

# CHAPTER I

## INTRODUCTION

### 1.1 Background

Traditional phenolic materials, which are the condensation reaction products of phenol and formaldehyde, exhibit good heat-resistant, flame retardant, and dielectric properties. They are widely used in electrical devices, appliances, and construction. The use of inexpensive raw materials is of particular attraction. While the advantages of phenolic resins are the main reason for the longevity of these resins, they have also shortcomings. These include release of water and ammonia during polymerization, poor molecular design flexibility, poor shelf life, and brittleness.

Polybenzoxazines offer an alternative to traditional phenolic resins and other thermosetting resins such as epoxies and unsaturated polyester resins. Benzoxazine was first synthesized by Holly and Cope in (1944) from a phenolic derivative, a primary amine and formaldehyde. However, the use of benzoxazine as precursor to phenolic resin did not start until when Shreiber (1973) reported the formation of oligomeric phenolic compounds made from benzoxazines. Riess et al. (1986) studied the synthesis and reaction of monofunctional benzoxazine compounds. They reported that monofunctional benzoxazines formed only oligomeric materials. They theorized that the side reactions of the ring opening compete with chain propagation leading to low molecular weight.

While benzoxazine chemistry is not new, the physical and mechanical properties of polybenzoxazines were not reported until Ning and Ishida (1994) studied bifunctional benzoxazine precursors. The bifunctional benzoxazine leads to large molecular weight polymer. Polybenzoxazines, the novel phenolic resins, provide a chemical and structural framework with great molecular design flexibility reported by Ning and Ishida (1994). The benzoxazine precursors exhibit low viscosity which is advantageous from processing point of view.

The majority of monomers undergo volumetric shrinkage upon polymerization. However, zero shrinkage or even volumetric expansion may be desirable in many applications, such as coatings, composites, and precision casting. Shrinkage causes residual stress that may lead to premature debonding and microcracks. Shrinkage occurs because the monomer molecules change from a Van der Waals distance to a covalent distance of separation and may lose small molecules by condensation polymerization. Shrinkage also occurs when the conformation of the polymer occupies a smaller free volume.

Bailey et al. (1973,1990) reported that spiro ortho esters and spiro ortho carbonates that polymerize via ring-opening reaction show volumetric expansion. They hypothesized that the strained ring of the monomer opened thus occupying a larger volume. These spiro ortho compounds were often mixed with epoxy resins in order to counter the shrinkage of the epoxy. An example is where various amounts of norbornene-spiro-orthocarbonate (NSOC) was copolymerized with an epoxy resin investigated by He and his coworkers (1981,1991). They found that the polymer density at room temperature was lower than the monomer while the  $T_g$  and mechanical

properties decreased as the amount of NSOC increased. In addition to the aforementioned mechanism of volumetric expansion, it is thought that the reduction of shrinkage in the glassy state ( $<T_g$ ) during cooling process by lowering the  $T_g$  of the copolymer significantly contributed to the observed results. The shrinkage in the glass region leads to internal stress since the molecular motion of the network segments was mostly restricted in this region. In general, as in the studies by He and Zhou (1991) and Shimbo et al. (1981, 1985), better mechanical properties are reported with the materials showing lower shrinkages .

The room temperature density ( $\rho_{RT}$ ) of an epoxy resin with various curing conditions was studied by Pang and Gillham (1989). The  $\rho_{RT}$  of a polymer depends on many factors, such as curing time, curing temperature, and cooling rate after the curing reaction. They found that, at low  $T_C$ , the  $\rho_{RT}$  of both fast and slow-cooled specimens increased gradually with curing time due to the densification of the material in the liquid and rubbery states. The density levels off when the material reaches the glassy state at a specified  $T_C$ . A different event occurs at moderate  $T_C$ . However, the increased  $\rho_{RT}$  as a function of curing time is found in fast-cooled samples. This is contrary to the slow-cooled samples where the  $\rho_{RT}$  decreased as a function of curing time. Both the fast and slow-cooled samples showed decreased  $\rho_{RT}$  at a higher  $T_C$ . These phenomena can be explained by the effect of glass transition temperature and crosslink density on the thermal shrinkage during the cooling step of polymerization cycle.

Ishida and Allen (in press), using dilatometric measurements, reported that the maximum shrinkage for isothermally cured B-a or its volumetric expansion coefficient in the glassy state were lower than epoxy. The B-a materials are polymerized with low shrinkage under isothermal conditions. The crosslink density of the cured B-a is significantly lower than is typically seen in crosslinked epoxies when the materials with similar  $T_g$  is compared.

Ishida and Low (submitted) reported the effect of intramolecular hydrogen bonding on volumetric expansion of benzoxazines by systematically varying the type of the primary amines used in synthesis. Intramolecular hydrogen bonding occurs in these materials between the phenolic OH and nitrogen of the Mannich base as studied by Dunkers and his coworkers (accepted). The strength of this hydrogen bonding depends on the electronegativity of the amine group that is attached to the nitrogen. The stronger the hydrogen bonding, the greater the volumetric expansion. In addition, the steric effect of the amine group also influences the volumetric changes during cure.

## **1.2 Objective**

The aim of this paper is to study the volumetric properties of a benzoxazine as it undergoes polymerization as well as the nature of their apparent expansion or near zero shrinkage. The effect of curing conditions on volumetric expansion and the glass transition temperature of a polybenzoxazine is studied by varying the curing time and temperature.