied the effect of the filler-treatment method on composite

properties. Two general methods are usually given for the incorporation of silane coupling agents: pretreatment of the filler or integral addition to the resin. It was concluded that superior flexural-strength properties were obtained with pretreated mineral filled polyester composites compared with integrally added methacryloxypropyltrimethoxysilane (MPS) at equivalent loadings. The performance differences were most pronounced at lower silane concentrations. Disadvantages of the integral-addition method are inefficient use of silane, incorporation of volatile by-products, prolonged mixing requirements, and the need for other additives. Varma *et al.* (1989) studied the mechanical properties and some characteristics of hybrid composites of glass and jute fabric modified by treatment with γ -aminopropyltrimethoxy silane, isopropyltriisostearoyltitanate, and tolylenediisocyanate, which were fabricated using unsaturated polyester resin. It was concluded that titanate treatment of jute fabric gives an improvement in mechanical properties and a better retention of mechanical properties in humid environments.

Ghosh and Ganguly (1993) compared the grafting of polyacrylonitrile and poly(methyl methacrylate) onto the fiber surface by using phenol and resorcinol formaldehyde resins. Results of the study showed that composites consisting of modified fiber and polyester resin had increased strength when both phenol-formaldehyde and resorcinol-formaldehyde resins were used. Chen and Porter (1994) showed that composites with kenaf fibers provide a promising way to improve the stiffness of polyethylene. The crystallization kinetics of PE in the composites suggested that the interfacial bonding between kenaf and PE appears to be unfavorable. Bledzki *et al.* (1996) studied methods of fiber modification for making natural fiber composites which are divided into two methods: (1) physical methods such as plasma method which changes the charges on the fiber surface, and (2) chemical methods by using coupling agents such as methylol compounds, triazine compounds, and silanes. These

coupling agents connect to the fiber by covalent bonds. Devi *et al.* (1997) modified pineapple leaf fiber (PALF) by using two types of silane coupling agent and by acetylation. The results of the study showed that silane coupling agent, which can connect to polyester resin by covalent bonds, developed optimum strength, while silane coupling agents which cannot connect to it by covalent bonds exhibited lower strength. Furthermore the optimum length of the fiber required to obtain PALF-polyester composites of maximum properties was found to be 30 mm at a fiber content of 30 wt%. Mitra *et al.* (1998) studied jute-reinforced composites by coating the fiber surface with phenol-formaldehyde resin. It was observed that the composite had higher strength but lower water absorption.

To date, there has been no papers reported on natural fibers for use as a reinforcement in polybenzoxazine resin. In this research, a study is made of the mechanical properties and water absorption of composites made from kenaf fiber and polybenzoxazine resin. The composites will be prepared using a resin transfer molding technique. Properties of polybenzoxazine composites will also be compared with that of conventional unsaturated polyester composites.