

CHAPTER I

INTRODUCTION

Phenolic resin was the first synthetic polymer derived from a condensation of phenol and formaldehyde in the presence of acid or alkaline catalysts. The first commercial phenolic product was developed by Baekeland in 1907, and up to now is one of the most widely used thermosetting resins.

The major advantages of phenolics are ; high temperature resistance, dimensional stability, flame retardancy, low smoke emission, chemical resistance, and electrical insulation properties. Thus, traditional phenolic resins have been used in many applications such as construction and automotive industries, electrical and electronic devices, coatings, adhesives, and aircraft interiors.

However, traditional phenolic resins still have many shortcomings. These include the need of strong acid or alkaline catalysts in the synthesis step, the release of by-products such as water or ammonia during the condensation polymerization, volumetric shrinkage during the processing step, and their brittleness and limited shelf-life. Since the structure of typical phenolic resin is mainly dependent on phenol and formaldehyde, which cannot be varied so much, it is difficult to overcome these problems.

Oxazine-based phenolic resins are an alternative to traditional phenolics. It is synthesized by the ring-opening polymerization of aromatic

oxazines, which can be modified by changing the functional groups on the backbone. Furthermore, it does not produce reaction by-products and can be synthesized without strong acid or alkaline catalysts.

Aromatic oxazines were first synthesized in 1944 by Holly and Cope through Mannich reactions from phenol, formaldehyde, and amines. Subsequently, Burke and co-workers (1949) synthesized many benzoxazines and naphthoxazines and found that benzoxazines reacts almost specifically with the ortho position of phenolic component to form a dimer with methylene-amine-methylene bridge structure. The low molecular weight oligomers from benzoxazine were first reported by Schreiber (1973). Reiss and co-workers (1985) investigated the polymerization of mono-functional benzoxazines with and without phenol as an initiator, while a linear polymer with low molecular weight, below 4,000, was obtained.

In 1994, Ning and Ishida made a significant advancement to this aromatic oxazine polymer by synthesizing polyfunctional benzoxazines via a thermally initiated ring-opening mechanism to obtain high molecular weight polybenzoxazines. It should be noted that polyfunctional benzoxazines offer tremendous molecular design flexibility by the variation of functional groups. Furthermore, the synthesis step does not produce any reaction by-products and there is no strong acid or alkaline catalysts requirements. A unique property of benzoxazine resins is the near-zero shrinkage, even expansion sometimes, upon ring-opening polymerization (D.J. Allen, 1996 and H.Y. Low, 1997). Moreover, polybenzoxazines are also prepared from the other phenolic derivatives which are inexpensive and readily available raw materials as alternative materials to phenol.

Ishida et al. have shown that polyfunctional benzoxazines exhibit excellent mechanical properties. Physical and mechanical characterization revealed that these materials have high glass transition temperatures (T_g), high moduli, low water absorption, and good dielectric properties (D.J. Allen, 1996). Reaction mechanisms, crystal structures, and spectral assignments were studied through model compounds (J. Dunker, 1995). The mechanical, physical, and rheological properties of polybenzoxazines and their copolymers with epoxies have been measured (D.J. Allen, 1996). Copolymerization of polybenzoxazines with epoxies is another approach to develop composite materials. It is found that these materials showed improvements in T_g , flexural stress, and flexural strain at break. Kinetics studies of the curing system were performed using differential scanning calorimetry (Y. Rodriguez, 1995). High performance polybenzoxazine and polynaphthoxazine are successfully prepared using an autoclave process (S.B. Shen, 1996).

In conventional composites, the fibers are made of glass, aramid, boron, carbon and graphite. However, for maximum utilization, a matrix to embed such strong fibers is required to produce a strong and stiff product for engineering applications. The fiber reinforced composite may then achieve high strength and stiffness due to the fibers. However, price performance is one of the conditions to be considered together with the improvement of quality. In this case, low cost natural fibers may be used as reinforcements in polymer composites. Compared to inorganic fillers, the main advantage of these natural fibers is the reduction in weight of the composite due to the low density, whilst it provides high specific strength and modulus. Thus, natural fiber is an attractive alternative to other expensive fillers such as glass.

The chemical repeat unit of a cellulose macromolecule is β -D-glucose, which contains three hydroxyl groups (Figure 1.1). Cellulose is a long-chain polymer in the pyranose form linked together by 1,4' glycosidic bonds to form cellobiose residues which are the repeating units in the cellulose chain. The hydroxyl groups in cellulose structure form intramolecular hydrogen bonds and intermolecular hydrogen bonds between those cellulose molecules as well as with hydroxyl groups from the atmosphere.

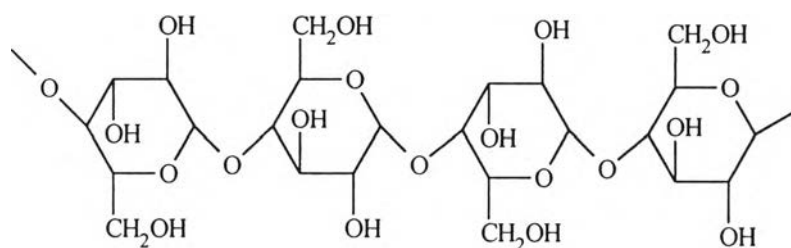


Figure 1.1 Structure of cellulose contains β -(1 \rightarrow 4)-D-glucose units.

Traditionally, phenolic resins are attractive for the reinforcing plastics industry, particularly with natural fibers. The hydrophilic structure of non-cured phenolic resins characterizes them as suitable materials for the impregnation of paper and cotton fabrics for use in the manufacture of electrical and decorative laminates, molded parts, filter paper and battery separators. Low molecular weight components, preferably mononuclear phenolic methylols, penetrate into the capillary cavities of cellulose fibers and fill the cavities, whereas resins of higher molecular weight are applied for coating the fibers and make them water-repellent. During cure, a chemical reaction between cellulose and phenolic methylol groups probably occurs which contributes to the increased water- and chemical resistance.

As a novel type of phenolic resins, benzoxazines are found to be excellent matrices for both glass fiber (H.Y. Low, M.S. Thesis) and carbon fiber reinforced composites (S.B. Shen, 1996). Taking the points mentioned above into consideration, the paper reinforced polybenzoxazine composite is expected to provide advantages and specific properties that have never been found in traditional paper reinforced phenolic materials.

The objective of this study is the development of natural fiber reinforced polybenzoxazines. In this work, two benzoxazine monomers are used to prepare paper composites which are benzoxazines based on bisphenol-A with aniline (B-a) and bisphenol-A with methylamine (B-m). Both monomers are characterized by FTIR (Fourier transform infrared spectroscopy). The density and water absorption values are measured systematically. Dynamic mechanical analysis (DMA) is carried out to study the dynamic mechanical properties of the composite in terms of storage modulus (G'), loss modulus (G'') and T_g . Flexural tests are also carried out to evaluate the mechanical properties of the composites. Scanning electron microscope (SEM) was also used to study the fiber/matrix interfacial property.