# CHAPTER I

INTRODUCTION

Composites, which is a heterogeneous substance consisting of two or more materials and the combination brings about new desirable properties, have many advantages over synthetic polymers and copolymers such as less density, reinforcement of the resin resulting in increased mechanical properties and size stability. Composites usually consist of polymer matrix, reinforcing material, and additives. For the polymer matrix, phenolic resins are widely used because of their good heat resistance, low flammability and low smoke generation. However, these kinds of resin have many problems. Those include need of strong catalysts, production of reaction byproducts during polymerization, poor molecular design flexibility and limited shelf life. Nowadays polybenzoxazine has been developed and studied as a novel class of phenolic resins to overcome the shortcomings of the traditional novolacs and resoles (Ning and Ishida, 1994, and Ishida and Allen, 1996). It has good dimensional stability, high heat resistance, low moisture absorption and no volatiles formation, thus polybenzoxazine is an attractive candidate for applications.

1.1 Benzoxazine

The benzoxazine ring is a six-membered heterocyclic ring with N and O as two of the constitutive elements. Benzoxazines are synthesized via Mannich condensation of phenol, formaldehyde and primary amine and polymerized by ring-opening polymerization as shown in Figure 1. The basic chemical repeat unit contains a phenolic and tertiary amine unit both of which have been considered the chemical groups responsible for good anti-flammability characteristics.
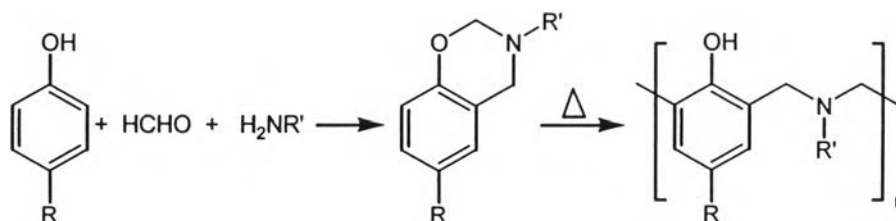
Figure 1.1 Synthesis of benzoxazine monomers and polybenzoxazine.

There are a number of possible isomeric benzoxazines depending on the relative positions of the two heteroatoms and the degree of oxidation of this oxazine ring system.

1.2 Sisal Fiber

Among the reinforcing materials of glass fiber, carbon fiber and aramid fiber, glass fiber is the most widely used because of its low cost and comparable mechanical properties. However, in recent years, there has been a growing interest for the use of natural fibers in composite applications, especially in the automotive industry. The properties of natural fiber compared with glass fiber are shown in Table 1.1.

Table 1.1 Comparison between natural fibers and glass fibers (Wambua *et al.*, 2003)

Property	Natural fibers (NF)	Glass fibers
Density	Low	Twice that of NF
Cost	Low	Low, but higher than NF
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO_2 neutral	Yes	No
Abrasion to machine	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Non biodegradable

Natural fiber-reinforced composites present many advantages compared to synthetic fiber-reinforced ones such as low tool wear, low density, cheap cost, availability and biodegradability. The principal advantage of natural fiber-reinforced polymer composites stems from their ability to absorb tremendous amounts of energy during impact fracture.

In this study, sisal fibers were used as the composite reinforcement. Sisal fiber is a leave fiber from *Agave sisalana*. It has round or crescent-shaped cross sections consisting of sharply polygonal ultimates containing large, rounded lumens (Lewin and Pearce, 1998). The fibers compose of 73.1% cellulose, 13.3% hemicellulose, 11.0% lignin, 0.9% pectin, and 1.6% extractives (Mark *et al.*, 1987). This kind of fibers is cheaper and lighter than glass fiber. Compared with other natural fibers growing in Thailand, sisal fiber is the one that has relatively high strength, modulus and percent elongation at break as shown in Table 1.2.

Table 1.2 Properties of natural fibers in relation to E-glass (Wambua *et al.*, 2003)

Properties	E-glass	Sisal	Jute	Ramie	Cotton
Density (g/cm^3)	2.55	1.33	1.48	1.5	1.51
Tensile strength (MPa)	2400	600-700	400-800	500	400
E-Modulus (GPa)	73	38	10-30	44	12
Elongation at failure (%)	3	2-3	1.8	2	3-10

Generally, natural fibers are three-dimensional polymeric composites consisting of cellulose microfibrils in a natural amorphous phenolic polymer matrix of lignin, hemicellulose and small amounts of extractives and ash. The strength and stiffness of the fibers are provided by hydrogen bonds and other linkages. The overall properties of the fibers depend on the individual properties of each component.

Cellulose, which is the essential component of all plant-fibers, is a linear condensation polymer consisting of D-anhydroglucopyranose units joined together by β-1,4-glycosidic bonds. The mechanical properties of natural fibers depend on its cellulose type, because each type of cellulose has its own cell geometry and the geometrical conditions determine the mechanical properties. Hemicellulose is responsible for the biodegradation, moisture absorption and thermal degradation of the natural fiber. On the other hand, lignin (or pectin) is quite thermally stable and responsible for thermal degradation at higher temperature. Lignin serves the dual purpose of binding and stiffening wood fibers, it imparts rigidity to the cell walls and acts as a binder between wood cells, creating a composite material that is

outstandingly resistant to compression, impact, and bending. The lignin component is also responsible for the characteristic color changes and responsible for the UV degradation of the fiber.

1.3 Surface Modifications of Natural Fibers

The performance and properties of composite materials depend on the properties of the individual components and their interfacial compatibility. The role of the matrix in a fiber-reinforced composite is to transfer the load to the stiff fibers through shear stresses at the interface. Insufficient adhesion between hydrophobic polymers and hydrophilic fibers results in poor mechanical properties of the composites. Adhesion between fiber and matrix can be attributed to some combination of the following mechanisms.

Adsorption and wetting. It is essential that the fibers be wet by the resin during the manufacturing process.

Chemical bonding. The strength of the final bond will reflect any chemical reaction that has occurred between fiber, fiber coating, and resin during processing.

Mechanical adhesion. Bonding of the matrix to the irregular surfaces characteristic of some carbon and organic fibers can occur via mechanical interlocking.

Interdiffusion. It is possible for the molecules of one surface to diffuse into the other, resulting in the formation of a bond.

Electrostatic attraction. Adhesion between fiber and resin may be promoted, at least initially, by a difference in electrostatic charge between the two materials.

The quality of the fiber–matrix interface is significant for the application of natural fibers as reinforcement fibers for plastics. Physical and chemical methods can be used to optimize this interface (Bledzki and Gassan, 1999). These modification methods are of different efficiency for the adhesion between matrix and fiber.

1.3.1 Physical Methods

Physical methods, such as stretching, calendering, thermotreatment, and the production of hybrid yarns do not change the chemical composition of the

fibers. Physical treatments change structure, surface morphology and mechanical properties of the fiber and thereby influence the mechanical bonding to polymers.

Electric discharge (corona, cold plasma) changes the surface energy of the cellulose fibers and in case of wood surface activation increases polarity fiber surface (Gassan and Gutowski, 2000).

Mercerization is an alkali treatment of cellulose-fibers to produce great swelling with resultant changes in the fine structure, dimension, morphology and mechanical properties.

1.3.2 Chemical Methods

This method brings compatibility by introducing a third material that has properties intermediate between polarized cellulose fiber and hydrophobic polymers.

1.3.2.1 Change of surface tension

The surface energy of fibers is closely related to the hydrophilicity of the fiber. This method decreases hydrophilicity by introducing hydrophobic group to cellulose fibers with, for example, stearic acid (Zafeiropoulos *et al.*, 2002) and aminofunctional silanes (Valadez-Gonzalez *et al.*, 1999).

1.3.2.2 Impregnation of fibers

A better combination of fiber and polymer is achieved by impregnation of the reinforcing fabrics with a polymer compatible to the polymer matrix. For this purpose polymer solutions or dispersions of low viscosity are used. The lack of solvents limits the use of this method.

1.3.2.3 Chemical coupling

This method improves the interfacial adhesion by treating the fiber surface treated with a compound that forms a bridge of chemical bonds between fiber and matrix.

Graft copolymerization. This reaction is initiated by free radicals of the cellulose molecule which are then treated with a suitable solution (compatible with the polymer matrix), for example vinyl monomer, acrylonitrile (Ghosh and Ganguly, 1993), and maleic anhydride (Mishra *et al.*, 2000). After this treatment the surface energy of the fibers is increased to a level much closer to the

surface energy of the matrix. Thus, a better wettability and a higher interfacial adhesion are obtained.

Treatment with isocyanates. Isocyanate containing chemical groups compatible with a resin form covalent bonds with cellulose hydroxyl groups. The mechanical properties of composites can be improved by this treatment (Sreekala and Thomas, 2003).

Organosilanes as coupling agents. Most of the silane coupling agents can be represented by R-$(CH_2)_n$ -Si(OR')$_3$ where n = 0–3, OR' is the hydrolyzable alkoxy group, and R the functional organic group reacting with the polymer. This could be a co-polymerization, and/or the formation of an interpenetrating network. Alkoxysilanes undergo hydrolysis, condensation and the bond formation stage. Silanols with hydroxyls of the fiber surface can also form polysiloxane structures (Plueddemann, 1982).

1.4 Scope of Research Work

The interest of using cellulose fibers as reinforcement in both thermoplastic and thermosets is constantly growing. However, very limited studies have been reported in the literature on the use of cellulose fiber in polybenzoxazine and no one has investigated the effect of surface modification on the mechanical properties of natural fiber-polybenzoxazine composites. In this research work, the diamined-based benzoxazine monomer was synthesized. Sisal fiber was incorporated in a polybenzoxazine/epoxy resin matrix to form a unidirectionally reinforced composite. The surface treatments with alkaline and a silane coupling agent were applied to this system and the effect of treatment on the mechanical properties of the composites was studied.