Chapter 3  Epoxy Drying and Coalescence

The primary differences between solventborne and waterborne impregnating resins arise from the distinct drying characteristics of the polymer solutions and the presence of residual surfactant in the latex system. This chapter will examine the drying processes in these two resin systems, and the roles of DICY curing agent and surfactant in those processes. Specifically, the drying and coalescence of latex systems will be reviewed. The implications of DICY and surfactant segregation on electrical and adhesive performance are examined. A two-stage drying model is to be employed, both as a process development tool and as an analytical technique to better understand the physics of drying in the latex epoxy resin.

3.1  Background and Literature Review

3.1.1  Solventborne Resins

Although a variety of epoxy chemistries are used in PCB manufacture, 94% of all epoxy resins supplied in the United States are of the bisphenol A (BPA) and brominated BPA types.1 The epoxy shown in Figure 3.1 is of the di-functional structoterminal type where the R-group represents hydrogen atoms in standard BPA and bromine atoms in flame-retardant brominated BPA.

![Figure 3.1: DGEBA epoxy resin](image)

The number of BPA repeat units, described by n in Figure 3.1, controls the properties of the resin and its curing mechanisms. In general, epoxy resins with smaller values of n possess lower viscosities and form networks through the epoxide groups while larger n value epoxies are more viscous and can be cured through hydroxyl reactions. The epoxide equivalent weight, or molecular weight per epoxide (WPE), describes the effect of varied n values. Commercial BPA resins are available in a range of WPEs. Resins with WPEs of about 180 to 350, which are liquids to semisolids at room temperature, are used in laminating and encapsulating applications which require low viscosity and good flow qualities.2 Higher WPE resins are often used as coatings. EPON 828, a non-brominated BPA resin with an average WPE of 185-192 (average n value of 0.15) has been chosen as the model resin system in this study.

3.1.2  Curing Agents

In light of the potential difficulties in dealing with DICY as the primary curing agent in PCB fabrication, as will be described below, it is necessary that DICY’s advantages are outlined and some alternative curing agents described. Figure 3.2 depicts the chemical structure of DICY. The greatest advantage of DICY as a
curing agent is its latency, allowing its mixture into one-package adhesive and impregnating epoxy resins, with a shelf life of up to one year at room temperature. A primary reason for this latency is the relative insolubility of DICY in non-polar epoxy resins. Only ~0.04 parts-per-hundred weight (phr) DICY is soluble in Epon 828 resin at 25°C, increasing to just ~0.6 phr at 150°C as shown in Figure 3.3. Since

\[
\begin{array}{c}
\text{N} \\
\text{N} - \text{C} - \text{N} - \text{C} \equiv \text{N} \\
\text{H}
\end{array}
\]

**Figure 3.2: Dicyandiamide**

DICY is commonly used in concentrations of 2-6 phr, it must either be milled into solid resins or dissolved in a polar solvent before its inclusion into a liquid epoxy resin. Note the relatively high solubility of DICY in water and dimethylformamide (DMF) as compared to 828 resin shown in Figure 3.3; these are the solvents used in this study for the latex and solventborne resins, respectively. Another aspect of DICY’s ambient latency is that virtually all of its reaction with epoxide groups occurs at temperatures over 100°C, with complete network formation typically occurring between 175°C to 180°C in air.²

Despite the widespread use of DICY, its curing mechanisms with epoxy are still unclear due their great complexity. It is believed that cross-linking occurs via an autocatalytic reaction in which the cyanamide
groups of the DICY are consumed; with several references providing details of several proposed reaction pathways. Another proposed cross-linking mechanism is Figure 3.4: One proposed DICY-epoxide cross-linking structure

The cure of epoxy/DICY systems can be accelerated by the addition of substituted ureas, imidazoles (2-methylimidazole, 2-MI, at 0.1 - 0.4 wt %), and tertiary amines (benzyldimethylamine at 0.1-0.5 wt %). The interaction of DICY and surfactant during epoxy cure has been studied in the context of increasing DICY’s solubility in the resin using a surfactant. The addition of 1.2 and 6 wt % surfactant decreased the cure kinetic activation energies relative to pure epoxy/DICY, but resulted in lower overall cure rates. It was theorized that DICY’s solubility was increased in epoxy resin by the surfactant addition, but that a film of surfactant resident at the DICY/epoxy interface impeded reaction. Although it is not a primary point of investigation in the proposed study, this phenomenon could influence some of the results in the latex epoxy study.

Alternative curing agent formulations for glass/epoxy PCB laminates include 4,4’-diaminodiphenylsulfone (DDS)/boron trifluoride monoethylamine (BF$_3$-MEA) and chlorendic anhydride (CA). DDS cured epoxies result in excellent high temperature performance, having neat resin heat deflection temperatures of approximately 175°C at loadings of 30 phr. BF$_3$-MEA is added in concentrations of 1-3 phr to accelerate the DDS/epoxy cure. The recommended cure cycle for DDS/BF$_3$-MEA/DGEBA is 2 hours at 125°C followed by a postcure of 2 hours at 200°C. Of importance to laminate production is the ability of this curing agent to B-stage at 125°C and remain useful in the prepreg form for 10 to 20 days. CA is attractive for applications in which flame resistance is required. Since CA has a very high reactivity at its dissolution temperature in BPA resins (100-120°C), it is blended in an 80/20 ratio with lower melt temperature anhydride curing agents to provide longer pot life. Gelation in a CA/DGEBA system can begin in a matter of hours at room temperature, but complete cure is achieved in 4 hours at 150°C.
3.1.3 Waterborne Latex Resins

Organic solvents that evaporate at relatively low temperatures are currently used to lower the viscosity of liquid BPA resin, to dissolve solid brominated fire retardant resins, and to provide adequate flow during reinforcement impregnation. Clearly, water is an environmentally attractive alternative for replacing these organic solvents. Unfortunately, the resins most commonly employed in PCB manufacture are essentially insoluble in water. Therefore, particles of the resin must be dispersed in the water phase with the aid of surfactants. Although anionic and cationic surfactants are widely used in polymer emulsions, the epoxy resins examined in this study are dispersed with nonionic surfactants.10,11 Nonionic surfactants are desirable for two reasons: 1) these dispersions are sterically stabilized and are therefore more stable with respect to pH variation, dilution, or curing agent addition 11, and 2) ionic species are undesirable for use in PCB from an electrical performance standpoint. Although the particular nonionic surfactant used in the proprietary formulations of the commercial epoxy emulsions used in this work is not known, it is likely very similar (if not identical) to Triton X-100 (octyl-phenol ethoxylate) shown in Figure 3.5. The native surfactant concentration in these commercial epoxy emulsions is approximately 5 wt %.12 The effect of varied surfactant concentration in latex epoxies is a significant part of this study; Triton X-100 was chosen as the surfactant for addition to the emulsions.

![Figure 3.5: Triton X-100](image)

Emulsions of epoxy resins are produced by adding surfactant to the resin, the water phase, or both, then stirring the two phases under high shear. This breaks the resin into small droplets that are stabilized in the water medium by the surfactant, which has spread on the droplet surfaces, thereby creating epoxy micelles.7 Depending upon factors such as particle size, pH, and surfactant type, the emulsion may possess only limited stability before flocculating or phase separating through coagulation. Therefore, cosolvents such as glycols, and glycol ethers and esters may also be added to stabilize the emulsion.7 These cosolvents usually evaporate along with the water during coalescence. Other possible additives might include biocides to prevent fungal growth and antifoaming agents to aid in processing. Although these components are typically added in small quantities relative to the resin and surfactant, the possibility of their presence in proprietary commercial systems such as those used in this study must be acknowledged.

3.1.3.1 Film Formation: Drying and Latex Coalescence

The nature of epoxy-containing micelles dispersed in water is fundamentally different from that of epoxy molecules in organic solutions. Epoxy molecules dissolved in a one-phase organic-based solution are mixed on the molecular level while emulsions are composed of micelles formed by small surfactant-coated
liquid epoxy resin droplets suspended in an aqueous phase. Accordingly, processes of film formation that occur during drying in the waterborne latex and solventborne systems are very different.

3.1.3.1 Solventborne Film Drying

The drying of solventborne polymers has been widely studied \(^{13,14}\), but is still a subject of interest due to its complexity. A study by Ion and Vergnaud of solventborne paint drying, which is closely related to the drying of solventborne epoxy films in this work, models the process as one-dimensional diffusion with a diffusion coefficient that is a function of solvent concentration and temperature.\(^{14}\) Semi-empirical and numerical methods were employed to analyze the kinetics of drying of solventborne varnishes, resulting in exponential functions for mass % solids (equivalently mass % solvent) as a function of drying time. Exponential decay functions for first order solvent drying kinetics are characteristic of diffusion problems; this is not the case for latex drying as will be described in later sections. Solvent diffusivity could be modeled as the product of Arrhenius functions of temperature and solvent concentration:

\[
D = a \exp\left(\frac{-b}{T}\right) \exp\left(\frac{-d}{C}\right)
\]

where \(D\) is the solvent diffusivity \([\text{cm}^2/\text{s}]\), \(T\) is absolute temperature \([\text{K}]\), \(C\) is solvent concentration \([\text{cm}^3/\text{cm}^3]\), and \(a\) \([\text{cm}^2/\text{s}]\), \(b\) \([\text{K}]\), and \(d\) \([\text{cm}^3/\text{cm}^3]\), are constants. Vergnaud found a similar diffusivity dependency on temperature and solvent concentration in a study of xylene and benzene drying in fire retardant coatings.\(^ {13}\) The Clausius-Clapeyron relation, in which the rate of evaporation from a pure liquid increases as the vapor pressure of the liquid’s free surface increases, can describe thermal activation of vapor pressure through the Arrhenius form\(^ {13}\)

\[
\frac{q_1}{q_2} = \exp\left(\frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)
\]

where \(q_1\) and \(q_2\) are the solvent mass flux rate per unit area at \(T_1\) and \(T_2\), respectively, \(\Delta H_{\text{vap}}\) is the heat of vaporization of the liquid, \(R\) is the gas constant.

3.1.3.2 Latex Film Drying and Coalescence

Waterborne film formation proceeds through three stages: water evaporation and colloid concentration, coalescence, and molecular interdiffusion.\(^ {15}\) During the water evaporation stage, the spherical micelles of surfactant stabilized resin slide past one another displacing voids, thereby forming a densely packed lattice. In the absence of the suspending free water, the particle surfaces begin to impinge and exert inter-particle forces. Coalescence begins when the bound water molecules associated with the hydrophilic surfactant on the particle surface evaporate. Polymer-water interfacial tension generates capillary forces that encourage intimate contact between the particle surfaces, creating further polymer-polymer surface energetic interfacial attraction. Once the water phase has been displaced from the particle-particle interface, the polymer chains interdiffuse, forming a continuous phase. In lower molecular weight epoxies with
relatively large molecular mobility, a continuous phase quite similar to a solvent cast film remains following latex film formation.

These three stages of coalescence can be viewed as corresponding to the regimes of progressive latex drying. Croll has identified the four stages of drying illustrated in Figure 3.6 and detailed schematically in Figure 3.7.\textsuperscript{16,17} Regime I is relatively short-lived, consisting of well-separated micelles in a water emulsion. The drying rate corresponding to Regime I is very close to that of free water evaporation. Once a layer of impinging particles forms, the evaporating water from the lower water rich zone is required to percolate through channels at the interstices of particles in the “skin” layer. This period of percolation-limited water transport is designated as Regime II drying in which the drying rate is constant but is significantly decreased from Regime I. Regime II can be viewed as a period in which a transition front between impinging particles and a water-rich reservoir propagates toward the supporting substrate. As the subsurface water-rich zone is depleted, the only remaining water is located in the interstices of the coalescing lattice. This water can still percolate, but is limited by interaction with the particle surfaces. Thus, Regime III is characterized as a falling-rate drying period in which the drying rate is proportional to the concentration of water available to percolate. Regime III continues in an asymptotic approach to complete dryness in which the polymer particles fully coalesce and interdiffuse. Regimes II and III form the phenomenological basis for the two-stage drying model employed in this study. The result is a “dry” film of constant mass, designated as Regime IV, in which some small equilibrium quantity of water, depending on the drying conditions, remains in the polymer. Regimes II and III constitute the basis for a mathematical model of drying developed in Section 3.2.4.

![Figure 3.6: The four regimes of latex drying and the stages corresponding to the two-stage model](image-url)
Croll’s view of drying assumes uniform evaporation over an entire planar film surface. Although this view serves as a successful basis for constructing a workable drying model, it neglects some potentially important aspects of latex drying. When a latex emulsion is poured into a mold with vertical walls a concave meniscus is formed at the walls that is thicker than the center of the mold. This distribution leads to initial drying in the center, with a drying front propagating outward in the plane of the film concurrent with receding front drying into the thickness. This mode of drying was observed in the late stages of the neat latex film drying in this study (since walled molds were used); although the resulting weight loss and model fits were dominated by other effects, non-uniform drying may play some role in interpretation as detailed in Section 3.2.5.1. Conversely, if a latex film is cast onto a glass plate with convex edges, the edges initially present greater surface area for evaporation and therefore dry first. This “ring” of dry zone will propagate inward with final drying in the center.

To this point the discussions of drying and film formation have centered on unfilled latex resins. While neat latex epoxy resins are significant from an adhesives standpoint and have been investigated in this study, the drying of latex impregnating resin systems is of greater importance in interlayer dielectric fabrication. Unfortunately, little published work is available on the drying of fiber-filled latex emulsion. Some understanding can be gained from studies of blend of “hard” and “soft” latex particles, that is, particles below and above their minimum film-formation temperature (MFT), respectively. The MFT of a polymer particle is closely related to its glass transition temperature $T_g$. When only hard particles comprise
a latex, drying is rapid due to the large capillaries at the undeformed particle interstices. Soft latex particles, such as the epoxy latex in this study, will deform during drying to form smaller capillaries reducing water percolation. Hence, the drying rate is lower than in the hard particle case. Winnik and Feng studied blends of hard and soft particles in which the soft particles deformed to fill the spaces around the hard particles. At low volume fractions of hard particles \( \Phi_H \) the drying rate was decreased from that of the pure soft particle latex, with the hard particles creating obstacles in the impinging lattice that increase the tortuosity of the water percolation path. Drying rates increase as \( \Phi_H \) increases to the point where the hard particles disrupt the long-range order of the lattice of soft particles. At high \( \Phi_H \) the drying rate once again decreases as the soft particles plug the pores around the hard particles. This model, shown schematically in Figure 3.8, may be applicable not only to the drying of fiber filled latex resins, but to resins in which a significant number of DICY crystals form in the bulk.

![Figure 3.8: Hard particle obstruction effect in soft latex particle drying](image)

### 3.1.3.2 Residual Surfactant Effects

Significant morphological differences remain between solvent cast and latex films. In studies of latex film formation, surfactant has been shown to segregate to both the film-air and the film-substrate interfaces and to remain either entrapped in inter-particle space or miscible with the polymer. Segregation of surfactant to the substrate-polymer interface can influence the adhesion strength of the system. Strengths decreased in pressure-sensitive adhesive bonds and acrylic film-glass bonds due to the formation of a weak boundary layer, while other surfactants increase adhesion of acrylic to glass through interactions between their hydrophilic part and polar groups on the glass surface. Jensen studied waterborne epoxy systems very similar to those of this study in which the surfactant appeared to be miscible with the cured resin and interacted with the glass reinforcing cloth at the resin/glass interface. Residual surfactant in cured epoxies acts as a plasticizer, reducing \( T_g \) with increasing surfactant concentration. Similar evidence will be presented in following chapters of this study.
The three stages of latex film formation provide the framework for the final distribution of surfactant in the dry film, as shown in Figure 3.9. During the drying stage, the initial distribution and progressive redistribution of surfactant occurs in four locations: the air/latex interface, the substrate/latex interface, the water/particle interface, and in the water phase. Early in drying, the surfactant is generally most concentrated at the water/particle interface, performing its role in dispersion. However, diffusing water can convey surfactant molecules to the air/latex interface. As the particles impinge and coalesce, surfactant is either displaced or desorbed from the particle surfaces along with bound water. This liberated water can again convey the surfactant to the air/latex interface, or it can concentrate the surfactant in the receding liquid water layer adjacent to the impermeable substrate/latex interface. The surfactant’s mobility, dependent upon molecular size and interaction with the polymer surfaces, influences the likelihood of diffusion to either the air- or substrate-latec interfaces, or entrapment in the bulk. Once coalescence is complete and molecular inter-diffusion occurs, the residual surfactant slowly expels to the bounding interfaces, forms a trapped separate phase in the bulk, or interacts with the polymer as a miscible plasticizer.

**Early Drying (Regime I)**

- Surfactant Emulsifies Epoxy Particles

**Transition Drying (Regime II)**

- Surfactant Conveyed to Air/Film by Evaporating Water
- Displacement from Coalescing Particles

**Late Stage Drying (Regime III)**

- Surfactant Trapped in Bulk Interstices
- Concentration in Receding Water Layer at Film/Substrate Interface

**Cured Film**

- Residual Separate Phase in the Cured Bulk
- Miscible Surfactant Plasticizes Cured Bulk

Figure 3.9: The distribution of surfactant during latex drying

Surfactant influences on latex drying mechanisms are complex. Coverage of the water surface by monolayers of oriented surfactant molecules can significantly reduce the rate of evaporation. Perhaps of greater importance in the later stages of drying is the osmotic pressure effect of water retention by hydrophilic surfactants. Isaacs found that a fatty-acid soap and sodium alginate thickener, added to styrene-butadiene rubber latex, slowed drying rates once the water mass fraction dropped to approximately 5 percent, due to the hydrophilic “binding” of water molecules. The presence of surfactant can actually increase drying rates in some systems. Percolation channels become constricted as soft latex particles...
impinge in the late stages of drying, leaving only a “membrane” of hydrophilic surfactant through which water transport can occur. The presence of surfactant in these membranes can increase drying rates compared to films of particles that contained no surfactant.\textsuperscript{18} In fact, in Winnik’s study drying rates increased with increasing surfactant concentration up to a saturation level well beyond the concentration necessary for complete emulsification of the latex particles. It is the formation of these membranes that is suspected to lead to large, segregated surfactant phases in systems. The surfactant comprising the membrane is displaced, during coalescence, to the surface by flowing along the same channels that conveyed the water during drying.\textsuperscript{28} In summary, the influence of surfactant on the drying rate and any relationship between drying behavior and surfactant surface concentration, is unclear and remains a subject of research.\textsuperscript{28,18,29}

Surfactant mobility is not limited to the drying period. It may continue to exude to the surface, or to substrate surfaces, following full coalescence. Juhue’ found that sodium dodecyl sulfate (SDS) surfactant remained mobile in fully dried poly(butyl methacrylate) (PBMA) latex films and exuded to the free surface upon annealing.\textsuperscript{29} The degree of exudation increased with elevated annealing temperature and longer times. It was hypothesized that the surfactant was transported to the surface through channels similar to those described in the drying process. Keintz and Holl have extensively studied the migration of various surfactants in poly(2-ethylhexyl methacrylate) latex films using Fourier Transform Infrared- Attenuated Total Reflection spectroscopy (FTIR-ATR).\textsuperscript{21} The presence and concentration of anionic, cationic, and nonionic surfactants, at the film-air and film-substrate interfaces, varied greatly depending on the material system. Results for the varied concentrations of the surfactant most similar to the one used in this study, ethoxylated nonyl phenol containing 10 ethoxy groups (NP10), are shown in Figure 3.10. Surfactant preferentially concentrated at the film-glass interface, although some film-air concentration was also observed. When a similar film containing 6.5 wt % NP10 was aged for several weeks at 23°C and 55% RH, as shown in Figure 3.11, surfactant migrated to the air-film interface.
Overall, interactions between residual surfactant and formed polymer films are very complex and are strongly dependent upon the material systems and process conditions. Therefore, it is difficult to predict the distribution of surfactant in a fully processed laminate fabricated using waterborne epoxy; the effects of residual surfactants on metal-foil conductor adhesion presented in Section 3.2.3 are an important component of the present study.
3.1.3.3 Electrical Performance

Due to its hydrophilic nature, residual surfactant in the cured epoxy could play a vital role in the uptake of water. In the context of a resin impregnated printed circuit laminate, absorbed moisture lowers the laminate’s dielectric strength and degrades electrical signal transmission due to dielectric heating losses.\(^{30}\) These performance concerns provide motivation for studying the effects of moist environments on the dielectric properties of the waterborne latex epoxy materials. Although the PCB material systems in this study are not designed for use as microwave circuit substrates, a microwave frequency dielectric measurement technique that is very sensitive to the presence of water will be used in investigating moisture effects on the materials’ dielectric properties.

Moisture ingress has been shown to greatly affect the properties of a dielectric material.\(^{31,32}\) The polar structure of water facilitates the instantaneous storage and absorption of radio frequency and microwave energy. At these frequencies the dielectric properties of water dominate those of most polymers and glass reinforcement materials. As shown in Table 3.1, the dielectric constant of free water at 1 GHz is more than 10 times greater than those of the epoxy and glass materials, while the dielectric loss is more than 100 times greater.\(^{30,33}\) Hence, the presence of free water in a dielectric material system can be clearly discerned using microwave frequency characterization.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\varepsilon')</th>
<th>(\varepsilon'')</th>
<th>(\tan \delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>3.5 - 4</td>
<td>0.05</td>
<td>0.015</td>
</tr>
<tr>
<td>Glass Cloth</td>
<td>6 - 6.5</td>
<td>0.025</td>
<td>0.004</td>
</tr>
<tr>
<td>Water</td>
<td>76</td>
<td>12</td>
<td>0.157</td>
</tr>
</tbody>
</table>

Table 3.1: Dielectric property comparison of common printed circuit component materials at 1 GHz

As water molecules initially enter into a material, they interact with, or are bound to, the surfaces that they encounter. This bound water can be energetically associated with other molecules through hydrogen or Van der Waals bonds, or physically adsorbed to the surface of the solid. As more moisture enters the bulk material, it forms a second phase in pores, capillaries, and other cavities. This second phase, free water, has properties that are essentially those of bulk liquid water.

When electric fields are applied to a moist solid material, the water dipoles tend to rotate in alignment with the fields. The dipoles in bound water at the surface of a material posses less rotational freedom than do the free water dipoles that reside in the capillaries and cavities, as illustrated in Figure 3.12. Greater rotational freedom is reflected in higher dielectric losses for samples that contain free water. As bound water molecules progressively cover the solid’s available free surfaces, the dielectric losses remain at a relatively constant value. A critical moisture content is reached when water concentration increases such
that additional water molecules are sufficiently separated from the binding solid surface that their dipoles possess more rotational freedom. Moisture concentrations above this critical point exhibit marked increases in dielectric loss.\textsuperscript{33}

Figure 3.12: Bound water associated with surfaces is incapable of freely rotating under the applied electric field. Away from the surface, the free water dipoles can more easily align with the applied field.

3.1.3.4 Curing Agent Solubility and Precipitate Morphology

Another important difference between solvent cast and latex films involves the behavior of insoluble third phase particles such as fillers or curing agents. This behavior has best been studied in the paint industry where insoluble pigments are supported in solvent-based and latex media. With solvent-based coatings, the dissolved supporting polymer binder medium is free to flow around the insoluble pigment particle during drying, even in the later stages when the binder viscosity increases.\textsuperscript{34} The ability of the solventborne polymer binder to flow allows a uniform deposition process, similar to precipitation, throughout the drying process. The binders in latex coatings can be viewed as “tacky spheres” supported in a water phase, which also supports the pigment particles. During drying, the binder spheres deform instead of flow around the pigments, suspending them at the latex particle boundaries. As the latex coalesces, the final distribution of pigment occurs; if the pigments are trapped into a widely spaced arrangement, the resulting paint film may be a chalky powder.
The epoxy resins in this study follow the paint analogy with the resin-insoluble DICY curing agent particles acting as the pigments. More precisely, DICY is dissolved in a solvent (or water) prior to addition to the epoxy resin (or emulsion). With solventborne resins, the insoluble DICY particles remain intimately mixed in the viscous resin, where the solvent deposited them, with only small-scale crystal formation. As the resin is heated during the cure cycle its viscosity passes through a minimum, whereupon the DICY can coalesce to form relatively large crystals on the substrate surface. The resulting ellipsoidal crystals are referred to in the literature as “cigar” inclusions.31,35 Walker and Cook, in a comparison of solvent- and waterborne epoxy coatings mixed with amine curing agents, found that the solventborne system maintained an isotropic solution during drying while the amines partitioned into “self-assembling aggregates” in the aqueous phase between the micelles, and on the free surface.36 A similar occurrence of curing agent partitioning has been observed in this study.

DICY phase behavior in the latex dispersion is complex and has not been addressed directly in the literature. The following description in based upon experimental observations to be detailed in following sections. A schematic comparison of curing agent precipitation during the two drying processes is shown in Figure 3.13. In the latex epoxy dispersions the DICY is not intimately mixed with the epoxy molecules, existing only in the aqueous phase surrounding the micelle. When the DICY falls out of the aqueous solution during drying, it is segregated to the particle boundaries in concentrations sufficient to form relatively large-scale planar crystals. The percolating water can also convey dissolved DICY to the drying surface, depositing it there in the form of crystals; a “crust” may form if enough DICY is deposited to form a continuous crystal phase. Deposition of DICY crystals on the free surface will have significant influence on adhesion, as will be outlined in Section 3.2.2.

As the resin’s viscosity drops during heating, these planar DICY crystals are more constrained than the DICY in the solventborne case and are therefore trapped in the forming network just as the analogous paint pigments were trapped in a widely dispersed arrangement. This trapping of the DICY may have positive effects as well. If the drying of the latex is rapid, then smaller, homogeneously dispersed crystals will be suspended in the resin. Such a uniform distribution of DICY would lead to greater availability of the curing agent during network formation, leading to higher cross-link density. The process of DICY sedimentation is very complex, depending upon DICY concentration, presence of cure accelerators and fillers, the nature of the substrate, and drying rate. Repercussions of DICY segregation on bulk epoxy morphology and adhesion are addressed in Section 3.2.2.
3.2 Results and Discussion

3.2.1 Dielectric Measurement Results

3.2.1.1 Moisture Effects

At the outset of this study it was suspected that residual surfactant in the cured waterborne epoxy might increase the affinity of the resin system for moisture, thereby degrading its electrical properties. To study this effect, samples of neat resin were prepared and subjected to soxhlet extraction to remove the residual surfactant that might be capable of moisture sorption; these samples were designated as “extracted” while samples from the same batch remained in as-made or “unextracted” condition. Neat resin was initially chosen for extraction instead of laminate materials to avoid the added complexity of water transport at the glass/epoxy interface.

Figure 3.14 depicts dielectric tan δ versus the fraction of water absorption as determined by mass uptake, on a dry weight basis, for each of the three neat resin conditions: waterborne extracted and unextracted, and solventborne. The relatively flat, linear portion of the tan δ vs. moisture at lower moisture content is characteristic of increasing bound water content. At higher moisture content, a demarcation in the slope of tan δ with increasing water content is observed, indicative of the presence of high-loss, free water dipoles.
The moisture fraction where these two lines intersect was taken as the critical moisture content of each system associated with saturation of the free surfaces by water molecules. The critical moisture weight fraction of the waterborne samples was 0.04 (4 wt%) in both the extracted and unextracted samples. Although limited data are available in the free water range for the solventborne material, an increase in tan δ slope at saturation indicates the critical moisture weight fraction to be approximately 0.024 (2.4 wt%).

The samples cast from latex absorbed more moisture and were also prone to absorb more free water than solventborne samples under identical moisture conditions. Little difference is evident in the tan δ behavior between extracted and unextracted samples. Evaluation of the samples’ masses before and after extraction revealed that as much as 1 wt% of the sample had been removed. Although the composition of the extracted fraction is not precisely known, the DICY curing agent is water soluble and residual surfactants may also be water-soluble. Hence it is likely that these components were extracted, their removal having little observable effect on the dielectric performance of the resin.
Figure 3.14: Tan δ vs. moisture sorption in neat epoxy resins showing the bound- to free water transition
A moderate amount of moisture was absorbed by the laminates with a maximum uptake of roughly 2 wt% in the solventborne epoxy/glass and 3 wt% in the waterborne epoxy/glass composites. The stated mass fractions have been calculated for the epoxy matrix material using a fiber mass fraction of 0.75 as determined by TGA. It is evident in Figure 3.15 that neither laminate exhibits the slope change in tan δ with increasing water content characteristic of the presence of gross free water volumes. The waterborne epoxy/glass composites reached a higher tan δ value concomitant with their higher moisture content, with a slight deviation in slope at the highest saturation point. This slight increase in tan δ does not suggest the large deviation in the slope of tan δ seen in the neat resins. An ensemble of neat resin and laminate tan δ values as a function of moisture is shown in Figure 3.16. It is quite significant that the equilibrium moisture in the glass-reinforced systems can essentially be accounted for by the water uptake in the epoxy matrix up to the ultimate saturation point and is not dominated by large-scale moisture migration at the fiber-epoxy interface. Only at the ultimate saturation point, which was achieved by immersion in boiling water, did any indication of a bound-to-free water transition occur. Under these conditions the glass-epoxy interface could have been damaged by the stresses associated with the harsh environment rather than by the weakness of a surfactant rich interface. This finding agrees well with the results of Jensen where the water diffusion coefficients for glass reinforced solvent- and waterborne epoxies indistinguishable.\textsuperscript{25} The absence of a large free water transition in the laminates suggests that moisture ingress is limited to relatively small voids, or disrupted fiber ends remnant from polishing, where the water can remain bound to a large surface area. No gross DICY crystals were evident upon viewing sections of the composites by optical or scanning electron microscopy.

Perhaps of greatest significance is the difference between the neat resin systems in critical moisture content and the magnitude of the tan δ increase in the free water regime. A higher critical moisture content suggests greater capacity for bound water, hence greater internal void surface area accessible to water ingress. Larger tan δ values in the free water regime suggest a greater total volume of water accessible voids. These factors indicate significant differences in the void morphology between the waterborne and the solventborne neat resins. Optical and scanning electron microscopy (SEM) were employed to determine these morphological differences.
3.2.1.2 DICY Inclusion Morphology

Neat resin samples used in the dielectric study were sectioned by cutting with a razor blade and examined using optical microscopy. The horizontal plane views, looking through the top of the sample as configured
in the casting mold, revealed large numbers of residual DICY crystals in both types of resin systems. Upon viewing these sections, the orientation and depth of these crystals were determined. The micrograph of a solvent-cast resin sample shown in Figure 3.17 contains a high density of small “X-shaped” crystals, primarily concentrated near the bottom surface of the sample where DICY precipitated during drying. This crystal morphology is commonly known as the DICY “cigar inclusion”.$^{35}$ Greater detail of these inclusions is shown in the section view SEM micrograph of Figure 3.19A where they are seen primarily to be voids, although one residual crystal is evident. Given the solubility of DICY in hot water, it is probable that most of the DICY crystals were dissolved and extracted during boiling, leaving near-surface ellipsoidal void spaces.

![Image of DICY crystals in solvent-cast resin](image)

**Figure 3.17: Optical micrograph of DICY “cigar inclusions” in cured solventborne epoxy resin**

A distinctly different DICY crystal morphology is found in the micrographs of a waterborne resin, an example of which is shown in Figure 3.18. The horizontal plane view contains a relatively large, irregularly shaped inclusion that is seen to be planar in the section view. This inclusion is actually a void space that was filled with water at the time of sample cleavage; note, in the horizontal plane view, the dark outline of the air bubble that formed just following sample cleavage. Greater detail of this crevice is shown in the section view SEM micrograph of Figure 3.19B where its length is seen to be many times that of the cigar inclusions of the solvent-cast resin. This void was either filled with a planar DICY crystal that was subsequently extracted, or it was opened by cure stresses acting on the thin, weak crystal layer. This difference in void morphology is responsible for the solventborne epoxy’s lower equilibrium water uptake and its weak bound-to-free water transition relative to the waterborne epoxies.
3.2.2 DICY Segregation and Adhesive Strength

As described above, residual DICY crystals in the cured waterborne resin can result in large planar voids within the bulk, while smaller precipitate voids can form in the solventborne resins. The discovery of large residual DICY crystals in the neat resins posed several questions: Would increased DICY concentrations in copper foil clad PCBs result in different inclusion morphologies as well? Would these inclusions disrupt the copper/laminate interface and decrease adhesion? Would the morphological differences in the neat resins affect water uptake behavior as much as the presence of residual surfactant?
To address these questions, the DICY concentration was increased from 3 phr to 4.5 phr in both the solvent- and waterborne impregnating resins during laminate fabrication. Upon peeling the foil from a PCB impregnated with 4.5 phr loaded solventborne resin, a relatively constant peel strength curve was observed (see Figure 3.20).

![Peel Strength vs Peel Distance](image)

**Figure 3.20:** Peel of copper foil from glass-epoxy PCB specimens exhibiting local DICY disruption of the adhesive interface.

The waterborne (4.5 phr DICY) impregnated PCB displayed maximum peel strengths similar to those of the other resin systems; however, local regions of greatly decreased strength were also observed. These weaker regions corresponded to relatively large DICY inclusions at the copper/laminate interface, as shown in the SEMs of Figure 3.21. Similar inclusions were not evident at the copper/laminate interface impregnated with the solventborne resin of the same DICY concentration. A PCB fabricated using waterborne resin with only a 3 phr DICY loading did not exhibit large inclusions following peel. Peel strengths shown in Figure 3.20 for this PCB were essentially the same as those measured for the solventborne impregnated system. These results suggest a lower DICY-segregation threshold concentration in the waterborne impregnating resins relative to solventborne system.
Figure 3.21: SEM images of laminate surfaces following 90° peel of copper foil. A) Solventborne epoxy with 4.5 wt% DICY, B) waterborne epoxy with 3 wt% DICY, C) waterborne epoxy with 4.5 wt% DICY

As detailed in Section 3.1.3.4, it is recognized that, in the latex epoxy dispersions, DICY is not intimately mixed with the epoxy molecules, existing only in the aqueous phase surrounding the micelle. During drying, the DICY is either conveyed to the surface in the percolating aqueous phase, or is concentrated at the inter-micelle boundaries. When the DICY precipitates, it is either segregated to the surface or to the particle boundaries in concentrations sufficient to form relatively large-scale planar crystals. As the resin’s viscosity drops during heating these planar DICY crystals are trapped in the forming network or form a “crust” on the same surface that ultimately will serve as a bonding interface during lamination, thus affecting adhesion. This study seeks to quantify the segregation threshold levels of DICY curing agent in the latex resins.

3.2.3 Residual Surfactant Effects on Adhesion

Copper clad PCB peel specimens containing varied amounts of surfactant were fabricated and tested to examine the stability of the copper-latex epoxy interface relative to that formed with solventborne epoxies. Surfactant concentrations were varied from approximately 5 wt% (native) to 15 wt% (10 phr post-added). Peel results for an etched strip from a 5 wt% surfactant specimen and two strips from the same 15 wt%
surfactant specimen are shown in Figure 3.22. Note that one strip of the 15 wt % specimen was tested in the as-made condition, while the 5 wt % specimen and a second strip of the 15 wt % specimen were aged for 8 hours at 180°C to simulate additional cure cycles. A relatively stable peel curve was obtained for the aged 5 wt % specimen. The as-made 15 wt % strip was slightly tougher due to plasticization of the epoxy adhesive as will be described in Chapter 4, resulting in a more jagged peel curve having a somewhat higher strength. The aged strip from the same 15 wt % specimen had a slightly reduced average strength in the stable peel regime, but exhibited a significant local weak zone near the start of the test. This zone was examined using SEM and optical microscopy to reveal oxidized regions on both the copper foil and laminate surfaces, as shown in Figure 3.23 and Figure 3.24. Note the oval-shaped region of disrupted copper surface connected to the strip edge by a narrow channel (circled in red) in the lower magnification SEM of Figure 3.23. At higher magnification this channel was seen to contain the needle-like crystals, characteristic of copper oxide, erupting through the stabilized nodular surface. This evidence, coupled with the discolored resin in Figure 3.24, indicated that a weakened zone likely caused by surfactant segregation. Analysis by X-ray Photoelectron Spectroscopy (XPS) of a 1mm x 1mm region, which included this zone and the surrounding normal foil prior to gold sputtering revealed the presence of organic carbon, but the absence of nitrogen indicative of curing agents. This led to the conclusion that this was a weakened location where surfactant phase separation disrupted the integrity of the copper-epoxy interphase beneath the peel strip and allowed oxygen diffusion. In the as-made condition, only 1 hour of elevated temperature exposure (normal cure) was not sufficient for large-scale subsurface copper oxide crystal growth. However, after 8 hours of elevated aging the copper oxide disruption of this zone was greatly advanced.
Figure 3.22: Peel of copper foil from glass-epoxy PCB specimens exhibiting local disruption of adhesive strength due to surfactant phase separation

Figure 3.23: Oxidized regions of stabilized copper foil corresponding to phase separation of surfactant at the copper-laminate interface of a 90° peel strip
This type of surfactant phase separation and oxidation was not observed in the peel testing of the native (5 wt %) surfactant emulsions and therefore is not an anticipated failure mode in actual practice. However, in later sections of this work a systematic study of adhesive durability was undertaken as a function of added surfactant. This preliminary result created concerns in preparing specimens for the durability study: would phase separation lead to similar local weak zones in all of the higher wt % surfactant specimens? It is important to note that the prepreg used to construct the peel specimens in which phase separation occurred was dried at room temperature. Drying conditions, as it turned out, were significant to the problem as will be described below. Since the drying and coalescence behavior of the latex is the key to both surfactant and DICY segregation, a two-stage drying model was employed in an attempt to quantify these effects.

3.2.4 Two-Stage Drying Model

A model proposed by Croll 17 and modified by Eckersley and Rudin 38 separates the latex drying process into two regimes: a constant rate stage followed by a falling rate period. The first, constant rate stage occurs as water evaporates from a dry/wet transition zone that recedes into the drying latex bulk. Croll envisioned the first stage ending when the transition zone reaches the impermeable substrate. The second stage then dominates with water percolating through the coalescing polymer bulk. Mathematically, Stage I is described by

\[
\frac{dm}{dt} = -Aq
\]

where \(m\) is the mass of water in the latex, \(t\) is the drying time, \(A\) is the surface area of the drying film, and \(q\) is the evaporation rate per unit area. Stage II follows first order kinetics as
where \( C \) is the water concentration present in the coalescing film. A development of these models and methods of implementation are presented in Appendix I.

This study seeks to employ the two-stage model as a method for gaining further understanding of the drying process in waterborne epoxy latex systems, and as a tool for determining acceptable processing parameters for the latex epoxies in adhesive applications. To compare different latex compositions and drying conditions, a metric must be defined that quantifies the deviation of experimental data from the model. The area of the region bounded by the experimental data and the model fit curves (Figure 3.25), in the normalized water mass fraction- normalized time plane, represents the retardation in drying rate of the latex-under-test versus that of an “ideal” latex as predicted by the two-stage model. Water mass fractions and drying times were normalized by the initial water mass fraction to minimize differences attributable to variations in dilution of the starting latex emulsion. This region, which is designated here as the deviation \( \Delta x \), is defined as:

\[
\Delta x = \int (\hat{x}_d - \hat{x}_m) \, d\hat{t}
\]

where \( \hat{x}_m \) and \( \hat{x}_d \) are the normalized water mass fractions corresponding to the model and the experimental data, respectively, and \( \hat{t} \) is time normalized by the initial water mass fraction. The deviation \( \Delta x \) has units of time.

Figure 3.25: Definition of the deviation (\( \Delta x \)) of experimental drying data from the two-stage model
3.2.5  *Latex Drying*

3.2.5.1  *Evaporation Rates*

It is clear from Equation 3.3 and Equation 3.4 that the key parameter of the two-stage model is the mass flux rate (drying rate) per area, $q$. It is of interest to understand how $q$ varies with the two external variables, temperature and relative humidity. The Clausius-Clapeyron relation for thermally activated evaporation is described by Equation 3.2 to be an Arrhenius function. Samples of deionized water were evaporated at three temperatures and a constant relative humidity of 15%. An Arrhenius fit of the resulting data, shown in Figure 3.26, has a slope with a correlation coefficient of 0.98 that corresponds to an activation energy of 38.0 kJ/mol, which is in good agreement with water’s latent enthalpy of vaporization of 40.6 kJ/mol. The error bars shown in Figure 3.26 correspond to the maximum standard deviation measured for DI water evaporation. Relative humidity’s role in evaporation can be understood by considering the simple linear mass transport boundary condition

\[ q = q_0 (C_s - C_\infty) \]  

where $q$ is the mass flux rate from within the volume, $q_0$ is the mass transfer coefficient of the vapor phase at the surface, $C_s$ is the vapor concentration at the surface, and $C_\infty$ is the vapor concentration of the environment well away from the surface. Since the environmental vapor concentration $C_\infty$ is proportional to the relative humidity, Equation 3.6 describes a linearly decreasing flux rate with increasing % RH. The mass transfer coefficient $q_0$ encompasses the effects of convection on the drying rate. This study was conducted in as near a static environment as possible where it was assumed that only natural convective circulation occurred. In practice, forced-air drying would be employed for process efficiency. In such a case the mass flux rate, $q$, would increase. Croll studied latex drying in two convective environments, “still air” and forced convection at a flow velocity of 1.8 m/s, and found that while the drying rates increased for the latter condition, the physics of film formation remained the same.

Experimental results for the drying of DI water at a constant 63°C and varied % RH are presented in the plot of Figure 3.27. The error bars shown in Figure 3.27 correspond to the maximum standard deviation measured for DI water evaporation. A reasonable linear trend ($R^2 = 0.93$) for water flux per area as a function of relative humidity has negative slope in agreement with Equation 3.6.
Figure 3.26: Arrhenius plot of deionized water evaporation at the three temperatures used in latex drying experiments.

Figure 3.27: Evaporation rates of deionized water at three relative humidities used in latex drying experiments demonstrating a linear relationship.
Croll found the Stage I drying rate of latex emulsions to be approximately 85% ± 15% of the drying rate of pure water in the same environment, independent of material system, in studies of paints and coatings.\textsuperscript{16,17} Winnik and Feng found that the drying rates of pure water and both hard and soft latex films were indistinguishable throughout Stage I drying.\textsuperscript{18} A comparison of typical drying rates, at 63°C and 15% RH, for pure DI water and waterborne epoxy latex resins containing 3 and 4.5 wt% DICY, is presented in Figure 3.28. Note the slightly greater slope in the pure-water drying curve compared to that of the latex resins; the latex resins have very similar drying rates. A summary of Stage I drying rates for epoxy latex resins at 15% RH is presented in Table 3.2. The drying rates presented are, with the exception of the neat resins at 32°C, the average of two or three experimentally determined values. The maximum standard deviation for any of the data sets represented 5.8% of the value of its mean; this error is assumed to represent the maximum error expected for the drying rates except as indicated in Table 3.2.

Results from neat resin drying experiments conducted at 45°C and 63°C agree well with Croll’s 85% drying rate ratio. Neat resin drying rates at 32°C, however, are much lower than those predicted by the 85% rule for pure water. These results suggest some alternate process occurring during drying at lower temperatures; it will be shown in following sections that DICY crystallization at the drying surface significantly impacts the measured mass flux rates. DICY surface segregation was observed visually in neat latex drying at 32°C, resulting in very long drying times and, in some aborted tests, incomplete drying as determined by the existence of opaque uncoalesced resin regions in films that had reached a quasi-equilibrium weight. It was determined that waterborne latex epoxy films of the thickness used in this study could not be produced reliably at 32°C, therefore films used in subsequent dielectric and dynamic mechanical analyses were dried at 63°C. The fact that DICY surface segregation at 32°C was pronounced even at the relatively low 3 wt% concentration indicates a kinetic component to the physics of the segregation process. Du Chesne suggests that fast formation of a “skin” layer by coalescing surface particles closes off many pores that could convey exuding surfactant, thereby resulting in smaller, more evenly distributed internal regions of surfactant.\textsuperscript{28} This same process may be occurring in the low-temperature drying of the neat latex resins; slower drying rates encountered at lower temperatures may allow pronounced DICY segregation prior to surface coalescence.
Drying of the glass supported latex resins at 45°C and 63°C yielded drying rate ratios lower than the 85% value (see Table 3.2), possibly due to three effects: 1) DICY surface segregation, 2) disruption of drying pore paths by the hard glass fibers, analogous to the hard segment argument posed in Section 3.1.3.1.2, and 3) the absence of edge drying. Since, at these temperatures, DICY formed a significant crust only at concentrations greater than 3 wt %, the contribution of DICY to rate depression in Stage I drying of glass-supported latex resins is reasoned to be small. Added water percolation path tortuosity is possible, due to the presence of the hard glass fibers. At higher temperature the driving force for percolation increases as per Equation 3.2. It is feasible that the effect of hard segment obstruction might therefore have a more pronounced influence with increasing temperature. It is believed that edge effect drying is the primary contributor to apparent drying rate ratio depression in the glass-supported systems; edge drying was observed in the neat resins as described in Section 3.1.3.1.2, but was not observed in the glass supported specimens. The glass cloth divided the drying latex resin bulk into many individual drying “cells” where lateral (in-plane) diffusion was minimized. Surprisingly, the drying rate for the 32°C glass-supported specimens was nearly that of pure water. It may be reasoned that the drying is slow enough at this relatively low temperature that hard segment obstruction has no appreciable effect. Note that the 85% value for drying rate ratio has been reported only in neat resin drying and may not hold in the drying of glass-supported latex for the reasons detailed above.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Material</th>
<th>Drying Rate (g/ cm²·s)</th>
<th>q/water [%]</th>
</tr>
</thead>
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<tr>
<td>32</td>
<td>DI Water</td>
<td>0.0131</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3 wt % DICY, Neat</td>
<td>0.0034*</td>
<td>26*</td>
</tr>
<tr>
<td></td>
<td>4.5 wt % DICY, Neat</td>
<td>0.0041*</td>
<td>31*</td>
</tr>
<tr>
<td></td>
<td>3 wt % DICY, Glass</td>
<td>0.0123</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>4.5 wt % DICY, Glass</td>
<td>0.0129</td>
<td>98</td>
</tr>
<tr>
<td>45</td>
<td>DI Water</td>
<td>0.029</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3 wt % DICY, Neat</td>
<td>0.0251</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>4.5 wt % DICY, Neat</td>
<td>0.0236</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>3 wt % DICY, Glass</td>
<td>0.0203</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>4.5 wt % DICY, Glass</td>
<td>0.0199</td>
<td>69</td>
</tr>
<tr>
<td>63</td>
<td>DI Water</td>
<td>0.0525</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3 wt % DICY, Neat</td>
<td>0.0430</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>4.5 wt % DICY, Neat</td>
<td>0.0458</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>3 wt % DICY, Glass</td>
<td>0.0287</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>4.5 wt % DICY, Glass</td>
<td>0.0311</td>
<td>59</td>
</tr>
</tbody>
</table>

Table 3.2: Stage I Drying Rates at 15% RH (Max. Error 5.8%, * indicates unknown error bound)

3.2.5.2 Latex System Comparisons

The two-stage drying model equations can be solved in terms of water mass fraction as a function of time as detailed in Appendix I.\textsuperscript{38} It is of interest to verify that the two-stage model is not a mathematical construct that could just as correctly be described by exponential drying as encountered in solventborne drying. A comparison of neat water-and solventborne volatile mass fraction vs. time is shown in Figure 3.29. A two-stage model curve fits the latex data with excellent agreement. Data for a comparable solventborne sample was fit using the two-stage model, resulting in a significant under-prediction of solvent mass fraction with time. When the solventborne data is instead fit with a single term exponential decay function the agreement is greatly improved. This comparison illustrates the fundamental differences between the physics of latex and solution drying.
3.2.5.2.1 DICY Concentration

Experimental data and model predictions for two neat latex epoxy formulations, containing DICY concentrations of 1 and 3 wt % and dried at 63°C and 15% relative humidity, are shown in Figure 3.30. All latex epoxies studied as a function of DICY concentration contained only native (5 wt %) surfactant. The Stage I model agrees very well with the data at higher water mass fractions, while the lower mass fraction data slightly deviate from the Stage II model. Overall, the model agreement is excellent, suggesting that a fundamental two-stage drying process accurately describes drying in this latex epoxy system. Data measured for neat resin samples containing higher DICY concentrations of 4.5 and 6 wt % are shown in Figure 3.31 accompanied by their corresponding model predictions. Stage I predictions are quite good; however, the Stage II models significantly underestimate the actual water mass fraction in the drying film. It was observed that crystals had formed within the bulk and on the surface of these higher DICY content films following drying and coalescence. It is hypothesized that this surface layer of DICY forms a barrier to moisture evaporation, thus slowing mass loss during Stage II. The 4.5 wt % DICY experimental data deviated from the model well into Stage II, suggesting that significant surface segregation does not occur until some critical concentration of DICY is reached in the percolating water. It is important to note that the Stage I drying rates shown in Table 3.2 for the 3 and 4.5 wt % are the same, within experimental error.
This hypothesis is reinforced by observing that the 6 wt % experimental data deviated from the model at roughly the same point in normalized time, but “earlier” in terms of the transition from Stage I to Stage II.

Figure 3.30: Two-stage drying model predictions and experimental data for neat latex epoxy resins containing 1 and 3 wt % DICY.
Films of the 3, 4.5 and 6 wt % DICY loaded resins were cured and their drying surfaces examined using SEM; micrographs of these surfaces are shown in Figure 3.32. Note the flat, smooth surface of the 3 wt % film, followed by the progressive roughening of the surface caused by the presence of remnant DICY crust in the 4.5 and 6 wt % micrographs.
Given that the two-stage model was developed for unfilled latex films, it is significant that it also works very well in describing the drying of the glass-reinforced latex epoxies in this study. The model is implemented by simply subtracting the mass of the dry glass cloth from the starting wet mass of the prepreg, then entering the remaining latex resin mass into the model as if it were a neat film. Although this simplification would seem to neglect the influence of the glass fibers, it must be recalled that the model is semi-empirical; the influence of the glass cloth will be reflected in the initial water flux rates, \( q \), used to construct the model (Appendix I). Experimental data for drying glass/latex epoxy containing varied DICY concentration are shown in Figure 3.33 with the corresponding two-stage models. Note that the 3 wt % DICY loaded resin/glass data are in excellent agreement with the model. As in the neat resins, the 4.5 and 6 wt % DICY material drying results diverged from the model prediction in the Stage II regime. The cause of the drying retardation is DICY crystal formation on the surface, as is shown in Figure 3.34B.
A summary of the deviations $\Delta_x$, as defined in Equation 3.5, from the two-stage drying model for neat and glass reinforced epoxy latex, as a function of DICY concentration, is presented in Figure 3.35. A significant trend of increasing deviation with DICY concentration is observed for the neat resins with an apparent threshold between 3 and 4.5 wt% at 63°C and 15% RH. A similar, if not as pronounced, threshold between 3 and 4.5 wt% DICY can be seen for the glass-latex epoxy system. The smaller $\Delta_x$ magnitude in the glass-reinforced material may result from disruption of the DICY crust formation by the fibers later in Stage II drying, thereby allowing marginally better water transport. In the final analysis, the
A two-stage model successfully identified the threshold of DICY concentration corresponding to observations of surface segregation.

![Figure 3.35: Experimental deviation from the two-stage model in neat and glass-supported epoxy latex resins as a function of DICY concentration. Drying conditions: 63°C, 15 % RH](image)

The results of Figure 3.35 represent only a single condition of temperature and relative humidity. It is of interest to understand how the critical DICY threshold changes depending upon the drying conditions. A summary of deviation $\Delta_x$ as a function of temperature, at 15 % RH, for 3 and 4.5 wt % DICY loaded neat latex resin is shown in Figure 3.36. As seen in Figure 3.35, for 63°C drying the latex containing a 3 wt % DICY concentration corresponds to a small $\Delta_x$, while $\Delta_x$ for the 4.5 wt % latex is significantly larger. As temperatures decrease, $\Delta_x$ increases monotonically in both material systems. Since the Stage I drying rate ratios for these systems agreed well with the 85 % value at 63°C and 45°C, these dramatically larger deviations suggest that critical DICY threshold values are related to Stage II drying kinetics. As discussed previously, the faster a coalesced “skin” layer forms on the surface, the less material is conveyed to the surface. The large $\Delta_x$ observed in the latex dried at 32°C is expected given the very low Stage I drying rates discussed previously. Deviation results for glass-supported latex resins, as a function of temperature at 15 % RH, are shown in Figure 3.37. Note that trends in $\Delta_x$ similar to those observed in the neat reins systems are evident, though the magnitudes of these deviations are smaller. If drying kinetics are a
controlling factor in determining threshold DICY concentration, then variations in relative humidity should also have an effect.

Figure 3.36: Experimental deviation from the two-stage model in neat epoxy latex resins as a function of drying temperature. Drying conditions: 15 % RH.
Deviation values at 63°C for neat latex resins loaded with 3 and 4.5 wt % DICY, as a function of relative humidity, are presented in Figure 3.38. In the 3 wt % latex, $\Delta_x$ is consistently small; the two-stage model actually appears to have over-predicted the measured drying behavior at 25 % RH, though this variation is within experimental error. Note that, for the 1.5 % RH condition, the $\Delta_x$ associated with the 4.5 wt % DICY loaded latex is as small as those for the 3 wt % DICY resins. This result suggests minimal surface segregation of DICY in the 4.5 wt% DICY neat resin dried at 1.5% RH, which was borne out by optical microscopy as shown in Figure 3.39A where no surface crystals are evident. Deviations increase in the 4.5 wt % DICY system as relative humidity rises, though the increase is not as dramatic as that for elevated temperature. The optical micrograph of Figure 3.39B confirms DICY crystal “crust” formation in the neat resin dried at 15%RH. This trend is consistent in terms of drying kinetics: the thermal dependence of drying is exponential (Arrhenius) while relative humidity dependence is only linear. Glass-latex resin deviations as a function of relative humidity at 63°C, are shown in Figure 3.40. Uniformly small $\Delta_x$ values are observed in the 3 wt % DICY loaded system. Deviations for the 4.5 wt % DICY loaded material are larger than those for the 3 wt % loaded latex, suggesting that the threshold DICY concentration for the glass-supported resins is somewhat lower than that of the neat resin. Interestingly, the difference in deviation magnitude between neat and glass-supported materials as a function of % RH at constant temperature is not nearly as large as that observed between these systems as temperature was varied at
constant % RH. In summary, there is a DICY concentration threshold above which surface crystallization occurs during Stage II drying. This surface segregation depends upon the kinetics of drying as reflected in results observed for drying under different environmental conditions.

Figure 3.38: Experimental deviation from the two-stage model in neat epoxy latex resins as a function of the relative humidity of the drying environment. Drying conditions: 63°C.

Figure 3.39: Optical micrographs of cured neat latex epoxy resin containing 4.5 wt % DICY dried at 63°C and A) 1.5 % RH and B) 15 % RH
Figure 3.40: Experimental deviation from the two-stage model in glass-supported epoxy latex resins as a function of the relative humidity of the drying environment. Drying conditions: 63°C.

3.2.5.2.2 Surfactant Concentration

Two-stage drying model fits to neat latex epoxy resin drying data, for varied surfactant concentration, are presented in Figure 3.41 and Figure 3.42. All latex epoxies used in the study of surfactant concentration contain 3 wt % DICY. Results for the neat latex resin containing only native surfactant (5 wt %) demonstrate excellent agreement with the model, as is expected from the previous results. Further addition of surfactant results in increased $\Delta x$, suggesting surfactant retardation of moisture transport during Stage II drying. There was no evidence that exudation of surfactant to the surface, analogous to DICY segregation, was responsible for the observed increase in deviation. Neat films of varied surfactant content produced during the drying study were cured and removed from the mold without disturbing the free surface. These films were first weighed, then the free surface was either rinsed with DI water alone, rinsed with DI water and wiped with a lint free tissue, or rinsed with acetone. Following overnight drying at 90 °C the samples were reweighed. No appreciable or systematic change in mass was observed. A sample of pure Triton X-100 was weighed, subjected to the identical curing conditions as the films, cooled, and reweighed.
Although the surfactant browned slightly, mass changes were recorded to be less than 5%; such a small change in mass proves that the surfactant did not evaporate during the curing of the epoxy films. Therefore, it can be concluded that the cured films did not possess significant surface concentrations of surfactant following drying. It will be shown in Chapter 4 that, in the neat latex resins, the location of the surfactant can be accounted for by interaction with the bulk epoxy network. The reason for the increased $\Delta$, is attributed to stronger retention of water by the increasingly concentrated aqueous surfactant solutions in the receding wet zone. This receding zone exists during Stage II drying, which is where the experimental data deviate from the models. A similar process, in which mobile excess surfactant concentrates in the aqueous phase instead of associating with the hydrophobic dry polymer, has been suggested by Kientz and Holl to explain surfactant segregation to the glass support substrate instead of to the free surface.

Figure 3.41: Two-stage drying model predictions and experimental data for neat latex epoxy resins containing 5 wt % and 7.5 wt % surfactant.
Figure 3.42: Two-stage drying model predictions and experimental data for neat latex epoxy resins containing 10 wt % and 15 wt % surfactant.

Two-stage model fits of glass-supported latex resins dried at 63°C and 15 % RH, containing a range of surfactant, are shown in Figure 3.43. The glass-latex material containing only native surfactant (5 wt %) agrees very well with the two-stage model. As in the neat resin case, increased surfactant concentration correlated with increased $\Delta x$. It is believed that the arguments against surface segregation of surfactant during drying, as detailed above for neat resins, apply to the glass-supported resins as well. The hypothesis of surfactant concentration in the receding aqueous phase, followed by segregation to the substrate (the glass fibers in this case), is important in interpreting results to be presented in later sections. This phenomenon would explain the phase separation effect shown in the aged peel results of Section 3.2.2.

Recall that the PCB peel specimen containing 15 wt % surfactant exhibited copper/epoxy interfacial phase separation and subsequent oxidation following thermal aging. It is reasonable to hypothesize that excess surfactant, segregated to the interphase of the glass fibers, migrated to the interphase during the lamination process to form a weak zone. A summary of the deviations measured for both the neat and glass-supported latex resins is presented in Figure 3.44. A general increase in $\Delta x$ is observed with increasing surfactant concentration in both the supported and neat resins.
Figure 3.43: Two-stage drying model predictions and experimental data for glass-supported latex epoxy resins containing 5, 10, and 15 wt % surfactant.
3.3 Summary

Given that the molecular structure of the epoxies used in both solventborne and waterborne latex laminating resins is the same, potential performance dissimilarity must arise from 1) differences in the physics of film formation or 2) the presence of additives residual from the emulsion. Fundamental differences exist between drying and film formation processes of solventborne and waterborne latex resins. When a solid, resin-insoluble curing agent, such as DICY, is used in the laminating resin formulation these differences in the drying process can lead to distinct, and potentially disadvantageous, crystal sediments. Small ellipsoidal sediment crystals form in neat solventborne resins, while large planar DICY crystal morphologies have been observed in the bulk of cured, neat waterborne latex epoxies. These distinct morphologies lead to different levels of moisture sensitivity in the neat resins, thereby resulting in significantly degraded electrical performance. Glass reinforced PCB laminates fabricated using waterborne latex resins did not contain large crystal morphologies in their bulk, but DICY segregation and crystallization on the surface of prepreg materials have been observed. These crystals locally decrease the adhesive strength of copper/epoxy bonds in PCB laminates.
A better knowledge of the drying process in latex epoxy systems is the key to understanding surface DICY segregation. Preliminary studies suggested the existence of a threshold DICY concentration below which no surface crust was formed; therefore, a method was sought by which this threshold, and the effects of varied drying conditions on it, could be identified. A two-stage drying model was instrumental in quantifying the threshold conditions for DICY segregation in drying and coalescing latex epoxy resins. The application of this approach to the drying of both neat and glass-supported latex epoxy was successful; it has been employed not only as an engineering tool for identifying suitable drying conditions, but has provided some insight into the drying process as well. Drying experiments in which the DICY concentration in the latex resin, as well as the temperature and relative humidity were varied, revealed that drying kinetics likely plays an important role in determining the critical threshold for surface segregation. Conditions favoring faster drying (higher temperature and lower relative humidity) lead to reduced surface DICY segregation. It is hypothesized that these conditions result in the rapid formation of a coalesced “skin” layer, and quicker coalescence of the bulk latex, thereby trapping DICY in the lattice before it can be conveyed to the surface by percolating water.

Surfactant residual from the emulsification process is an obvious issue of concern in replacing solventborne resins with waterborne latex epoxies. A series of PCB laminates were fabricated, using latex epoxy resins containing varied surfactant concentrations, as part of a study of surfactant effects in copper/epoxy adhesion. A preliminary peel test of PCB laminates containing elevated surfactant concentration (15 wt %) showed signs of surfactant phase separation at the copper-epoxy interface. This interface was susceptible to oxidative degradation following elevated temperature aging. No such surfactant phase separation was observed in laminates fabricated using latex resins with native surfactant (5 wt %); this phenomenon is not anticipated to be a problem in actual practice. Nevertheless, a further study into the systematic effects of surfactant on adhesion is the focus of another section of this work. Therefore, the two-stage model was employed in an analysis of surfactant concentration on drying behavior to determine whether surface phase separation occurred during coalescence. Although the drying behavior of higher-surfactant resins deviated from the model in a manner analogous to resins that formed surface DICY crusts, no surface segregation of surfactant was observed. It has been hypothesized that drying rates for latex resins containing greater surfactant concentration were retarded by the presence of hydrophilic surfactants in the receding wet zone during Stage II drying. Ultimately, upon complete drying, this surfactant would either be driven to the support substrate (glass fibers in the case of prepreg materials) or would become miscible in the epoxy bulk. This conclusion will be important in understanding surfactant-related influences on the adhesive and electrical properties of PCB laminates reported elsewhere in this study.

3.4 References
2 Shell Technical Note: SC:67-81, Shell Chemical Company.
12 Private communication, Shell Technical Information.