

Low Temperature Curing of Epoxies with Microwaves

Robert L. Hubbard and Iftikhar Ahmad
 Lambda Technologies, Inc.
 860 Aviation Pkwy. Suite 900
 Morrisville, NC 27560
 (919) 462-1919
 (919) 462-1929 fax
bhubbard@microcure.com

Renzhe Zhao and Qing Ji
 Henkel Corporation
 15350 Barranca Pkwy.
 Irvine, CA 92618
 (949) 789-2567
 (949) 789-2595 fax
Renzhe.Zhao@us.henkel.com

Abstract

There is increasing interest in using lower temperature processing in microelectronics packaging today. Some new technology devices are intolerant of temperatures above 200 °C or even 100 °C. There are also devices that require a low thermal budget (time-temperature) to maintain performance tolerances or to avoid unwanted intermetallic compound formation. Finally there are package processes that are simplified by having the ability to maintain low temperatures at critical steps. It has been well established that variable frequency microwave (VFM) technology can cure epoxy materials in a wide variety of applications at much faster times (<10%) than that of convection or IR heating. This work describes the lower shrinkage and lower stress that results by curing flip-chip underfills and package encapsulants at lower temperatures and faster times with VFM technology. An hypothesis for the mechanism of microwave cure of epoxies and the comparison to the resultant thermal and mechanical properties of the fully cured epoxies is discussed.

Key words: epoxy, underfill, encapsulant, low-temperature, shrinkage, stress, microwave, VFM

Introduction

The microwave heating mechanism is based on the excitement of molecular dipoles and their subsequent dielectric loss to molecular rotations¹. This direct increase in the entropy of the system at each molecular dipole site causes more rapid collisions of reacting molecules at the proper reaction orientation at a lower bulk temperature of the material. Epoxy-based adhesives can be fully cured in minutes rather than hours (Table 1).

Application	Convection	VFM
Flip Chip	30-120 min	10-30 min
Encapsulation	2-3 hrs	2-10 min

Glob top	1-2 hrs	5-10 min
Die attach	10-240 min	1-10 min
Silicones	8-20 hrs	20-40 min
Wafer films	3-5 hrs	1-2 hrs
Flex tape	4-5 hrs	10-20 min
Smart card	6-12 hrs	2-5 min

Table 1

Microwave curing has a selective nature. Only materials that have available, polarizable electrons

and the flexibility of molecular rotation, will be heated (Figure 1). Un-cured polar polymers and doped silicon are good examples of susceptible materials but glasses, metals, and fully cured polymers are not. A variable frequency microwave (VFM) technology was developed to prevent the arcing of metals and to provide a uniform energy field particularly for use in microelectronics production processes. Many studies by semiconductor fabricators have shown no effect by VFM on the electrical or structural characteristics of semiconductor devices².

$$P_{av} = \omega \epsilon_0 \epsilon''_{eff} E_{rms}^2 V$$

P_{av} = ave power dissipated

ω = angular frequency

ϵ''_{eff} = dielectric loss factor

E = electric field intensity

V = volume of the load

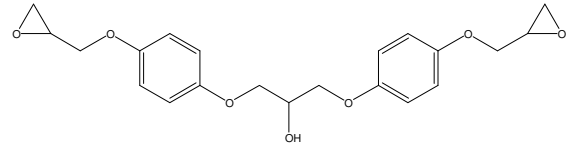
Figure 1

The abundance of uses for adhesives and encapsulants based on epoxy formulation has produced a wide range of materials from many suppliers. To achieve the desired adhesive and mechanical properties required for flip-chip underfill and die encapsulation, the cure temperatures are usually around 150-200°C for 2-3 hours. A lower temperature may be used but the cure times must extend into many hours or days. Incomplete cure can produce unwanted brittleness, low Tg, low adhesion, and solvent permeability. Flip-chip devices with low-k dielectrics are very sensitive to degraded material properties of improperly cured underfills.

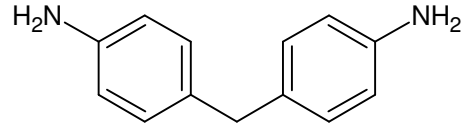
Several publications have described the full cure of polyimides and PBOs by VFM at half the normal convection temperatures³⁴. Lowering the cure temperature of epoxies with VFM might provide unique thermal or mechanical advantages over the standard cure. Since the cure at lower temperatures could still be done in a matter of minutes, the process would be practical for production.

The addition of an epoxy resin molecule (e.g. DGEBA) to a curing agent (e.g. MDA) can occur initially in a linear fashion before cross-linking to other chains. This would promote a larger "mesh" network polymer than if the initial curing produced shorter, more tightly entangled chains before cross-linking. At some time and temperature there is a sharp increase in viscosity (gellation) that essentially fixes the nature of the polymer network and determines its fundamental morphology. Further

heating serves to complete the conversion and cross-linking producing the required hard, solvent resistant, film properties.



DGEBA



MDA

Lee and Neville⁵ proposed that lower temperature curing of epoxies should produce more linear polymers and a lower cross-link density⁶ (Figure 2).

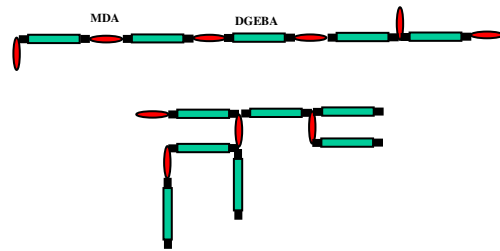


Figure 2

Longer chains between cross-links should produce higher toughness, greater elongation, less shrinkage, lower compression and tensile moduli, lower brittleness and less crack propagation (Figure 3)⁷. Since the introduction of fillers in epoxies has decreased the cross-link distance⁸, a lower temperature cure might restore some of these desirable properties.

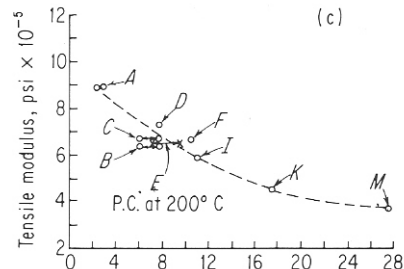


Figure 3

There is another explanation for a decrease in shrinkage and lowered stress in packages with epoxies cured by VFM. Figure 4 shows the general

features of a die attached by underfill and solder balls to an organic substrate. Under standard conditions, all of the components come under stress when cooling from 150°C to ambient since they all have differing thermal coefficients of expansion (and, more importantly, contraction). In the case of VFM curing of the system, only the die and underfill will be heated to 150°C since the organic board is mostly transparent to microwave energy. As the temperature of cure is lowered the “CTE-effect” would be expected to be even less.



Figure4

Experimental

VFM curing was done on a Lambda Technologies Microcure 2100-700 system. Ambient gas control or vacuum was not required. Four-thousand ninety-six frequencies were cycled between 5.8 and 7.0 GHz every 0.1 seconds for a residence time of 25 μs each. Part temperature was controlled in a closed-loop feedback system by measurement with a non-contact IR sensor and a fiber-optic contact probe on the back of the substrate was also monitored. A ramp rate of 1 °C/sec brought the part to soak temperature with a control of +/- 1 °C for the programmed time. Power was automatically adjusted to maintain temperature.

Cure profiles were determined by choosing temperatures 10-30 °C below the “onset” temperature given by the manufacturer or measured on the epoxy DSC trace. Times were estimated at 10% of recommended total cure times and adjusted for equivalent Tg to convection cure.

Results

The stress created by CTE mismatch between epoxy, silicon, and substrates in flip-chip assembly is partly relieved by adding fillers. The underfill CTE can be lowered to nearly 10 ppm/°C (below Tg). The selective heating of VFM is shown in Figure 5. In “Area a” on the left there is very little heating of the board. In “Area b” there is a flip-chip soldered die. In “Area c” on the right the heat of the epoxy underfill can be seen surrounded by much cooler board.

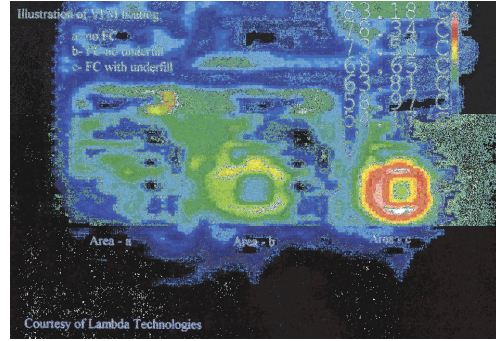


Figure5

The expansion/contraction estimates for convection curing and VFM curing at 150°C of a flip-chip system is shown in Table 2. Also shown are the measured adhesion and radius-of-curvature (ROC) of the die⁹ indicating die warpage. (Higher ROC is less warpage.)

	silicon	epoxy	board	Push-off (psi)	ROC (in)
CTE(ppm/°C)	3	10	18		
Convection	375 ppm	1250 ppm	2250 ppm	986	48
VFM	375 ppm	1250 ppm	522 ppm	1620	299

Table 2

Since the board temperature rise is only 29°C with VFM, the expansion/contraction of the die and board are nearly equivalent. With equivalent cures (same resultant Tg), the VFM cured package has nearly twice the adhesion¹⁰ and six times the ROC. This is even at an “equivalent” cure temperature. For a small die this lowered stress and shrinkage would not be significant but for larger die or larger distance-from-neutral-point bumps, this difference could have significant shear and drop-test ramifications. Full reliability tests are currently in progress on production flip-chip assemblies.

Epoxy encapsulation of die, for individual die, die array packaging, or between die, can cause warpage of the bulk material and shrinkage of the substrate. To determine the effect of lowering the cure temperature, an 18 mm x 5 mm four-layer substrate was populated with an array of 30 – 8 mm dice. The streets between the dice were filled with encapsulant by automatic dispensing.

The choice of the VFM curing temperatures were made by selecting points below the “onset” temperature but above the reaction initiation

temperature (see Figure 6). The intent was to choose temperatures before gelation could begin. At lower temperatures and with the speed of VFM, a substantial portion of curing is accomplished in a more fluid state.

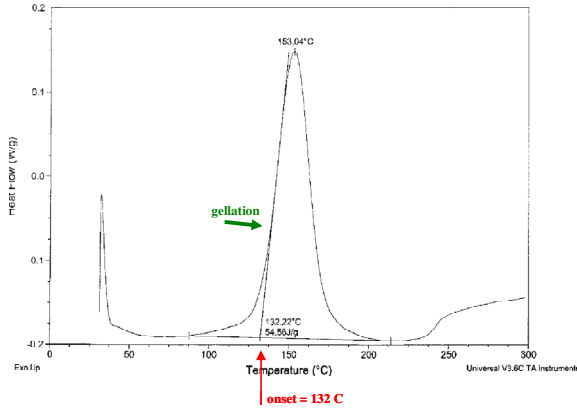


Figure 6

The results can be seen in Table 3. The samples were taken to equivalent cure (by Tg) and warpage of the substrate was measured on a flat-bed profilometer. The VFM cured boards were flat to the resolution of the machine.

	Cure (%)	Warpage
Convection: 145°C – 70 min	99.9	3.5 mm
VFM: 100°C / 3 min + 120°C / 4 min	99.9	< 0.5 mm

Table 3

Discussion

Advantages of curing an epoxy at a low temperature with VFM are reduced shrinkage, reduced stress and a more uniform film. Since all of the adhesive is heated at the same instant with microwave energy, the network formation is uniform throughout the bulk. With convection heating, the outside of the film is heated sooner and to a higher degree than the material on the inside. This causes a “skin” to form and non-uniform shrinkage. This may account for at least some of the observed warpage in the encapsulant described above. Further experiments are underway to measure flip-chip die ROC and encapsulant warpage under a variety of lower temperatures and cure profiles.

Additional experiments are underway to determine whether the predicted increased elongation, lowered modulus, and other thermo-mechanical property changes would result with lower temperature and faster cures. The relationship

between these properties and cross-link density should also reveal if there are fundamental differences in how the same chemical reactions take place in a polymer network exposed to microwave energies. Epoxy formulations in production applications are very complex but having an understanding of how microwave energy effects the core materials may assist in the design of custom VFM process profiles.

References

- ¹ A.C. Metaxas, R.J. Meredith, R.J., “Industrial Microwave Heating”, 1983, Peter Peregrinus Ltd., London.
- ² Unpublished proprietary results
- ³ R.L. Hubbard, Z. Fathi, J. Wander, T. Hattori, H. Matsutani, T. Ueno, C.E. Schuckert, “Low Temperature Cure of Aromatic Polyimides”, Symposium on Polymers for Microelectronics, Winterthur, DE, May 5-7 2003.
- ⁴ R.L. Hubbard, I. Ahmad, K Hicks, M. Ohe, T. Kawamura, “Low Temperature Curing of Polybenzoxazole (PBO) Films on Wafers”, Symposium on Polymers for Microelectronics, Winterthur, DE, May 3-5 2006.
- ⁵ H. Lee, K. Neville, “Handbook of Epoxy Resins”, pg. 6-7, 1967, McGraw-Hill, New York.
- ⁶ Burhans, et.al., “Designing Epoxy Resins Specifically for Filament-wound Deep Sumbergence Applications, RIP Division of SPI, Chicago, February.
- ⁷ H. Lee, K. Neville, “Handbook of Epoxy Resins”, pg. 6-19, 1967, McGraw-Hill, New York.
- ⁸ Kumins, “Long Range Effects of Polymer Pigment Interaction in the Solid State”, *Office.Dig.*, November.
- ⁹ See also Fathi et.al., Proceedings of Electronic Packaging Materials Science IX Symposium, Boston, Eds., pg 125, 1997.
- ¹⁰ See also B. Pan, et.al., “Variable Frequency Microwave For Chip-on-Board Glob Top Curing”, Proceedings of NEPCON West, 1998.