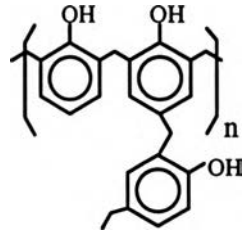
CHAPTER I

INTRODUCTION

1.1 Phenolic Resins



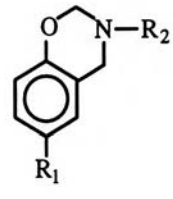
(1)

Phenolics (1), thermosetting resins, are derived from a condensation of a phenol and an aldehyde, especially formaldehyde, in the presence of an acidic or basic catalyst. They were developed over 75 years ago by Bayer. In 1905, Backeland initiated the first commercial phenolic product by using phenol and formaldehyde as starting materials. He also established the important differences between acid and alkaline catalyzed products, as well as the importance of excess phenol and formadehyde in producing intermediates.

Phenolic resins are employed in a wide range of applications from commodity construction materials to high chemical and temperature resistance, flame retardance and dielectric insulation and also the relative inexpensive raw materials.

Nevertheless, phenolics also have several undesirable drawbacks. There is a great dependence on catalyst in the reaction either by acids yielding low molecular weight prepolymer so called novolacs or by base leading to resoles. Toxicity by ingestion, inhalation and skin absorption of phenol is significant. Water as a by-product is generated upon curing, usually in the form of steam because of high processing temperature. Apart from having limited shelf life, phenolics are too brittle in pure form.

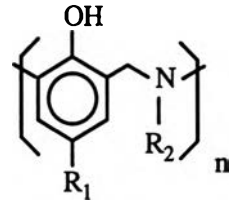
1.2 Benzoxazine



(2)

A phenolic derivative, a primary amine and formaldehyde from a ring compound via Mannich reaction, is termed benzoxazine (2). Benzoxazine based phenolic resin overcomes those drawbacks of the traditional phenolics. It was found to react with the ortho position of a phenolic compound to form a dimer with methylene-amine-mathylene bridge structure. Its processe has no volatiles during curing because it proceeds by ring opening polymerization. Due to the synthesis by Mannich condensation of a phenol, formaldehyde, and an amine, they do have much more molecular design flexibility than a novolac and resoles materials. Benzoxazine was first synthesized by Holly and Cope (1944). Ning and Ishida (1994) synthesized polyfunctional benzoxazines which polymerized to higher weight crosslinked polybenzoxazines possessing excellent mechanical and physical properties.

1.3 Polybenzoxazine



(3)

The polybenzoxazines (3) are a newly developed class of thermosetting resins that are based on the ring-opening polymerization of benzoxazine precursors. A number of polybenzoxazine properties are superior to those of epoxy resins and conventional phenolics. Physical and mechanical characterization have revealed that these new materials posses high glass transition temperatures, high moduli, low water absorption values, and good dielectric properties, in addition to near-zero shrinkage or a slight expansion upon cure (D. J. Allen, 1994). It is also superior to conventional phenolic resin in process control since it releases no by-product during reactions. Furthermore, because of the low viscosity, it offers good processability for composite manufacturing.

1.4 Polybenzoxazine Filled with Calcium Carbonate Composite

For economical reasons, particulate inorganic fillers are often added to commercial thermoplastic and thermosetting resins. Calcium carbonate ($CaCO_3$) is the most widely used filler since it is available at low costs and produced in a broad range of particle size distribution. However, there is usually a trade-off involved with certainly important properties, such as toughness and strength, which usually deteriorate. In selecting a filler,

particle size must be considered. Filler of large particle size may tend to be filtered out from the resin flow through the reinforcing material during cure. This would result in an uneven distribution of filler.

The objective of this paper is to investigate the effect of $CaCO_3$ on the static mechanical and dynamic mechanical properties of a polybenzoxazine. This work also studies the role of the particle size of the filler and the effect of the interface on the properties of the composite including tensile modulus and yield stress analysed on the basis of theoretical predictions for two-phase systems. The degree of discontinuity in the structure is assessed on the basis of the stress concentration factor. Flexural properties and Izod impact strength values are also evaluated. Furthermore, the rheological behaviors of a purified benzoxazine monomer and 18% oligomer are studied to compare with a novolac resin, as well.