



CHAPTER II

THEORY

2.1 Materials

2.1.1 Polybenzoxazine Resin

Polybenzoxazines are promising as a novel route to phenolic resins because of their tremendously flexible molecular design, their versatile performance and their well balanced thermal and mechanical performance [5]. In addition to the advantages of traditional phenolic resins, such as heat resistance, good electronic properties and flame retardance, polybenzoxazines also have such unique characteristics as low absorption of water, dimensional stability and near-zero shrinkage or expansion upon curing, which overcome the shortcomings of traditional phenolic resins. Furthermore, they do not need strong acid catalysts for polymerization and do not produce by-products during polymerization [9].

Despite their high performance, the crosslinking densities of benzoxazine resins are believed to be considerably lower than those of ordinary thermosetting resins. As high performance thermosetting resins, their properties can be improved by tightening their network structure. Some authors have investigated the copolymerization of benzoxazine resin with epoxy resin. The crosslinking density and glass-transition temperature of these copolymers were higher than those of the polybenzoxazine homopolymer, and their heat resistance and mechanical properties were also better [10].

In addition, the presence of epoxy resin significantly improves the processability of benzoxazine resins but the resulting binary mixtures require higher curing temperatures than the pure benzoxazine resin. Phenolic resin has been used as a crosslinker for epoxy resin and has been reported to be a catalyst for benzoxazine resin [11]. So, ternary systems based on benzoxazine, epoxy and phenolic resins have been developed [12].

The copolymerization of these benzoxazine–novolac systems with epoxy resins requires high amounts of epoxy resins if the mechanical and thermal properties are to be good.

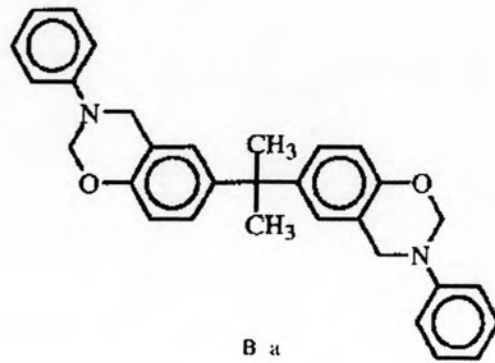


Figure 2.1 ; Benzoxazine-novolac chemical structure

These compounds are synthesized from phenols, formaldehyde and amines [5].

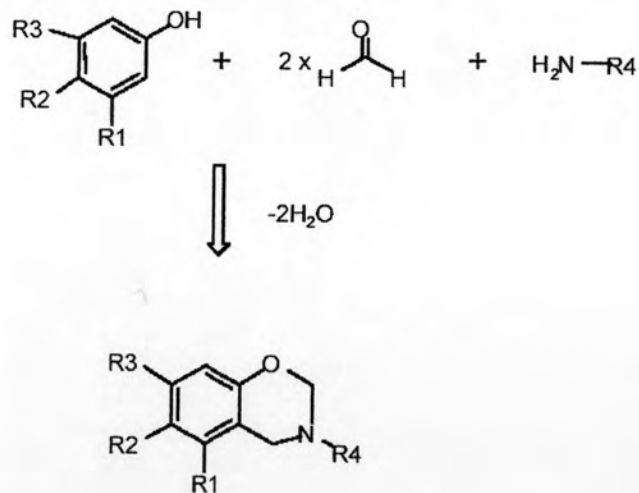


Figure 2.2 ; Synthesis of Benzoxazine

Upon heating homopolymerize to form high molecular weight polymers or in case we use multifunctional phenols and/or multifunctional amines we get highly crosslinked polymers [5].

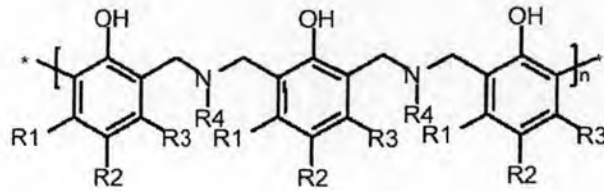


Figure 2.3: Homopolymerization of Benzoxazine

2.1.2 Epoxy Resin

Difunctional epoxy begins with brominated bisphenol-A epoxy resins and are formulated with accelerators, (2-methylimidazole) and hardeners, dicyandiamide aka (dicy). There are now a variety of epoxy resins, distributed roughly by glass transition temperature, (T_g) into three basic categories [3]:

1. Low end difunctionals, (T_g range 110-130°C)
2. Difunctional systems blended with tetrafunctional or multifunctional resins (T_g range 135-160°C)
3. Pure multifunctional epoxy systems; (T_g 170°C or above). Tetrafunctional modified systems offer higher T_g and better resistance to many of the solvents and chemicals used in board manufacture. Mid-range bifunctional modified systems offer improved performance in higher layer count designs, and multifunctionals result in improved yields on high layer count designs where multifunctionals reliability and resistance to misalignment are problematic. Epoxies with more than two epoxide moieties (groups) per molecule can react to form three-dimensional lattices and we often refer to them in terms of that multiple functionality (tetrafunctionals, multifunctionals, etc.).

Multifunctional epoxy resins have long been used where higher temperature performance and high modulus is required. These systems however are limited in their use because of their inherent brittleness. Improvement in toughness can be accomplished through a number of techniques, which are effective in difunctional and more linear systems such as those based on bisphenol A.

The most widely used multifunctional epoxy resins are those based on phenol novolacs. Because of their high cross-link density they are often preferred for applications where high temperature resistance, chemical resistance and high modulus are required. These properties also tend to be associated with brittleness. Typical current applications include [6]:

1. Composites (sporting goods, aerospace, automotive)
2. High temperature adhesives
3. Electronic encapsulation
4. Corrosion resistant coatings and linings
5. Friction materials

Epoxidized phenol novolacs are resins produced by the condensation of phenol with formaldehyde and subsequent reaction with epichlorohydrin. On the other hand, Bisphenol A is the starting phenolic for the most widely used epoxy resin and is manufactured by reacting phenol with acetone. This sequence is shown in Figure 2.4 [6].

BISPHENOL A SYNTHESIS

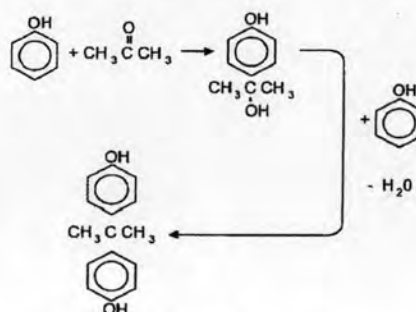


Figure 2.4 ; Bisphenol A synthesis

In the current commercial process Bisphenol A is supplied for epoxy resin production at greater than 98% difunctional content. Phenol novolacs are always characterized by much higher degrees of multifunctional content. Because formaldehyde is smaller than acetone and less hindered in its reaction with phenol, multiple formaldehyde reactions on phenol and multiple condensations with phenol can occur as illustrated in Figure 2.5 [6].

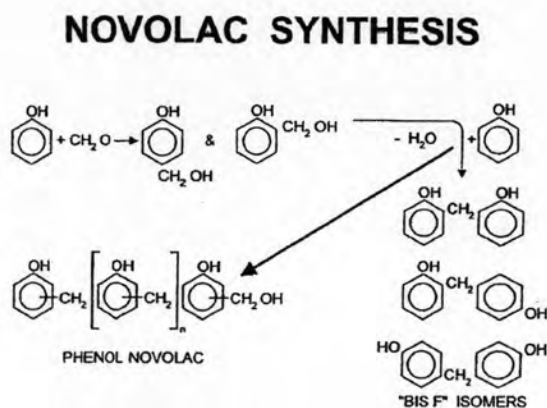


Figure 2.5 ; Novolac Synthesis

Conversion of bisphenol A to the epoxy yields substantially a linear resin. Aromatic glycidyl ether resins, both epoxy phenol novolac resins (EPN) and epoxy cresol novolac resins (ECN) have attained commercial importance. The former are made by glycidylation of the phenol-formaldehyde condensates (novolac) obtained from acid-catalyzed resinification of phenol and formaldehyde. The products produce random *ortho*- and *para*-methylene bridges (phenolic resins)[7]. The epoxidation of phenol novolacs yields a mixture of di- and poly-functional resins as shown in figure 2.6 [6].

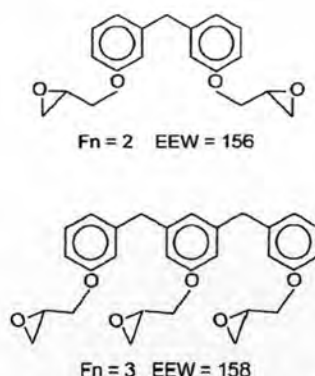


Figure 2.6 ; Conversion of Bisphenol A to the epoxy

An increase in the molecular weight of the novolac increases the functionality of the resin. Epoxidation with an excess of epichlorohydrin minimizes the reaction of the phenolic OH groups with glycidylated phenol groups and prevents branching. The epoxidation is similar to the procedure described for bisphenol A. EPN resins range from a high viscosity liquid of $n = 0.2$ to a solid of n value >3 [7].

2.1.3 Reinforcements

a. Glass Fabric Basics [3]

The used of fiberglass fabric styles in the manufacture of prepreg and laminate. The most selection is based on the thickness they will contribute to the finished laminate or printed wiring board or on the amount of resin they hold for filling and bonding. Specific choices often depend not only on building thickness but also on secondary properties such as stiffness, dielectric constant, CTE control, dimensional stability and cost.

Fiberglass fabric starts out on a "warp beam" containing thousands of individual strands of yarn rolled onto a master beam, or roll. These yarns will compose the machine direction of the fabric, or more correctly, the "warp direction". The warp yarns are then "slashed" run through a solution of sizing agents and lubricants which protects them from damage during weaving.

In the actual weaving process the warp beam is mounted at the back of a loom and the "fill" yarns are inserted as the warp yarns are passed through from back to front. In the older style Draper looms, a wooden shuttle containing the fill yarn was slapped back and forth from side to side of the loom to insert the fill yarns and alternating warp yarns moved up and down in

a mechanical frame to create the traditional "plain weave". This resulted in a woven, or "Drapered", edge.

In the newer air jet or water jet looms, the fill yarns move across the loom on jets of air or water and are cut off individually leaving a fringed edge. A single warp beam may contain several thousand yards of warp yarns and may represent as much as a week's weaving time for a single loom. After weaving, electrical grade glasses must be "scoured" to remove excess sizing from the warp yarns and then heat cleaned to remove the rest of it.

After scouring and heat cleaning (a lengthy stay in an oven at elevated temperature) the weaver treats the fabric with organosilane finishing agents to provide a fabric surface which can be wet by and bonded to various resin systems.

Glass manufacturers apply high temperature finishes to glass intended for polyimide Manufacturers so that the bonds will survive the use conditions that the polyimide will see. The finish on a fiberglass fabric represents only a very tiny amount of material (a fraction of a percent of the raw weight) but vitally affects how the resin will wet the surface during prepregging. Prepreg with repellent spots or streaks (which often show up on heating even if they are not evident initially) is generally a result of either poor scouring and heat cleaning or inadequate silane treatment.

b. E-glass

"E" glass, electrical or E-glass, so named because its chemical composition makes it an excellent electrical insulator, is particularly well suited to applications in which radio-signal transparency is desired, such as aircraft radomes, antennae and computer circuit boards. However, it is also the most economical glass fiber for composites, offering sufficient strength in most applications at a relatively low cost. Over time, it has become the standard form of fiberglass, accounting for more than 90 percent of all glass-fiber reinforcements. At least 50 percent of E-glass fibers are silica oxide; the remainders are composed of oxides of aluminum, boron, calcium and other compounds, including limestone, fluorspar, boric acid and clay [13].

c. S-glass [3]

"S" Glass, more accurately, S2-Glass is a "high strength" glass fiber originally developed for the structural field. It differs in both composition and properties from E-Glass. Compositionally, S2-Glass has a higher percentage of both Silicon Dioxide and Aluminum Oxide than E-Glass. It is more difficult to manufacture than E-glass because it has a much higher melting point and requires special tooling in the drawing operation.

Pure platinum tooling is required, which means that it is expensive, and which also means that nobody will have an "extra" die on hand. Relatively small amounts of S2-Glass are woven for electrical grade applications each year and relatively large minimum purchases are required (relative to most program requirements).

S2-Glass has a lower dielectric constant and dissipation factor than E-Glass because of the higher silicon dioxide percentage. It also has a lower CTE than E-glass. In practical terms it will knock off about 2 ppm/ °C in CTE value in a typical MLB with an average 50% resin content.

Likewise, for equivalent constructions, it will reduce dielectric constant by about 0.2. Finishes can be put on S2-Glass the same as for E-glass, which means that it will be essentially compatible with all the basic resin systems. When incremental an improvement in dielectric constant and CTE is worth a significant price increase, because, at least as of this writing, S2-Glass costs several times as much as E-glass and as mentioned, requires large minimum purchases [3].