

Moisture Absorption Properties of Laminates Used in Chip Packaging Applications

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Abstract

Plastic laminates are increasingly used as interposers within chip packaging applications. As a component within the package, the laminate is subjected to package moisture sensitivity testing. The moisture requirements of chip packaging laminates are related to ambient moisture absorption and thermal cycling. Printed wiring board (PWB) laminates, however, are gauged on properties relating to wet processes such as resist developing, copper etching, and pumice scrubbing. Consequently, printed wiring board moisture absorption test methods differ from chip packaging test conditions.

The moisture absorption properties within a bismaleimide/triazine laminate was investigated under pressure cooker conditions (121°C, 2 atm) and compared to absorption properties measured under chip package moisture sensitivity tests (as specified by the JEDEC Solids State Engineering Council). For pressure cooker testing, silane coupling agent and construction were the dominant factors contributing to laminate integrity. Exposure to JEDEC conditions, however, showed that moisture absorption into the laminate is dominated by the bulk resin matrix. Furthermore, moisture behavior under packaging conditions is characterized by Fickian diffusion yielding characteristic diffusivity and saturation parameters.

Introduction

The current study investigates moisture absorption properties in a new bismaleimide triazine (BT) based laminate, specifically formulated for chip packaging applications. The laminate possess excellent thermal properties (T_g approaching 200°C), superior electrical performance, and low moisture absorption. Moisture absorption is investigated under pressure vessel (cooker) test conditions established by the Institute for Interconnecting and Packaging Electronic Circuits (IPC) and compared to the absorption properties measured under the JEDEC Solids State Engineering Council (JEDEC) Level 1, 2, and 3 conditions. Results give significant insight into the importance of the glass resin interface within a chip packaging laminate.

Background

Laminates traditionally used in printed wiring boards (PWB) are seeing increased use as interposers within silicon chip packaging. Laminates are attractive for chip packaging because the cost of a PWB-type laminate is significantly lower than the all ceramic substrates typically used for this application. As chip packaging has evolved from both a materials and processing stand point, laminates have become the standard in packages such as the immensely popular Plastic Ball Grid Array (PBGA).¹ Future packaging directions using flip chip attach will also

require low cost solutions and most likely will be dominated by PWB-type laminates.¹

As a component within a chip package, the laminate will be subjected to stringent moisture sensitivity testing. Moisture sensitivity is an issue because a chip package is exposed to solder reflow temperatures in excess of 200°C. At these high reflow temperatures, absorbed moisture may cause package cracking as the water becomes vapor. Within the PBGA package family, moisture induced failure has been primarily linked to water absorbed in the die attach adhesive which causes large internal pressures under reflow.² PBGA packages typically crack to alleviate these pressures. Since moisture typically enters a PBGA package through the laminate substrate, an understanding of the moisture absorption processes in chip packaging laminates will enhance development of improved high density interposers.³

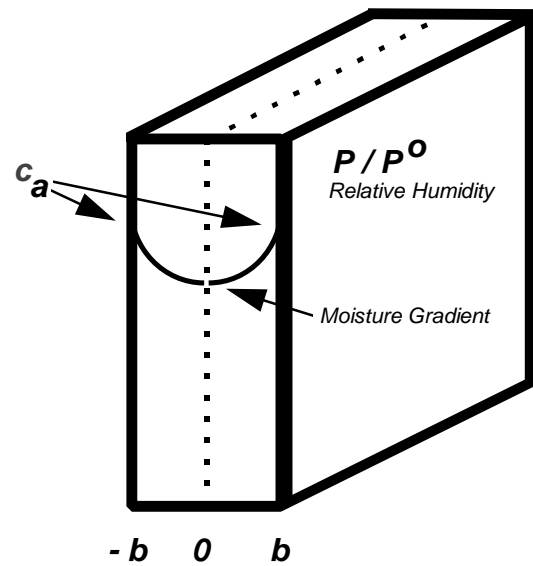
PWB-type laminates are frequently manufactured as fiber glass reinforced polymeric substrates with fillers being added to improve electrical properties or enhance board processing. In a typical glass reinforced laminate, the system is generally modeled as having three phases: the glass fiber, the resin matrix, and an interface region between the resin and glass. The interface region serves as an adhesion layer binding the resin to the glass and is

formed by a coupling agent coated on the glass fibers. Coupling agents are silanes with a hydrolyzable silicon end group which reacts with the glass surface and a reactive organic end group which bonds to the resin matrix. The interface is complicated and involves both chemisorbed as well as physically absorbed coupling agent.^{5,6} The interface region most likely has a gradation from a very rich silane layer at the glass surface to an increasingly polymer rich resin - silane interpenetrating network (IPN) before the pure resin matrix.⁷ The importance of this region to moisture absorption characteristics has been widely investigated.

Moisture permeation into a chip packaging laminate can proceed by absorption into the resin - glass interface region or into the resin matrix. When the reinforcement is glass, the moisture absorption in this phase is negligible. Moisture absorption at the interface can be rapid with a high final equilibrium moisture content.^{4,8,9,10,11} This process may not be significant to the overall laminate moisture absorption properties, however, do to the thin nature of the interface region compared to the bulk resin. For example, the interface could be as thin as 30 Angstroms which equates to less than 1% by volume of the resin.⁹ Undoubtedly, the interface integrity is important. If no coupling agent is used or the interface is damaged, moisture absorption can be significantly increased.¹² With an optimized interface, however, the interface absorption has been shown to be negligible, and the resin matrix dominates the laminate moisture absorption properties.^{12,13,14}

Laminate moisture absorption theories have considered the resin matrix moisture absorption as a chemical versus physical behavior. Water bound to the resin (chemical absorption) is typically characterized by absorption hysteresis with a step-wise uptake over time.¹³ Physical absorption is completely reversible with a smooth moisture uptake and has been modeled as a Fickian diffusion process in a wide variety of PWB laminates.^{12,14,15} Fickian diffusion processes are represented by Fick's law and the many readily available solutions.

Moisture absorption in an unclad one dimensional laminate under constant temperature and humidity conditions is depicted in Figure 1.



Laminate of Thickness 2b

Figure 1 - Unclad Laminate

Upon initial humid environment exposure, the laminate surface equilibrates with the environment by rapid convective mass transport, and moisture begins to diffuse into the laminate along chemical potential gradients. This one dimensional absorption process is mathematically governed by Fick's law:¹⁶

Equation 1

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

$$c = c_i \quad @ \quad -b < x < b \quad \& \quad t \geq 0$$

$$c = c_a \quad @ \quad x = -b \text{ or } b \quad \& \quad t > 0$$

The solution to this Fick's second law problem is well known:

Equation 2

$$\frac{C_t}{C_l} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 p^2} e^{-\frac{D(2n+1)^2 p^2 t}{4b^2}}$$

where C_t is the average absorbed moisture concentration at time t , C_l is the equilibrium (saturation) moisture absorption, D is the diffusion coefficient, and b is half the laminate thickness. The rate of moisture absorption is controlled by the time constant which includes the diffusion coefficient and the laminate thickness. After infinite time in a given

environment, the laminate will have a moisture level defined by the equilibrium absorption. To model the moisture absorption process, the laminate can be exposed to a humid environment, and the weight gain can be measured until equilibrium is reached. From the resulting graphs, the above equation can be fit to the data determining the diffusion coefficient and equilibrium moisture absorption value.^{12,14,15}

Sample Preparation

Chip packaging laminates clad on two sides were manufactured with the BT resin system. Core constructions were chosen to meet PBGA specifications and pressed with 1/2 oz. copper. Two constructions were investigated along with three different silane coupling agents coated on the glass. Table 1 summarizes the laminates investigated. Before all moisture absorption experiments, the copper was etched using standard etching practices.

	Table 1. Laminate Constructions		
	Coupling A	Coupling B	Coupling C
Three ply Two plies 2116 (outer) with one ply 7628 inner	Sample A	Sample B	
Four ply Four plies 2116.	Sample C		Sample D

Results and Discussion – IPC Pressure Vessel The laminate constructions were subjected to the IPC Pressure Vessel test, 2.6.16 of IPC-TM-650. The testing protocol, commonly known as a “pressure cooker test”, requires 4” X 4” unclad laminates be subjected to a 2 atm (14psig), 121°C moisture atmosphere for 96 hours. After 96 hours the samples are visually inspected. In addition, laminate cross sections can be taken and examined under 100 – 200X magnification to further define voids and resin to reinforcement separation. Compared to unconditioned samples, the appearance of measling, weave exposure, and loss of surface resin is graded qualitatively using a scale from 1 - 5:

Grade 5: No measling, delamination, weave exposure, voiding or other degradation in excess of that observed on the unconditioned sample.

Grade 4: Very slight measling; or slight weave exposure.

Grade 3: Slight measling or weave exposure; or maximum of 3 voids no greater than 0.010 inch.

Grade 2: Moderate measling or weave exposure; or more than 3 voids no greater than 0.020inch.

Grade 1: Heavy measling and weave exposure; or voids greater than 0.020 inch; blisters or delamination.

Samples exposed to the pressure cooker test were compared by visual inspection of the surfaces as well as through cross sections. Visual comparison between the four conditions showed significant differences in measling with no severe delamination or blistering. Table 2 summarizes the visual grading results. Cross sections of the conditions were potted in a clear epoxy, a laminate edge polished smooth, and the laminate edge viewed under a reflective scope at 200X magnification. Figures 2a – 2d indicate the typical defects observed using this technique.

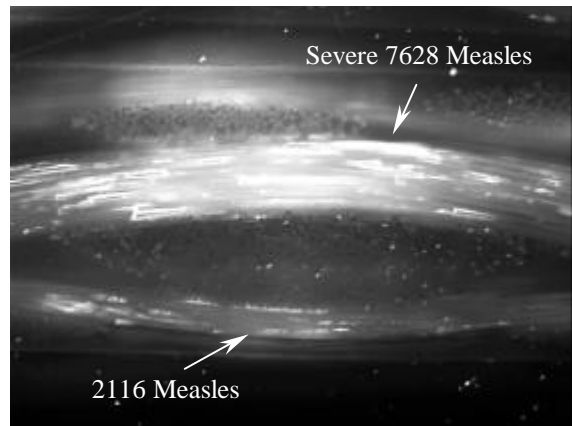


Figure 2a – Sample A Cross Section

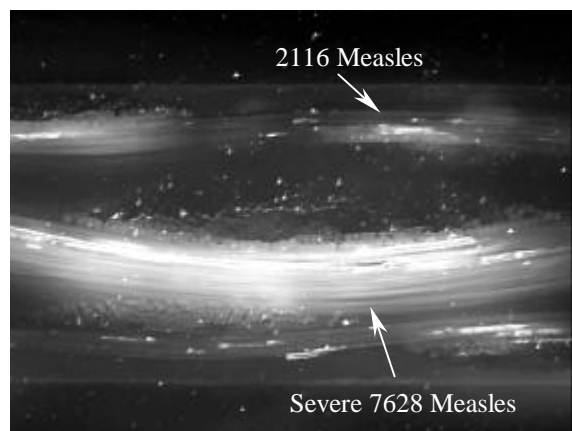


Figure 2b – Sample B Cross Section

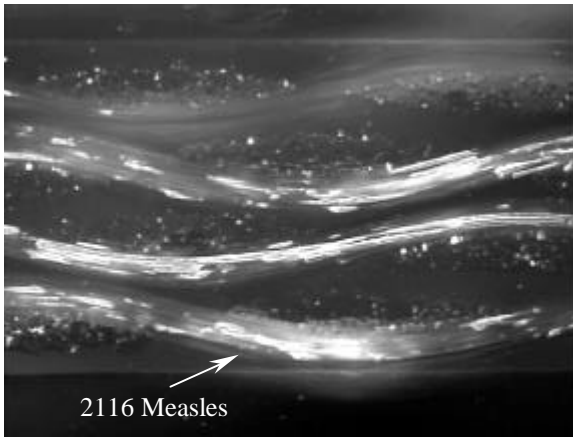


Figure 2c – Sample C Cross Section

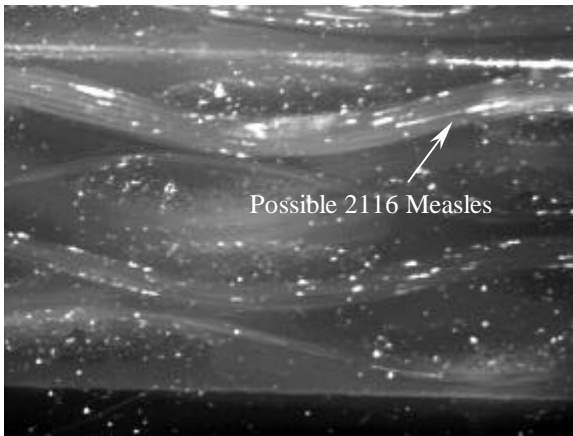


Figure 2d – Sample D Cross Section

The laminate constructions were important in improving the test results. By studying the cross sections, the three layer cores showed void formation mainly along the 7628 glass yarns culminating at the weave knuckle. When voids were present in the 2116 glass in either construction, the defects were small and throughout the yarn. Constructions based on finer 2116 glass (Sample C) appear to be more resistant to pressure cooker testing than the heavier 7628 glass (Sample A).

The largest improvement in pressure cooker resistance came when the glass coupling agent was changed. Higher visual ratings were apparent when comparing Sample B to A and Sample D to C and were accompanied by much lower void formation. Changing the coupling agent on the four ply construction produced Sample D, and significantly increased the visual inspection to a pass rating. The choice of coupling agent significantly affects the glass - resin interface indicating the importance of this region to passing the pressure cooker test.

Table 2 - Pressure Cooker Visual Results

	Coupling A	Coupling B	Coupling C
Three ply Two plies 2116 (outer) with one ply 7628 inner	1.0	2.0	
Four ply Four plies 2116.	3.0		5.0

Results and Discussion – JEDEC

The laminate moisture absorption properties were measured at temperature and humidity conditions set by the JEDEC Solid State Products Engineering Council for testing chip packages. These conditions (summarized in Table 3), are used to test package moisture resistance under solder reflow conditions.

Table 3 - JEDEC Conditions

	Level 1	Level 2	Level 3
Temperature (°C)	85	85	30
Humidity (% Relative)	85	60	60

Laminate samples were prepared square (approximately two inches on a side with edges and glass fibers perpendicular), and the edges were polished smooth using 400 grit paper. Per the package standard test protocol, all laminates were first dried at 125°C for 24 to 48 hours. Samples were cooled then to room temperature under a dry desiccated environment, the laminate thickness was measured using a micrometer, and an initial laminate mass was recorded (100 µg accuracy). Temperature and humidity conditions were accomplished using an Espec Model SH-240 humidity chamber. Samples were periodically removed from the chamber, the mass was measured, and the sample were promptly returned to the environment. At the completion of uptake experiments, each sample’s resin content was determined by burning off the resin at 700°C and measuring the glass mass remaining. Table 4 summarizes the nominal laminate thicknesses and resin contents.

Table 4 - Laminate Properties

	Sample A & B	Sample C & D
Thickness (inches)	0.0143	0.0157
Resin Content (wt. %)	40.1	44.0

Moisture permeation into the laminates was measured until a final equilibrium value was reached. Figure 3 gives a typical set of data demonstrated on Sample D. The moisture uptake in

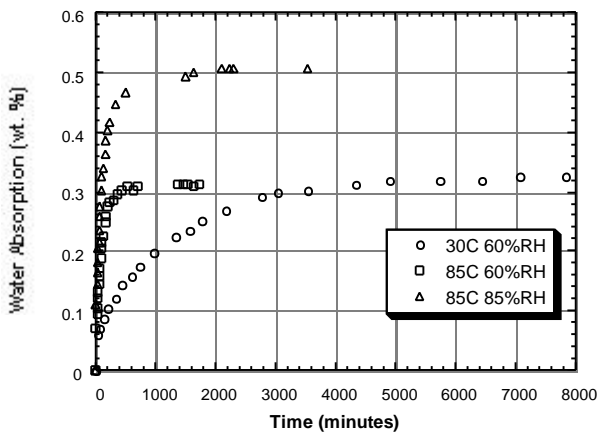


Figure 3 – Sample D Absorption Curves

all conditions was observed to proceed smoothly and to asymptotically approach a final absorption weight (typical of a Fickian diffusion process). Whether the absorption process was one dimensional or involved appreciable edge effects was investigated using two inch square copper clad samples. The cladding effectively blocked the moisture diffusion process into the laminate faces. Consequently the laminate showed very little moisture absorption as

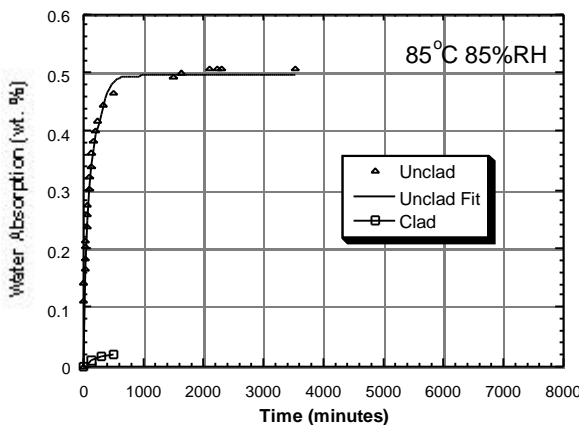


Figure 4 – Sample D Edge Effects

demonstrated in Figure 4. Since edge diffusional effects were negligible in these experiments, the diffusion process was modeled as being one dimensional. To ensure the characteristic diffusion length did not change during the experiment, after reaching saturation the laminate thickness was measured and compared to the initial value. In all cases, the laminates showed a small negligible increase in thickness much less than 1%.

Equation 2 was fit to the absorption curves by minimizing the sum of square error between the equation and the data. Both the equilibrium moisture concentration and the diffusivity were allowed to vary during the fit even though a final equilibrium value was evident from the data. The Fickian diffusion model was found to fit the data very well as demonstrated in Figure 5. All samples produced similar agreement to the model.

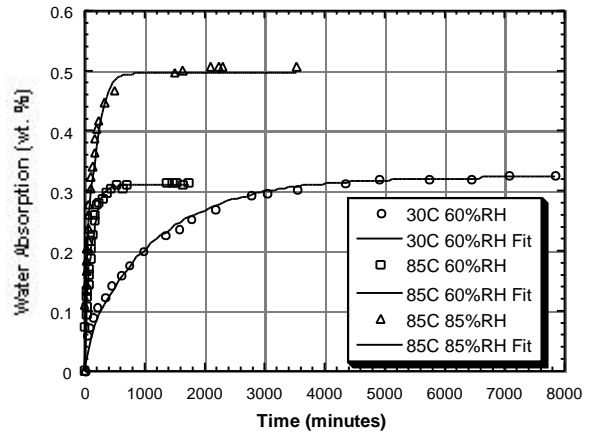


Figure 5 – Sample D Fit to Fickian Model

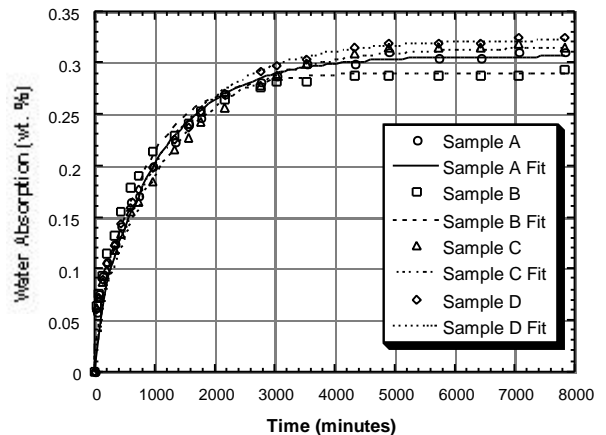


Figure 6 – Construction Comparison

Comparing absorption curves between the different laminate conditions revealed only small deviations (Figure 6). Varying the construction or the interface coupling agent did not compromise the Fickian diffusion behavior.

Comparison of the absorption curves in Figure 5 suggests that JEDEC level conditions impacted the moisture uptake process. Increasing temperature from Level 3 to Level 2 increased the rate to equilibrium without significantly affecting the saturation value. Diffusion coefficients were determined on the order of 2×10^{-8} sqcm/s at 85°C and 2×10^{-9} sqcm/s at 60°C. Increasing the relative humidity from Level 2 to Level 1 increased the

saturation value but did not appear to affect the uptake rate. Saturation values were typically determined to be 0.5% at 85%RH and 0.3% at 60% RH. These trends on temperature and humidity effects in BT laminates are in agreement with other investigations.¹⁴

Since the rate of moisture permeation characterized by the diffusion coefficient varied insignificantly between the different laminate conditions, a resin dominated moisture absorption process is indicated. Table 5 lists diffusion coefficients at Level 3 conditions and shows little variation between samples. Using a three ply laminate compared with a four ply construction had very little affect on the diffusion process. The laminate constructions had similar resin contents which translate to similar resin volume fractions. Laminate diffusion coefficients depend on the resin volume fraction with less than a linear dependence.^{14,16} Consequently, the effect of small changes in resin volume fraction is lost within the experimental error of this study. More importantly, diffusion coefficients were independent of the glass resin interface at all JEDEC levels indicating the resin dominated the moisture diffusion.

Determining the barrier energy to diffusion substantiates a resin controlled process. In Figure 7, the diffusion coefficients at Level 2 and Level 3 are plotted in accordance with an activated energy process, and similar slopes are apparent between

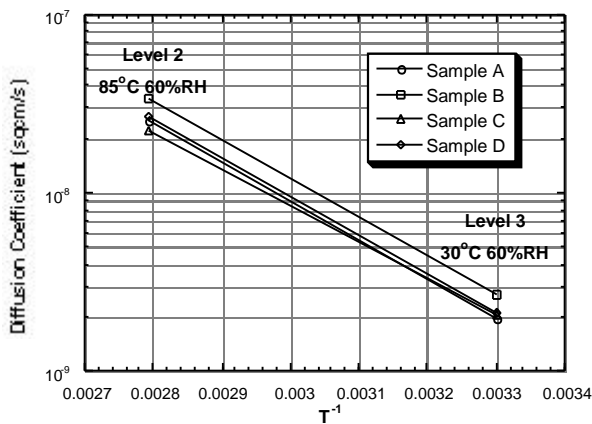


Figure 7 – Diffusion Activation Energy

laminate conditions. The resulting activation energies summarized in Table 6 are almost identical which indicates that the diffusing water molecules are within the same phase independent of the resin glass interface.

Table 5 – Diffusivity at 30°C, 60%RH, (cm²/s)

	Coupling A	Coupling B	Coupling C
Three ply Two plies 2116 (outer) with one ply 7628 inner	1.97 X 10 ⁻⁹	2.70 X 10 ⁻⁹	
Four ply Four plies 2116.	2.05 X 10 ⁻⁹		2.16 X 10 ⁻⁹

Table 6 - Activation Energies, (kcal/gmole)

	Coupling A	Coupling B	Coupling C
Three ply Two plies 2116 (outer) with one ply 7628 inner	10.06	9.88	
Four ply Four plies 2116.	9.37		9.88

Finally, further evidence of moisture primarily residing in the resin is found by studying the saturation values. Figure 8 compares the moisture saturation at Level 1 and Level 2 conditions with the lines indicating general trends. The four ply constructions appear to absorb more moisture compared to the three ply materials. Higher

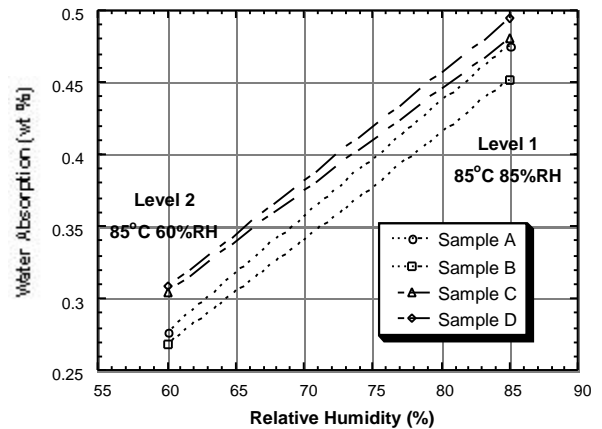


Figure 8 – Saturation Values

moisture absorption is primarily linked to the higher resin contents noted in Table 4. Assuming the bulk of the moisture resides in the resin phase, the saturation values can be adjusted by resin weight fractions to compare differing resin content laminates.^{14,16} In this study, the four ply saturation

values can be multiplied by $40.1/44.0 = 0.91$ for comparison to the three ply materials. Using this correction factor on the data in Figure 8, the saturation values for the two different constructions overlay, thus, indicating that neither the construction or the coupling agent affects the saturation moisture absorption.

Conclusions

Within a glass reinforced BT laminate, moisture absorption properties are affected by the absorption conditions, laminate construction, and the resin glass interface. For pressure cooker testing, silane coupling agents and laminate construction are dominant factors contributing to laminate integrity. Exposure to JEDEC conditions, however, gives moisture absorption into the laminate dominated by the bulk resin matrix. No effect on JEDEC moisture absorption properties is apparent by changing the coupling agent. Furthermore, moisture behavior under packaging conditions is characterized by Fickian diffusion yielding characteristic diffusivity and saturation parameters. The pressure cooker test appears to pickup weaknesses in the glass resin interface while the JEDEC moisture absorption conditions are dominated by the resin phase.

References

1. "Choose One....", Market report available from Prismark Partners LLC, Cold Spring Harbor, NY, July 1997.
2. Miles, Barry, and Bruce Freyman, "The Elimination of the Popcorn Phenomenon in Overmolded Plastic Pad Array Carriers (OMPAC)", *Proceedings of the IEPC*, Sept. 1992.
3. Hawkins, George, Gans Ganesan, Gary Lewis, and Howard Berg, "The PBGA: A Systematic Study of Moisture Resistance", *International Journal of Microcircuits and Electronic Packaging*, Vol. 18, Number 2, Second Quarter 1995.
4. Woo, M. and Piggott, M. R., "Water Absorption of Resins and Composites: IV. Water Transport in Fiber Reinforced Plastics", *Journal of Composites Technology and Research*, Vol. 10, No. 1, Spring 1988.
5. Koenig, Jack L. and Hamid Emadipour, "Mechanical Characterization of the Interfacial Strength of Glass Reinforced Composites", *Polymer Composites*, Vol. 6, No. 3, July 1985.

6. Ikuta, N., T. Hori, H. Naitoh, Y. Kera, E. Nishio and I. Abe, "Fixation of Silane Coupling Agents to Glass Fiber in Silane Treatment Process", *The Fourth International Conference on Composite Interfaces*, 1992.
7. Culler, S. R., H. Ishida, and J. L. Koenig, "FT-IR Characterization of the Reaction at the Silane / Matrix Resin Interface of Composite Materials", *Journal of Colloid and Interface Science*, Vol. 109, No. 1, January 1986.
8. Stoudt, M. R., E. Escalante and R. E. Ricker, "The Influence of Water on the Mechanical Properties of a Glass-Epoxy Matrix Composite", *Advanced Composite Materials*, Vol. 19, 1991.
9. Wu, Wen-li, Williams J. Orts, Charles J. Majkrzak, and Donald L. Hunston, "Water Absorption at a Polyimide / Silicon Wafer Interface", *Polymer Engineering and Science*, Vol. 35, No. 12, June 1995.
10. Rothwall, W. P., D. R. Holecek, and J. A. Kershaw, "NMR Imaging: Study of Fluid Absorption by Polymer Composites", *Journal of Polymer Science: Polymer Letter Edition*, Vol. 22, 1984.
11. Hoh, Ka-Pi, Brian Perry, George Rotter, Hatsuo Ishida, and Jack L. Koenig, "NOTE Analysis of Composite Processing Using Magnetic Resonance Imaging", *Journal of Adhesion*, Vol. 27, 1989.
12. Boudreau, R. J., "Glass Fabric Finishes: Effects on the Kinetics of Water Absorption and Laminate Physical and Electrical Properties", *Printed Circuit World Convention II*, June 1981.
13. Marsh, L. L., R. Lasky, D. P. Scraphim, and G. S. Springer, "Moisture Solubility and Diffusion in Epoxy and Epoxy-glass Composites", *IBM Journal of Research Development*, Vol. 28, 1984.
14. Liu, P. C., D. W. Wang, E. D. Livingston, and W. T. Chen, "Moisture Absorption Behavior of Printed Circuit Laminate Materials", *Proceedings of the International Electronics Packaging Conference*, American Society of Mechanical Engineers, September, 1993.
15. Aditya, P. K., and P. K. Sinha, "Diffusion Coefficients of Polymeric Composites Subjected to Periodic Hydrothermal Exposure", *Journal of Reinforced Plastics and Composites*, Vol. 11, September 1992.

16. Shen, Chi-Hung, and George S. Springer, "Moisture Absorption and Desorption of Composite Materials", *Journal of Composite Materials*, Vol. 10, January 1976.

ADDITIONAL INFORMATION

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