CHAPTER 1

INTRODUCTION

1.1. The Significance of Kinetics Study

Nowadays thermosetting polymers, which exhibit crosslinked chains by chemical bonds forming a three dimensional network, have received a strong attention particularly in the field of automotive, aerospace, construction, and electronic industries because of the potential applications of these materials. The processing of these materials is complicated due to the involvement of complex chemical reactions and hazardous conditions. In order to improve the material properties and applicabilities, reinforcements, fillers, pigments, and other additives are added into the polymer matrix. In addition, preparing polymer blends or polymer composites can alter various properties of polymers. As a result of those modification and treatment, a large number of chemical reactions and changes in physical and chemical properties of the final polymers are obtained. Thus, the understanding of curing reaction is crucial in the analysis, control, and design of processing operations. The kinetic study involves an insight knowledge of the chemical reactions, which play an important role in the curing process allowing development of quantitative models possible for prediction of a thermal curing process. Insight understanding on reaction kinetics is essential for a study of the relationship between material properties and extent of the reaction. The characterization of thermosetting polymers is necessary for a better understanding of structure-property relationships and improvement in product quality.

A variety of experimental techniques have been developed in order to monitor the curing reaction of thermosetting polymers. These techniques include chromatography, infrared spectroscopy, nuclear magnetic resonance spectroscopy, Raman spectroscopy, differential scanning calorimetry (DSC), dielectric measurements, and rheokinetic measurement.

Differential scanning calorimetry directly measures thermal properties of a material as a function of temperature. Properties such as heat of cure, glass transition temperature (T_g), percent crystallinity, melting point, and degree of curing can be calculated from the experimental results. However this technique cannot be employed for identifying the chemical characteristic of observed transitions.

Fourier transform infrared (FT-IR) spectroscopy is applicable to structural characterization of polymer because the vibrational patterns in a polymer are closely related to those of monomers. During a variable temperature infrared spectroscopy study, some physical changes as a result of changes in temperature can be inferred or correlated to chemical characteristic *via* changes in the observed infrared spectra.

The combination of DSC and FT-IR techniques allows the study of structural changes in a material as the sample passes through various thermal transitions. In addition, FT-IR technique provides sufficient information by spectroscopic means to assign the different states of physical or chemical phenomena.

1.2. A Ternary System Based on Benzoxazine, Epoxy, and Phenolic Resins

Epoxy resin is a thermosetting polymer with an extremely wide range of molecular design. It has excellent mechanical and chemical properties such as high tensile and compressive strength, good chemical resistance, good adhesion to glass and metals, and high distortion temperature. The varieties of these properties make it meet requirements of demanding applications. These include areas as diverse as constructions, electronics, adhesives, and coatings. The superior mechanical and chemical properties possessed by epoxy resins are the results of curing process, in which low molecular weight of the resin is transformed into a finite molecular weight of polymer with a three dimensional network structure. However the usefulness of epoxy resins in many applications is limited by their inherent brittleness arising from the crosslinked structure.

Phenolic resin is widely used in industrial applications because of its inherent hardness, heat resistance, flame resistance, chemical resistance, dimensional stability, and good dielectric properties. The important advantages include inexpensive raw materials and easy fabricating process. These make the phenolic resin highly competitive in cost/performance index. However traditional phenolics derived from condensation reaction of precursors of either novolac and resole type resins exhibit the common shortcoming of brittleness, strong acidic catalyst, volumetric shrinkage, and volatile by-products (e.g., water and ammonia) generated by the condensation polymerization. The lacks of molecular design flexibility imposed by the phenolic chemistry have become another disadvantage of the material. This is apparent when one compares traditional phenolic resin to epoxy. Since the structure of typical phenolic resin is dependent on phenol and formaldehye that cannot be varied to a great extent.

Polybenzoxazine is a newly developed thermosetting polymer with interesting properties. As a novel class of phenolic resins, it has been developed and modified to overcome the shortcomings of traditional phenolic resins. Polybenzoxazine has excellent properties commonly found in the traditional phenolics such as heat resistance, good electrical properties and flame retardance. Furthermore polybenzoxazine has unique properties, unlike the traditional phenolics such as excellent dimensional stability, improved toughness, stable dielectric constant, near zero shrinkage, and low water absorption. The ease of processing is a major advantage of polybenzoxazine in comparison to other thermally stable polymers such as polyamide, polyphenylene, polyetherimide, and polybenzimdazole. Polybenzoxazine seems to combine the thermal properties and flame retardance of phenolics with the mechanical performance and design flexibility of advanced epoxy resins. Thus, it is possible to synthesize inherently non-flammable material exhibiting high char yield, superior mechanical properties and excellent processibility without sacrificing the advantage of traditional phenolics. In addition, polybenzoxazine can be synthesized from inexpensive raw materials and can be cured without strong acid or basic catalyst. It does not release by-products during polymerization due to ring-opening of polymerization. As a result, polybenzoxazine has become an attractive candidate for various advance applications. Despite of its high performance, polybenzoxazine shows surprisingly low crosslink density, as compare to ordinary thermosetting resins with similar properties. Moreover induction time of curing, cure time and cure temperature of this material are substantially high.

Recently, a new polymeric system based on the ternary mixture of benzoxazine, epoxy, and phenolic novolac resins, have shown promising properties suitable for a wide range of applications, particularly in a microelectronic application and a highly filled system. The addition of epoxy to benzoxazine network greatly increases the crosslink density of the material and strongly influences mechanical properties of the final product. The material properties present a high thermal stability, high glass transition temperature and low melt viscosity. These properties were reported to strongly dependent on the compositions of monomers in the resin mixture.[1]

1.3. The Objective of This Research

The objective of this research is to synthesize some ternary compounds based on benzoxazine, epoxy, and phenolic novolac resins and to investigate the reaction kinetics of these ternary compounds by DSC and FT-IR spectroscopy.

1.4. Scope of This Research

1. To prepare the new polymeric systems based on the ternary compounds of benzoxazine, epoxy, and phenolic novolac resins.
2. To investigate the reaction kinetics of the ternary compounds by DSC and FT-IR spectroscopy.