CHARPTER I

INTRODUCTION

1.1 General Introduction

Due to their superior high specific mechanical properties and ease of fabrication, polymer matrix composites such as epoxy, Kerimid 601 (polyimides), and cyanate ester, have been used for various applications ranging from aerospace structures to electronic packaging materials. The use of curing agents for epoxy and cyanate ester as well as the poor adhesion of polyimide, however, limit the utilization of those resins especially for high performance fiber composite applications. High levels of the properties by controlling the orientation of the reinforcing fiber have been studies by T. Takei and H. Hatta [6]. However, this experiment will intent to use new polymer matrix copolymers based on benzoxazine/epoxy resin for electronic industry products particularly as, printed circuit boards (PCBs) materials as this resin mixture has been reported to provide some interesting properties that overcome those shortcomings in traditional epoxy, cyanate esters or polyimide.

The popular names of many of the materials which comprise the majority of printed circuit boards (PCBs) laminates have often been generalized of the chemical names of the principal resin systems used such as "epoxy," "polyimide", "cyanate ester" and the like. In recent years the search for products suitable for high frequency performance has resulted in the use of new materials and combinations of materials that make the generalizations of the past more difficult to sustain. Various resins in use in the electronic laminate industry are thermosets (which means that they "cure" into a hard final product) rather than thermoplastics (which may be molten and re-molten many times) [38].

In practice, the ideal polymeric materials suitable for printed circuit board laminates should have some or all of the following characteristics [38]:

1. Glass transition temperature of the resin should be greater than 260°C but with a resin system that is tougher and less brittle than today's standard high temperature systems. Furthermore, the resin systems should possess minimal problems that occur due to "mixed" and "blended" systems which often retain many of the problems of their weakest elements. (At present the "pure" polyimides remain the best available materials.)

2. Dielectric constant and loss tangent should be under 3.0. The ideal would be an air dielectric with copper foil bonded on both sides, but there are still some technical limitations involved in solving the problem. At present, a pure Teflon® (DuPont) on fiberglass laminate, with a dielectric constant of 2.1 and dielectric loss of 0.0009, is the best available in wide commercial use.

3. Dimensional stability of the polymer used should be relatively high. Despite all phases of handling, processing and use, the material should retain its original size and dimension when returns to its original thermal conditions.

4. Low coefficient of thermal expansion that should be tailorable to match the expansion requirements of claddings, devices to be mounted on the surface and thermal planes buried in the interior. Current development target for leadless chip carrier attachment at 6.0 ppm/ °C is ideal. (At present, woven Kevlar-reinforced laminates with relatively low resin contents can provide the CTE value close to 6.0 ppm/°C requirement. Other materials such as quartz reinforcement, copper-invar-copper distributed constraining planes and Thermount® reinforcement achieve values as low as 9-11 ppm/°C (a substantial improvement over 17-18 ppm/°C for conventional epoxy or polyimide laminates.)

5. Low z-direction expansion should match that of the copper in the plated through holes to avoid serious problems during thermal processing steps such as solder reflow. The ideal material would have a very low z-direction CTE: in the order of 35 ppm/°C. (Below their

Tg's, most standard materials have CTE's of 50-60 ppm/°C, the higher z-direction effect coming from the in-plane constraint.)

6. Uncomplicated processing i.e. the materials should be able to be processed using conventional processing methods, etching and wet chemical processing, and lamination techniques. Process yields should be more than 95% even for complex limited production and prototype boards. The process should be forgiving. (At present nothing always meets this objective.)

Huntsman advanced structural composites business unit recently presented a paper at the recent SAMPE exhibition to develop a new resin transfer molding (RTM) system. The advanced structural materials group has been actively working in the development of high performance systems for resin transfer molding processes for aerospace and industrial composite applications. A new RTM system based on a novel benzoxazine/epoxy chemistry has been recently developed and is in the final phase of commercial introduction to the market place. This new system is processable at 177°C using traditional RTM techniques [39].

The cured composite properties proved to be superior to the traditional epoxy systems. The 177°C cured composite had glass transition temperatures (T_g) in excess of 200°C with excellent thermal mechanical properties. The cured neat resin modulus is also significantly higher than the traditional epoxy systems and in particular, modulus retention under hot wet conditions was also shown to be excellent [5]. This is supported by the fact that benzoxazine chemistry has very low moisture absorption characteristics. The overall composite's thermomechanical properties were shown to be superior and comparable to the high performance prepreg resin systems. The system also displayed superior thermal oxidative stability. The paper described in detail the chemistry, processing and performance of this benzoxazine system as well as the rational behind the selection of different components and their effect on the overall system properties. Details of neat resin and composite processing and processing kinetics are also discussed and are available from their website [39].

In this work, we will investigate the effect of multifunctional epoxy resin i.e. epoxy novolac cured by benzoxazine resin on their thermomechanical and some physical properties for printed circuit board applications. The effect of benzoxazine resin contents on those essential properties will be studied.

1.2 Objectives

1) To investigate the effect of composition ratio on processing behaviors, thermophysical and mechanical properties of benzoxazine/epoxy copolymers.

2) To study thermophysical and mechanical characteristics of benzoxazine/epoxy copolymers reinforced with glass fiber (cloth) for an application as printed circuit boards (PCBs).

1.3 Scope of the study

1) Synthesis of the benzoxazine polymer resins (BA-a type)
2) Preparation of copolymers between BA-a resin and epoxy resin of a novolac type.
3) Investigation of curing behaviors of the benzoxazine-epoxy mixtures i.e. 100:0, 80:20, 60:40 and 40:60. (DSC, FTIR)
4) Determination the thermal and physical properties for the fully cured copolymers by various weight ratios of benzoxazine and epoxy resins i.e. 100:0, 80:20, 60:40 and 40:60.
    - 4.1 Thermal expansion coefficient (TMA)
    - 4.2 Glass transition temperature (DSC, DMA)
    - 4.3 Thermal stability (TGA)
    - 4.4 Flexural properties
    - 4.5 Dynamic mechanical properties
    - 4.6 Density
    - 4.7 Water absorption

5) Examination of fiberglass reinforcement effect in term of processing, thermal and mechanical properties at about 80% by weight of the glass fiber.