

Chapter 1 Introduction

Epoxy resins represent one of the most important polymeric material systems in the electronics industry, serving as encapsulants, coatings, die-attach adhesives, transfer-molding compounds, and laminate impregnating resins. Often cited advantages of epoxies include¹: 1) adhesion to a variety of surfaces, 2) good corrosion protection, 3) excellent electrical performance for standard applications, 4) good mechanical performance and thermal stability to moderately high temperatures, 5) relatively low moisture absorption, 6) little cure shrinkage, and 7) versatility in resin, filler, and curing agent selection. Glass or paper reinforced epoxy-impregnated laminates form the structural core of printed circuit boards (PCBs) in the majority of modern electronic systems. Current impregnation techniques require that organic solvents be used to reduce resin viscosity for improved flow and wetting of the reinforcement material.

Recently, environmental concerns over the release of volatile organic compounds into the workplace environment have prompted PCB suppliers to consider waterborne replacements for solventborne impregnating, masking, and varnishing processes.² Such a solvent replacement strategy promises the additional financial benefits of lower healthcare-related costs arising from reduced worker exposure, and decreased fire risk and waste disposal costs. The benefits promised by waterborne epoxies can best be realized if: 1) their performance falls within the industry tolerances established for solventborne resin performance, and 2) if they can directly replace solventborne epoxies in the manufacturing process with a minimum of re-engineering effort or additional cost. A primary goal of the proposed research is to examine the performance of a waterborne epoxy in PCB lamination and adhesion relative to traditional solventborne resin.

1.1 Printed Circuit Board Base Materials

The base structure in the laminating process is the resin-preimpregnated reinforcement composite, known as prepreg. In the prepregging process, the reinforcement (paper or glass cloth) is dip impregnated by drawing it through a pan of resin, followed by squeeze-roller metering to ensure proper resin content. Forced-air or infrared heating is then employed to remove the residual solvent from the uncured prepreg. This heating step is controlled to achieve only partial cure, or the B-stage of the resin, resulting in a dry, non-tacky sheet which can be easily handled, but which possesses enough residual cure to flow readily during lamination. In a process known as “dry lay-up”, prepreg sheets are cut and stacked in quantities to achieve the desired final laminate thickness. The most common laminate used in the PCB industry, designated FR-4 (Flame Retardant Type-4), is composed of glass cloth impregnated with brominated diglycidyl ether of bisphenol A (DGEBA) epoxy resin containing the curing agents dicyandiamide (DICY) and an amine or imidazole cure accelerator.³ DICY has become the standard PCB curing agent because of its latency, providing a shelf life for B-staged prepreg of up to one year at room temperature.

Uncured stacks of B-staged prepreg are clad with copper foil on either one or both surfaces, and are then cured by hot pressing. These copper clad laminates are supplied to electronics manufacturers who mask the desired circuit pattern over the copper with a photo curable polymer coating. The masked board is subsequently exposed to etchant solutions that remove the exposed, undesired copper, leaving only the circuit conductor traces. The residual etch mask is then stripped from the copper traces using solvents or aqueous-alkaline solutions. Subsequent processing steps are application dependent. Although relatively simple, low-cost commodity PCBs utilize only one single- or double clad laminate. Greater emphasis is now being placed on multilayer technology.

1.2 Multilayer Printed Circuit Boards

Multilayer PCBs are common in the digital applications market, finding use in personal computers, supercomputers, and aerospace applications.⁴ A multilayer PCB structure is composed of both internal and external circuit planes connected by conductor-plated holes. Plated through-holes penetrate the entire PCB, while local holes, or vias, connect adjacent layers. “Buried vias” connect only internal planes and “blind vias” connect surface and internal planes, as shown in Figure 1.1.⁵ The number of layers can vary from 3 to as many as 50, with 12 to 15 layers being common.⁶

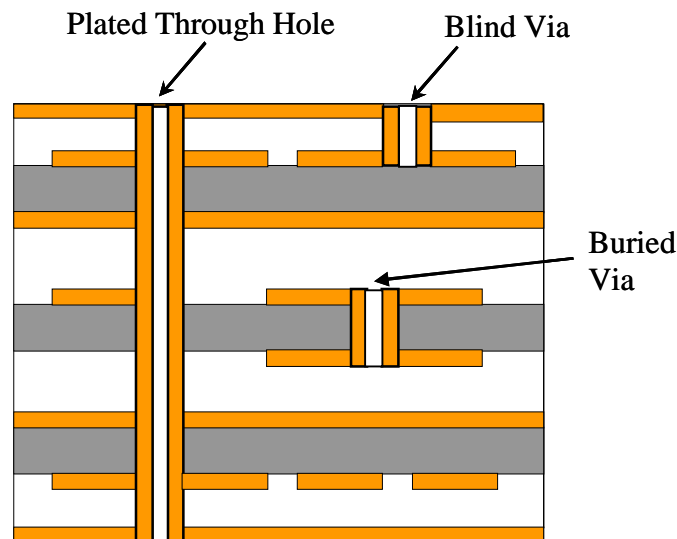


Figure 1.1: Schematic of a multilayer circuit board

Several multilayer production techniques exist. The “stack-up” process involves alternating several copper clad C-staged (fully cured) and etched boards with B-staged adhesive layers, then pressing to form a multilayer structure. A foil-capped stack-up, shown in Figure 1.2, is comprised of a series of circuit patterned boards adhered together with B-staged layers and laminated top and bottom with continuous

copper foil. This design, the most popular option, allows the electronics manufacturer to use the existing buried circuits and etch their own circuit patterns on the outer layers.⁵ Component-capped stack-ups are a similar type of multilayer PCB in which the outermost layers are pre-patterned. High frequency PCB transmission lines, known as striplines and microstrips, are constructed using the stack-up process. These multilayer circuits require exacting dimensions to achieve the proper electrical impedance critical for optimal electromagnetic wave propagation and are therefore constructed using base and adhesive layers with tightly controlled dielectric properties and thicknesses. In each of these stack-up fabrications the copper/epoxy interface experiences at least two thermal and pressure cycles associated with cure, as well as any thermal test cycling and high temperature solder applications.

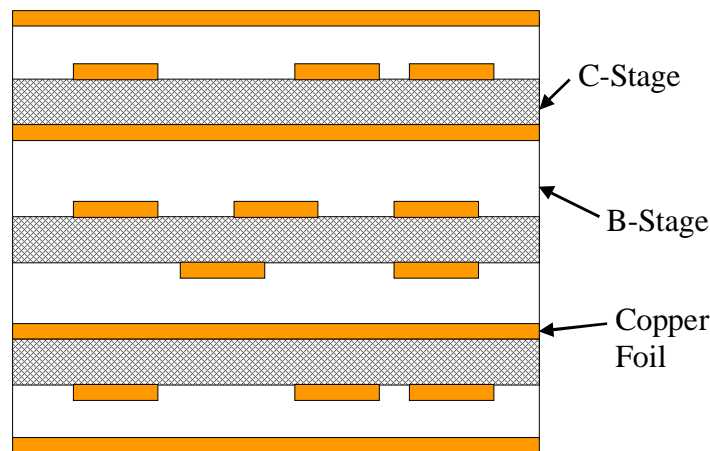


Figure 1.2: Foil-capped stack-up PCB construction

A second multilayer production technique, known as layer-by-layer buildup, involves bonding successive C-staged circuit layers onto previously adhered layers.⁷ Since each bonding cycle involves elevated cure temperature and pressure, the earliest bonded interfaces in the layer-by-layer process experience repeated environmental aging stresses. A layer-by-layer PCB construction is shown schematically in Figure 1.3. Inherent to multilayer laminate construction, regardless of the specific process, is the step of bonding an adhesive prepreg layer to the exposed copper surface of circuit traces or ground planes. Therefore, knowledge of the surface characteristics of the copper foil becomes critical. Standard commercial copper foils are electrodeposited with a variety of bulk grain structures, but are generally treated for adhesion on one side only.^{5,8} The adhesion-optimized surface is roughened and treated with zinc chromate adhesion promoters, yielding a “brass” composition on the surface that is relatively resistant to corrosion.⁹ The untreated side is smooth in texture and has a shiny, pink appearance; it exhibits poor adhesion due to minimal mechanical interlocking with the adhesive resin and is subject to oxidative degradation. Although double-treated foils are commercially available, they possess several disadvantages, including 1) greater cost, 2) increased mechanical fragility leading to processing difficulties, 3) difficulty in development of photo-resist masks resulting in higher probability of circuit defects, and 4) incompatibility with plating

processes during the processing of conductive vias.⁵ For these reasons most multilayer PCBs are constructed using single-treated copper foil with the untreated surface exposed for further lamination.

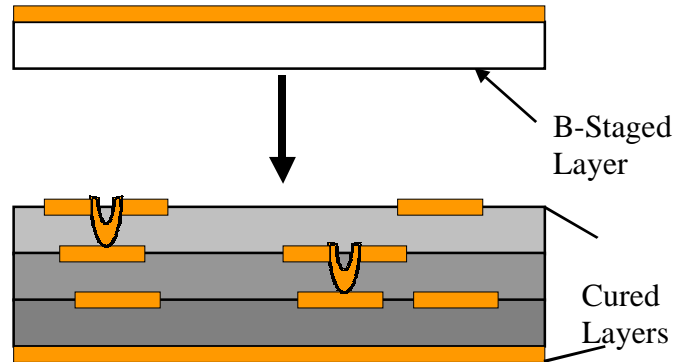


Figure 1.3: Layer-by-layer PCB construction

The greatest thermal and mechanical stresses imposed on the great majority of PCB constructions over their service lives occur during fabrication. This study seeks to identify any problems or improvements in the performance, both adhesive and electrical, of PCB laminates impregnated with waterborne latex epoxy versus traditional solventborne resins. To understand any post-fabrication performance differences, the fundamentally different processing behavior of the two resin systems must be examined.

1.3 Problem Description

The primary differences between the solventborne and waterborne epoxy impregnating resins under consideration in this study arise from the distinct physical compositions and drying characteristics of the polymer solution and the latex emulsion. Glass cloth impregnation by epoxy solutions in organic solvents is a well-characterized process, having been commercialized for many years. Substitution of a waterborne latex resin system will be successful only if process reengineering is minimal and material performance is equivalent or superior. Latex resin manufacturers have attempted to develop impregnating systems that can replace solution resin systems with minimal process redesign. However, the presence of residual surfactant from the emulsion poses a clear concern for obtaining acceptable material properties and adhesive durability. Another, less obvious problem involves the crystallization of insoluble solid dicyandiamide curing agent during drying and coalescence. These crystal precipitates are significantly different in morphology and much larger than those found in solution cast resins. Although alternate curing strategies can be used in some applications, the use of DICY, because of its unique latent nature, is likely to persist in PCB laminate manufacture.

The goal of this study is to identify changes in material properties and adhesive failure modes associated with residual surfactants and curing agent precipitates in copper clad PCB laminates, leading to the following thesis statement:

1.3.1 Thesis Statement

Waterborne latex epoxy impregnating resins can be demonstrated to meet or exceed the performance of solventborne resins in the context of the foil/laminate adhesive strength, adhesive thermal durability, and dielectric properties. This can be accomplished by characterizing the effects of both residual surfactant and DICY curing agent on latex resins used in the fabrication of copper foil-clad printed circuit boards.

1.4 References

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