

CHAPTER I

INTRODUCTION

For most applications, thermosetting resins are used to construct plastic tooling. Processing of thermosetting resins has received strong attention from the automotive, aerospace and construction industries due to the great potential of these products. These materials offer the advantages of strength, rigidity, dimensional stability, and higher operating temperatures than thermoplastics. They are generally supplied as liquid two-component systems except for modeling blocks and prepregs. Plastic tools can be constructed from various chemical classes of plastics. The most common types for rigid tool constructions are epoxy and unsaturated polyester resins. Flexible tooling applications may utilize modified versions of epoxy, unsaturated polyester resins or use silicone or polyurethane elastomers. For higher temperature systems, bismaleimides and cyanate esters are currently being investigated for possible tooling applications. Although in many cases the plastic is used in conjunction with wood, plaster, or metal, the finished product is usually classed as a plastic tool.

Phenolic resins were among the first commercial materials used in plastic tooling. Introduced in the late 1930s, they have been largely replaced by other classes of thermosetting resins. Their disadvantages include brittleness, long cure cycles, and corrosive nature of the acidic curing agent. The dimensional stability of the tool is limited by the migration of by-product water produced by the cure. Phenolic resins are used today mainly as impregnating matrices for laminated paper and wood modeling blocks. After unsaturated polyester resins became available in the early 1940s, they were used in a variety of plastics tooling applications, such as, the construction of

trimming, drilling, and checking fixtures. They are still used today in tool fabrication where broad tolerances are acceptable and low cost is important. The largest application for polyester tool is probably in the construction of molds for boats and similarly polyester shells. The high shrinkage of material during cure is not critical for these applications.

For the epoxy resins, they are the most versatile thermosetting tooling plastics. Since their introduction into plastic tooling in the late 1940s, these materials have become the mainstays of the industry. Advantages include low shrinkage, high flexural and compressive strength, good dimensional stability, and good chemical resistance. These properties make possible the accurate and stable reproduction of a model. Through the use of suitable fiber reinforcement, lightweight laminate tools with high mechanical characteristics can be readily produced. Most epoxy tooling materials also contain fillers. They control flow in the application, reduce shrinkage, improve wear resistance, modify strength properties, modify heat of reaction, control thermal conductivity and coefficient of thermal expansion, impart color, and reduce cost.

In the process, thermosetting resins undergo a volumetric shrinkage 3-15% during polymerization under even the best system. Upon curing, the most epoxy resins also undergo 2-7% volumetric shrinkage too. However, resins without shrinkage would be advantageous for such applications as precision castings, dental composites, rock cracking materials and high strength composites. The superior mechanical interlocking to a substrate that would be possible with zero shrinkage or expanding materials makes them ideally suited for high performance adhesives, sealants, and coatings.

Spiroorthoesters and spiroorthocarbonates (Bailey, 1977) were synthesized and polymerized via ring-opening reaction. The new materials have shown volumetric expansion property. It was hypothesized that the

strained ring of the monomers opened would thus occupy a larger volume. Although some type of spiroortho compounds show 2.7% of volumetric expansion, these substances have been found few useful applications besides complicated synthesis routes and low glass transition temperature (T_g). As homopolymers, these expanding polymers seem to have quite limited utility for mechanically demanding structural materials. As an additive into epoxy resins, they reduce shrinkage and improve the mechanical properties, for example, (Ishida, 1997) curing a copolymer of bisnorbornenyl spiroorthocarbonate and an epoxy, the resulting composite had higher impact strength and higher shear strength than the epoxy-carbon fiber composites.

The recently interesting benzoxazine materials were synthesized from phenol derivatives, primary amines and paraformaldehyde. Polybenzoxazines, the novel phenolic resins, as compared to epoxy resins and conventional phenolics, have indicated the excellent glass transition temperature (T_g), and moduli, low water absorption values, in addition to zero shrinkage or a slightly expansion upon cure (Holly, 1944; Ishida, 1995, 1996, 1997, 1998).

Similarly, new benzoxazines using aminospirosilicate derivatives as primary amines are expected to present zero shrinkage upon cure although aminospirosilicates have not yet investigated their shrinkage or expanding property. Then the aim of this research is therefore to investigate whether the aminospirosilicates and benzoxazines based on these aminospirosilicates show shrinkage or expanding property. The effects of curing conditions on the volumetric measurement of aminosilicates and benzoxazines are studied by varying curing time and temperature.