THE DYNAMICS OF LOW STRESS EPOXY CURING

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ABSTRACT

It is now possible to reduce the high stresses built into electronic assemblies by reducing the cure temperatures of epoxy adhesives and encapsulants. For the first time, an epoxy thermoset resin can be fully cured at temperatures well below its $T_{g\infty}$. Even though the cure temperatures are low and the cure times are not long, the extent of cure is complete; the stress advantages of low temperature cure are obtained; and several improvements in thermomechanical properties result. This study compares the use of a uniform variable frequency microwave (VFM) field cure to standard oven curing at temperatures below $T_{g\infty}$. Since commercial flip-chip under-fills have already been shown to be cured with VFM at low temperatures with lowered stress and improved reliability, it has now been found that the levels of silica filler can be reduced and elastomeric additives eliminated. Thinned, molded, epoxy-embedded silicon wafers were also shown to have lower warpage and much lower shrinkage stress even when just the post-mold cure was done with VFM at lower temperatures.

Key words: low stress, epoxy, under-fill, embedded wafers, microwaves, low temperature

INTRODUCTION

The use of epoxies in the consumer electronics industry is challenging. With the shift to more brittle low k dielectric materials and larger dice, the stresses produced in chip assembly are intensifying adhesion and reliability issues at die/adhesive/substrate interfaces. With the new trends to thinned dice in large wafers, and panel embedded packaging, there are stress induced increased warpage and bow issues in the epoxy encapsulants. In addition, multiple thermal excursions during assembly pose such difficult challenges that the assembly of electronic devices now accounts for a significant portion of the total cost of consumer electronics [1]. Packaging stress can also affect the electrical performance of some of the new device architectures.

Epoxy formulations have become quite complex, but their basic thermal behavior remains the same. The ultimate glass transition temperature ($T_{g\infty}$) needs to be high enough so that the epoxy does not soften during subsequent process steps and allow bonded joints and assembled parts to move with respect to each other. High curing temperatures are also necessary for full adhesion to all surfaces. It is well established that the thermal cure of thermosets, and in particular, epoxies, requires a cure temperature above the "ultimate" glass transition temperature ($T_{g\infty}$) to achieve full cure [2-4]. At lower cure temperatures, a vitrified (solid glass) state forms, so the reaction becomes controlled by diffusion of the reactants and is slowed by orders of magnitude (effectively stopped). At gelation, thermoset backbones become rigid, with crosslinking restricted to side-chain reactions. To continue the cure reaction requires increasing the temperature to increase molecular mobility. If vitrification occurs, chemical control of the reaction may be re-established by heating to 10-15 °C above $T_{g\infty}$. In practice with commercial epoxy adhesives, the actual cure temperatures are usually set to 50 °C higher than $T_{g\infty}$ to decrease the time of the cure process to two hours or less.

But high cure temperatures directly increase stress produced between joined materials with widely differing coefficients of thermal expansion (CTE). Another issue is the direct relationship between epoxy cure temperature and stress in the epoxy network itself. Shrinkage stress increases as the epoxy reaction product cools from the highest cure temperature in the gel state to ambient temperature [5]. As large complex silicon devices are incorporated into common consumer products, thermal stress issues become more costly to alleviate. Currently, low curing temperatures are being sought to allow the use of low temperature plastics, which save cost, weight, and space in consumer products. The use of epoxy embedded "fan-out" packaging in large panels for cost reduction faces the same warpage issues on a larger scale.

One suggestion has been to reduce the cure time with microwave energy. The opportunity offered by microwave curing of polymers is based on the inherently different heating mechanism involved. In contrast to conventional heating, which creates molecular translational energy, microwave fields excite polarizable electrons in molecules, which creates rotational motion from dielectric loss (E′′) [6]. This rotational energy provides increased collision frequency (Z) and more favorable alignment of the reactive species (ρ); factors that directly increase reaction rates according to the collision-modified Arrhenius equation 1.

$$k = Z \rho \, e^{(-Ea/RT)} \qquad (1)$$

Microwave excited rotations occur not only on the side chains but also along the backbones of polymers, greatly enhancing the mobility of the entire polymer network. By this means, microwave fields increase the mobility of the "infinite network" formed at gelation [7] so the cure can continue in the gel state at a lower temperature of the bulk material.

Until recently, highly conflicting results have been reported when microwave energy was used to increase the cure rate of epoxy resins [8-10]. For example, both low reaction rates and very high reaction rates were reported with accompanying speculations of reaction mechanisms and structural dependencies. Furthermore, the common use of a single frequency microwave generator requires that a single mode, in a very small area (less than 1 cm^3) be the focus of the experiment. As a result of this difficult experimental condition, it is not surprising that "hot spots" of activation and cure, represented by broad glass transitions, were found in the product DSC traces.

With the development more than two decades ago of variable frequency microwave (VFM) technology [11], it became possible to produce a highly uniform field over a volume of about 1 m^3 (a million-fold increase) from a single generator and waveguide. Consequently, sample temperature variations of only ± 1.7 °C have been measured across large cavity chambers from nearly wall to wall in all dimensions. The VFM microwave oven changes frequencies every 25 μs. This technology eliminates the possibility of metal arcing found in single frequency systems. With these uniform VFM fields, it has been reported that polymerization of epoxy thermosets [12], thermoplastic films [13] and other polymer systems [14] have been cured at temperatures well below the standard thermal cure, with high extent of cure. In addition, there is evidence of modified thermomechanical properties of these polymers; including lowered modulus with decreased crosslink density [15], and reduced coefficient of thermal expansion [16]. Finally, it is noted that a low temperature VFM epoxy cure resulting in a high $T_{g\infty}$ has been reported to produce lowered stress and increased reliability of an IBM microprocessor server module [17]. As a result of these and other benefits,

VFM technology has been incorporated into production manufacturing systems world-wide.

In a study of two fundamental reagents commonly used and often studied in epoxy adhesives (Figure 1) it was determined that there was no vitrification formed when the reaction temperature using VFM was substantially lower than the Tg∞ [18].
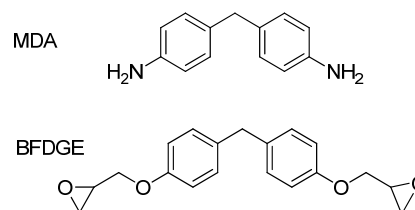

Figure 1. Structures of epoxide (BFDGE) and diamine (MDA) starting materials

The extent of reaction was complete as measured by DMA and FTIR. A higher ratio of linear chain growth to crosslink growth was confirmed by C-13 NMR. In contrast, the standard convection oven curing of these same two epoxy components produced increasing vitrification and cessation of cure as the cure temperature was decreased below Tg∞.

It should be noted that adhesion of epoxies is directly proportional to the number of hydroxyl functions produced in the cure reaction (Figure 2). If the cure reaction is incomplete, then the adhesion is incomplete to the same extent. Two step cures with a high temperature final step is often recommended by the material suppliers to complete adhesion.
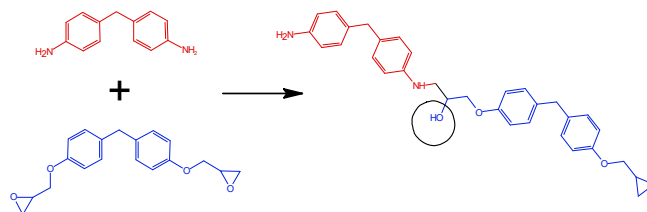

Figure 2: Hydroxyl (circled) produced during cure

Most of the additives in commercial epoxy resins are included to enhance package reliability. Historically, underfill materials had a high modulus to prevent crack propagation in solder joints; matched CTE with solder; and high Tg [19]. Newer low-k dielectric materials are very fragile which requires a lower modulus underfill to prevent crack propagation on the die and in the epoxy. Current underfills have very high silica loading (60-90%) to reduce the CTE even further as well as elastomer additives to reduce the modulus. Lowered modulus forces the cured epoxy Tg values down to 100 °C or less. Adding large amounts of silica and elastomers have adverse effects on the underfill flow and uniformity. The survival of the low-k dielectrics is now a trade-off with cracking of the epoxy and solder balls [20]. Figure 3 (courtesy IBM) clearly shows the

die and epoxy cracking and delamination failures (arrows) with high modulus underfills.
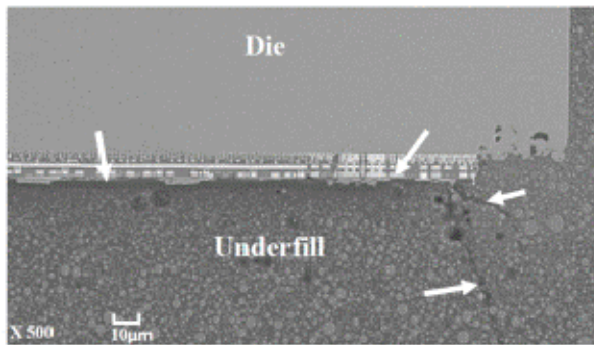

Figure 3: Epoxy stress fractures and de-laminations

There is currently no material solution that provides an epoxy material with low modulus, high Tg, low additives, and high adhesion that can be properly cured at a low temperature. These same issues confront the possibility of providing embedded dice in a molded epoxy format with all of the properties listed above, but in very large formats. Many assembly, reliability, and cost issues might be addressed with a low temperature cure and low modulus.

EXPERIMENTAL
The oven used for the thermal cure reactions had a digital readout and a separate thermocouple in the oven chamber was used for confirmation. The variable frequency microwave (VFM) curing system uses a digital closed loop control based on the continuously measured temperature of the sample. A non-contact infrared probe provided temperature control of $\pm$ 1°C after emissivity calibration with a GaAs fiber optic probe directly in contact with the sample at each soak temperature. Power (maximum 500W auto-leveled) was digitally controlled to produce ramp rates to soak with a precision of +/-2°C. Typical power levels necessary for the samples ranged from a few watts during ramp to several hundred, depending on the soak temperature. Reflected power from the reaction chamber (13" x 14" x 15") was found to always be less than 15%. Temperature variation within the microwave cavity had previously been measured to be ±1.7°C. The programmed temperature profiles ended at the conclusion of the soak temperature time, and the samples passively returned to ambient temperature within 2-3 minutes because the air, fixtures, and walls of the chamber were not heated during microwave irradiation of the sample.

The epoxy underfill material was from Namics Corporation with three different loading percentages of silica spheres and one sample without the standard elastomer additive. The epoxy embedded wafers were from a commercial proprietary source.

Samples for both oven and microwave cure were the same 42.5mm x 8mm x 1mm to facilitate measurement by DMA, with some of the length used to cut a sample for modulated-TMA. Teflon molds with cavities of these measurements were used for the curing experiments. The molds were cleaned and dried but not coated and the samples were easily removed with a spatula after cure. Teflon was used due to its microwave transparency and intermediate thermal conductivity. The molds were placed on Teflon rails in the center of the microwave chamber or on the center rack of the thermal oven.

DMA measurements of storage modulus (E′), loss modulus (E″), and tanδ (damping factor) were made using a 3 °C/min ramp from 20°C to 250°C at a 1Hz frequency by vertical clamped tension mode. Measurement of T_g was taken from the highest point of the tanδ peak and storage modulus was taken from a temperature 50 °C above the measured T_g.

Modulated-TMA was performed using a modulation of +/- 1.00 °C every 300 seconds and a ramp of 3 °C per minute. There was a 25 minute oscillation period at the beginning of each run at room temperature. Reversible expansion, non-reversible shrinkage, and total dimensional change were plotted for each sample.

Three 300 mm diameter epoxy wafers were thinned to 0.5 – 1.0 mm, after molding at Applied Materials. Warpage of these wafers was measured around the circumference of the wafer on an optical bench at the top ("noon") position and at every position corresponding to 1.5 hour clock positions.

RESULTS AND DISCUSSION
A summary of published results of low temperature VFM curing of commercial underfill materials is presented in Table 1 along with the recent model compound study. The model resin mixture did not have any of the standard additives that the commercial resins usually include such as colorants, silica filler, and elastomers. Since the silica fillers now represent most of the volume of most epoxies for underfill, encapsulation, and structural applications, it was important to evaluate the effects of these additives on the thermomechanical properties after cure with the VFM technology.

Table 1: Summary of commercial and model studies

Material	Oven	VFM	Tg∞ (°C)	Ref.
Henkel FP4527	165°C/30min	105°C/1hr	104	12
Henkel UF8830	150°C/2hrs	85°C/1hr	108	12
Namics U8410	165°C/2hr	115°C/1hr	117	15
"UF#B"	165°C/2hr	110°C/2hrs	98	18
"UF#C"	165°C/90min	110°C/90min	110	18
BFDGE/MDA	170°C/1hr	100°C/30min	133	19

Of particular interest for stress and reliability was the effect of both silica filler and elastomer additives on the storage modulus (E') above the Tg∞ point. The crosslink density of a thermoset can be directly determined, and the molecular weight of the crosslink calculated, from the storage modulus at 50°C above Tg∞ [21]. Table 2 highlights the modulus improvements in commercial underfills from the low temperature VFM cure references in Table 1, all with equivalent Tg∞.

Table 2: Low modulus in VFM cured commercial epoxies

	E'(MPa) – oven cure	E'(MPa) – VFM cure
Henkel UF8830	29	11
Namics U8410	71	40
UF#B	129	95

Increased package reliability with VFM cured epoxies has been at least partially attributed to this lower modulus at lower temperatures [18].

Silica loading

To determine the effect of silica loading and elastomer additives on the properties of cured epoxies, samples of the same underfill from Namics with 60%, 45% and 40% silica loading were shown to have even lower modulus with decreasing VFM cure temperature (Figure 4).
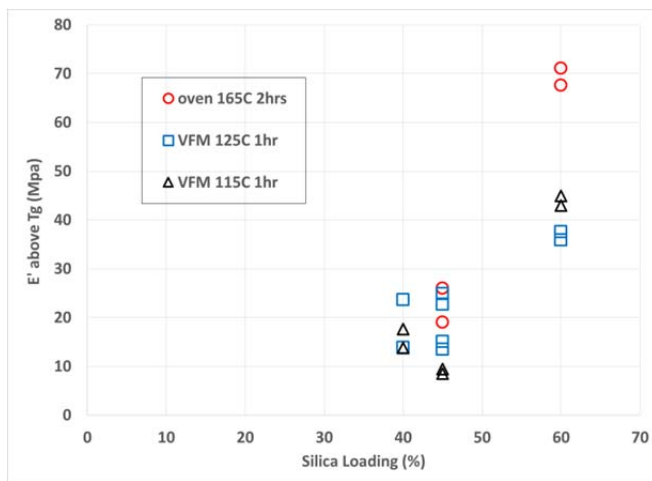

Figure 4: Silica loading effect on modulus of underfills

A closer examination of these results was provided by the use of a statistically designed experiment (DOE) on the VFM cure including the variable of silica loading (Table 3). The experiment was a randomized full factorial with three center points and replicates for a total of 21 trials.

Table 3: DOE on silica loading with VFM cure method

Variable	Low setting	High setting
Soak temperature	115 °C	125 °C
Cure time at soak	55 min	120 min
Silica loading	45%	60%

The most significant variable affecting storage modulus above Tg∞ was the silica loading (Figure 5). At all VFM cure temperatures and times the modulus was lower with the lower silica loading. This effect was expected because the silica is historically added to increase modulus around the solder joints but now is used to decrease the CTE of the epoxy. What is surprising is that the modulus stays low even at low temperatures and short VFM cure times. Modulus in these experiments was always substantially lower than oven cure samples.
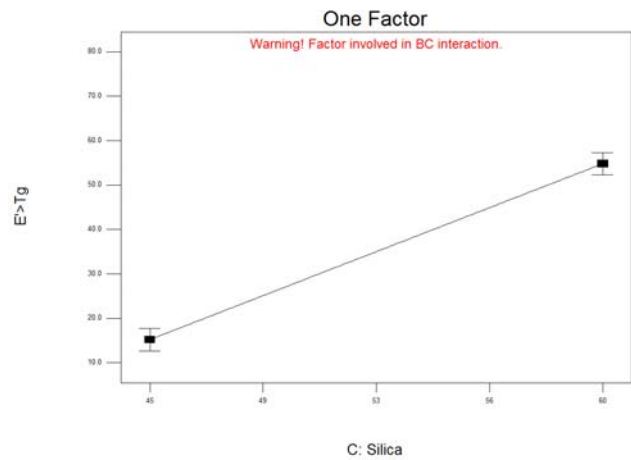

Figure 5: Effect of silica loading on storage modulus

There was a strong dependency of VFM cure time and silica loading but only at the 60% loading as seen in Figure 6. This was unchanged at either temperature (115 °C or 125 °C). In every case, the modulus (and crosslink density) of the VFM cured epoxies is half that with oven curing, and decreases further with decreasing silica loading, expanding on the data shown in Figure 4.
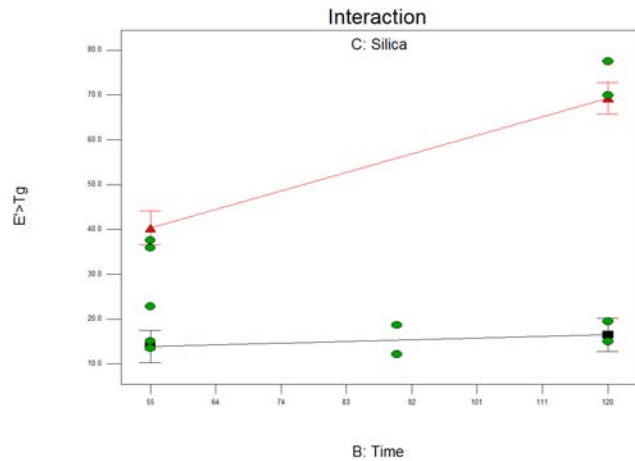

Figure 6: Dependence of VFM cure time with silica loading (red-60%, black-45%)

There are small but significant dependencies of time and temperature on the Tg∞ values. Figure 7 displays the time-silica dependency. This may just be due to the much lower heat capacity of silica compared than the epoxy.
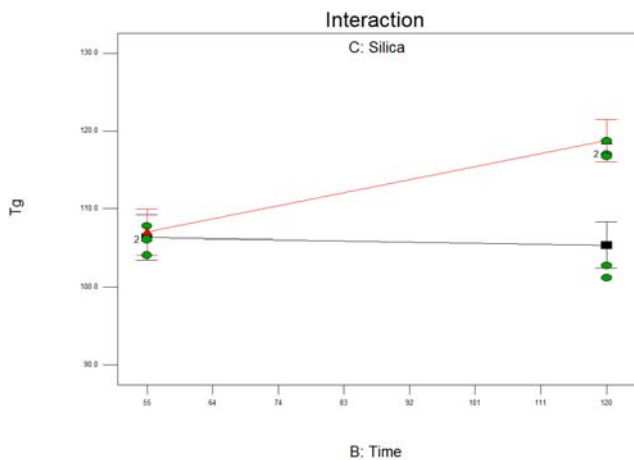
Figure 7: Dependency of time and silica loading on Tg∞ with VFM cure

Elastomer additives

The effect of eliminating elastomer additives was determined by the evaluation of an identical underfill sample without the elastomer additive as shown in Table 4. VFM cure of this underfill at a lower temperature achieves the same low modulus with or without the elastomer additive. All of these samples had the same 60% silica loading.

Table 4: Comparison with and without elastomer additive

	Elastomer	Cure (°C)	Time	E' (>Tg∞)
Oven cure	Y	165 °C	120 min	71 MPa
VFM cure	Y	115 °C	55 min	40 MPa
VFM cure	N	115 °C	55 min	35 MPa

Molded wafer post-mold curing

The silicon wafers embedded by Applied Materials were evaluated for warpage from post-mold cure (PMC) using VFM at low temperatures and a standard convection oven. The recommended mold cure for this application included a longer than usual time of 8-10 minutes at 120 °C. The recommended oven PMC for this material was 150 °C for one hour. Warpage measurements of the wafers after molding, but before PMC, were taken around the circumference of the wafer on an optical bench. Wafers were then treated with VFM PMC and re-measured as shown in Table 5. Instead of an expected increase in warpage from the PMC, warpage was reduced by several millimeters after VFM PMC.

Table 5: Warpage of epoxy embedded wafer before and after PMC with VFM

Location	Wafer 1	Wafer 1	Wafer 2	Wafer 2
Clock Dial	Before PMC	115°C/30min VFM PMC	Before PMC	115°C/60min VFM PMC
O'clock	Lift in mm	Lift in mm	Lift in mm	Lift in mm
12	3	2	0	0
1.5	1	0	3	2
3	1	4	3	2
4.5	4	1	0	0
6	0	3	4	4
7.5	4	3	2	1
9	5	0	2	1
10.5	1	3	3	3
Total	**19**	**16**	**17**	**13**

Samples from the middle and edges of the wafers were measured with modulated-TMA to determine the enthalpic relaxation shrinkage within the epoxy. Figure 8 displays the reversible thermal expansion and the non-reversible shrinkage components of one of the samples. The non-reversible shrinkage represents the one-time increase of heat shrinkage of the polymer network after PMC. The example in Figure 8 was taken from the middle of a wafer with standard oven PMC process at 150 °C which produced shrinkage of 1.3 μm (bottom curve in blue).
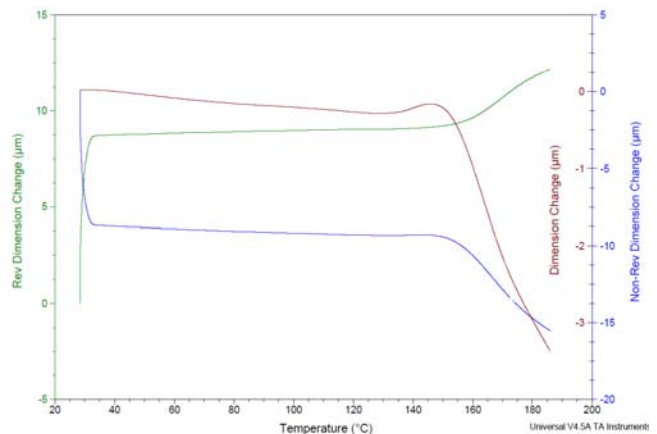

Figure 8: Modulated TMA of embedded wafer sample with oven PMC

A comparison was made of the non-reversible shrinkage of the thinned embedded wafer after molding with oven PMC at 150 °C for one hour, and with VFM PMC at 115 °C for 30 minutes and 60 minutes (Figure 9). The Tg∞ values of all PMC samples were 150 °C +/- 5 °C. The Tg values of the molded wafer before PMC was only about 10 °C lower than Tg∞ which indicates that the oven molding process of 120 °C for eight minutes had already substantially cured the epoxy.
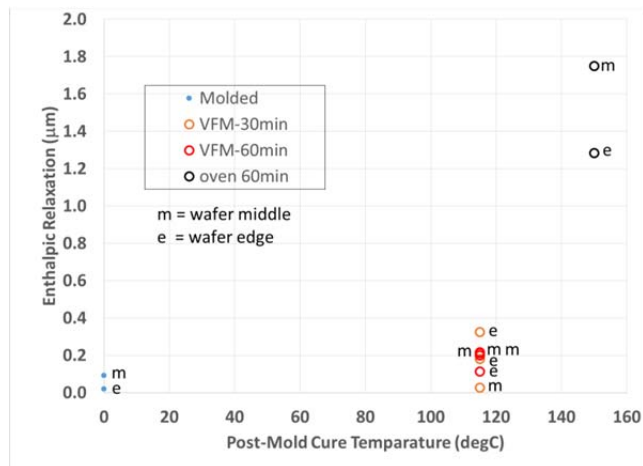

Figure 9: PMC shrinkage of embedded silicon wafers

Since the epoxy was substantially cured during the mold process, only a small amount of additional stress would have been expected during the PMC process even at 150 °C in an oven. It appears that the shrinkage stress added during oven PMC is still several times higher than with the low temperature VFM PMC. It can also be seen that the amount of time used for the VFM PMC was not a factor at 115 °C. The option of using low-temperature VFM for the whole molding process for lowest possible total warpage has not been investigated yet.

CONCLUSIONS
The low temperature processing capability of microwaves allows the users of commercial epoxy composites to obtain desirable high Tg∞ values with low modulus at reduced stress levels. The low modulus from lowered crosslink density is also produced at lowered silica loadings and without the need for elastomer additives in a commercial resin. Low warpage and reduced shrinkage stress was also demonstrated in post-mold cures of molded wafer level constructions.

ACKNOWLEDGEMENTS

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