The Dynamics of Low Stress Epoxy Curing

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Thermal and Chemical Stress in Joints

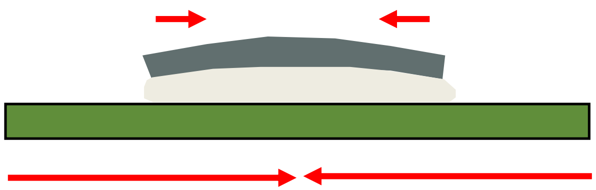
- Thermal stress is created by temperature excursions during assembly and product life
  - Joining materials with different CTEs can cause stress failures
  - Silicon and glass differ widely from organics and metals
- Chemical shrinkage stress is created during the cure of an epoxy (or any thermoset resin)
  - Temperature of cure and extent of cure directly affects chemical stress
  - The chemical structures of the starting materials affect chemical stress (and all the thermomechanical properties of an epoxy)

1. Once the extent of cure is complete, the stress properties do not change
2. Incompletely cured epoxy properties can change with higher temperature (extent of cure changes)

Compression Stress From "CTE–Mismatch"

- Co-efficient of thermal expansion mis-match between materials

die CTE = 3 ppm/°C
heated to 165°C



board CTE = 18 ppm/°C
heated to 165°C

165°C cure temp = 2100 ppm difference

100°C cure temp = 1125 ppm difference

- Lower the cure temperature
  - Lower stress from CTE mis-match
    - Cure time increases rapidly
    - Cure temp lower limit is Tg

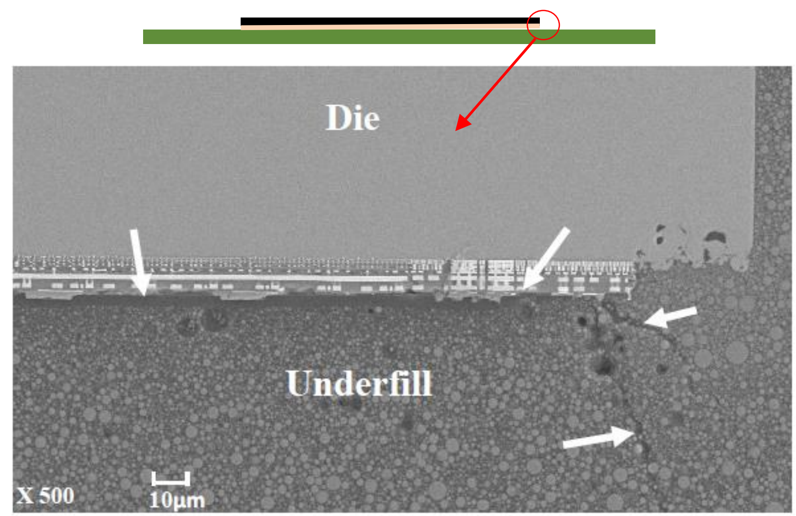
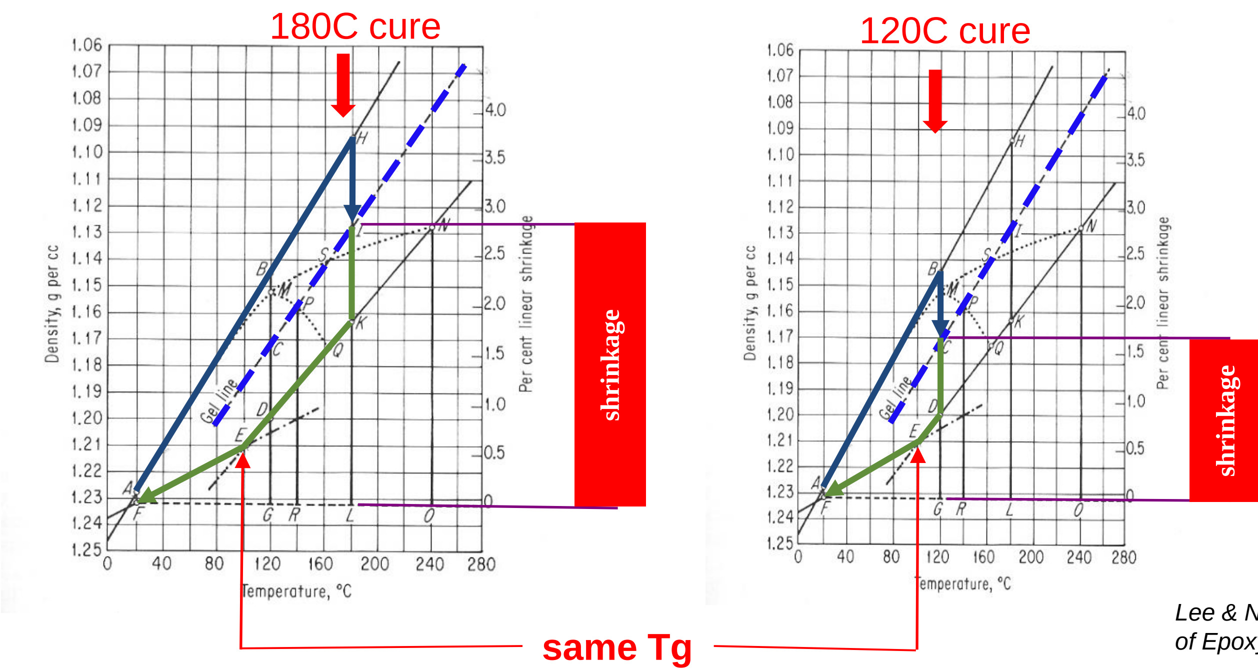


Fig. 5: A failed part of the control cell after 1000 cycles.
Courtesy: IBM

Epoxy Shrinkage Stress During Cure

- Cure temperature <u>directly</u> affects total shrinkage stress
  - Shrinkage begins at gelation point
  - Temperature difference between gelation and room temperature

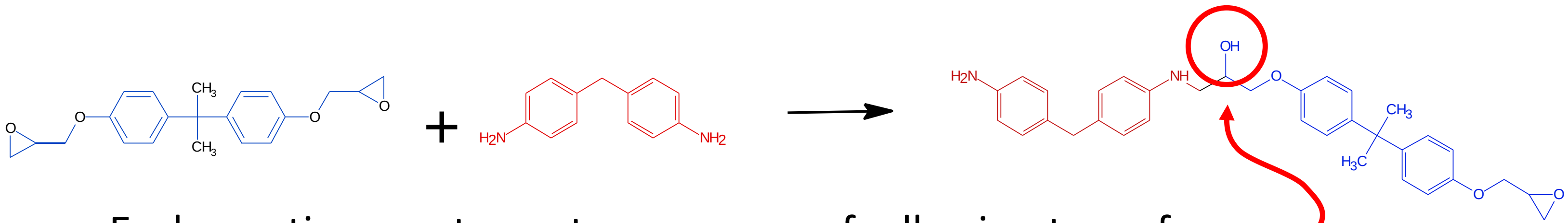


Lee & Neville, Handbook of Epoxy Resins, 1967.

- **Great! Let's all use lower cure temperatures!**

Adhesion Depends on Extent of Cure

- Resin (epoxide) and hardener (amine example):

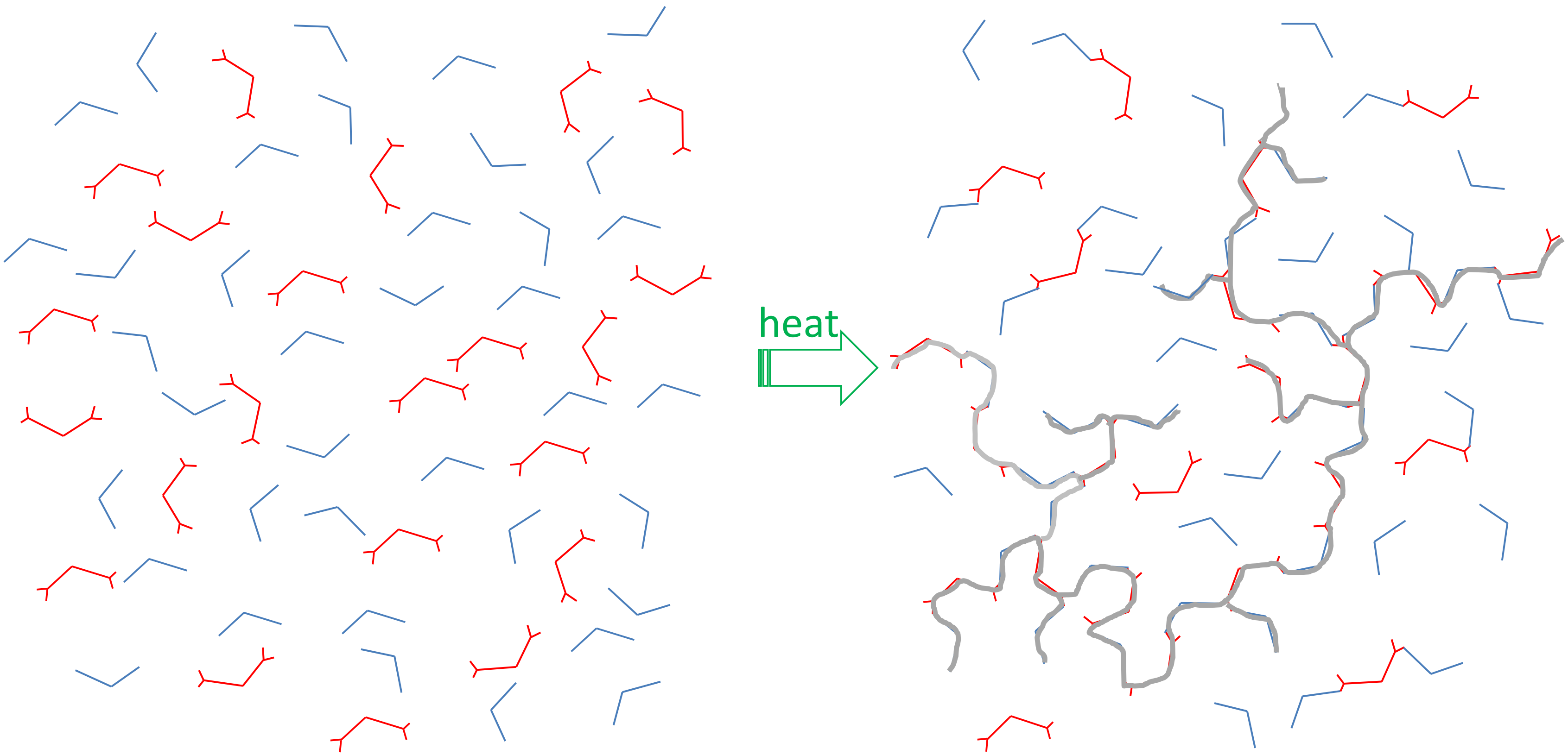


  - Each reaction creates a strong source of adhesion to surfaces

- Networks are formed from linear and crosslinked connections
  - More connections = greater adhesion
  - More connections = higher Tg (extent of cure)
- Increasing network density reaches the <u>critical point of gelation</u>
  - viscosity rises rapidly; mobility and reaction rate drops rapidly
  - As the cure Tg increases, the cure temperature must be increased

Fluid Resin to Rigid Gel

- A molecular backbone spanning the whole system defines "gelation".



- Backbone is now <u>rigid</u> so continued cure requires increasing temperatures.
- Cure temperatures are usually set 20-50°C above Tg∞ for <u>full cure</u>.

Problems with Incomplete Cure Reactions

- At the gel point the cure reaction may be only 30-50% complete
  - As the temperature is raised the reaction (and adhesion) can continue
  - If temperature is not kept 10-15°C above Tg, a **glass** (solid) forms
  - Time at a lower temperature must increase by 1000X
- Film adhesives are incompletely cured glasses (on purpose)

1. Adhesion will not increase without higher temperature
2. The incomplety cured joint will soften at low temperatures
3. If the joint temperature is raised above Tg at a later process step:

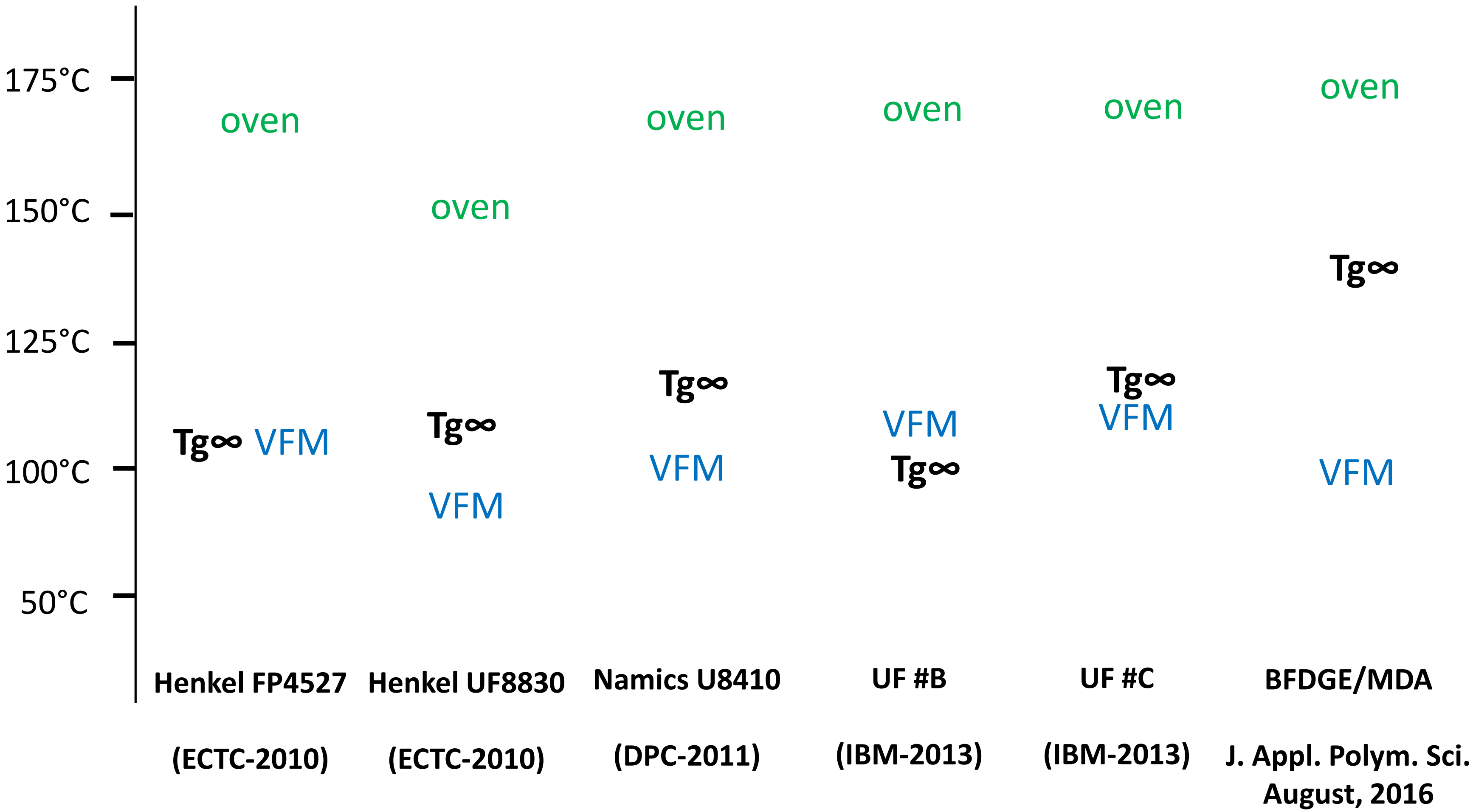
   The cure reaction will continue with:

   - Increased epoxy shrinkage
   - Decreased coefficient of thermal expansion
   - Potential movement and shifting of parts
   - Creation of voids and cracking in adhesive and between parts

Back to high temperature curing, and high total stress

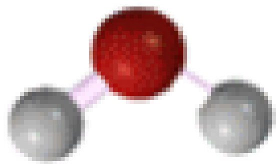
Low Temperature Cures with Microwaves

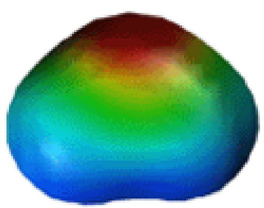
- Full cure measured as Tg∞ from DMA and ΔH from DSC (no glass formed)



Microwaves Create Molecular Rotation

Water (H_2O)

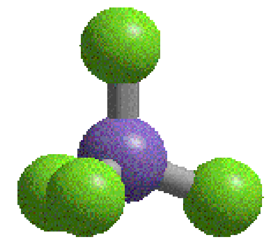


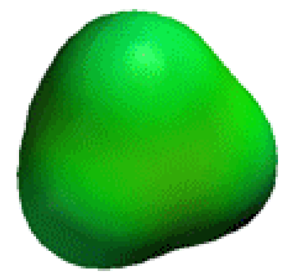


Dipole Moment = 1.86 D

Polarizability = 1.45 Å

Methane (CH_4)



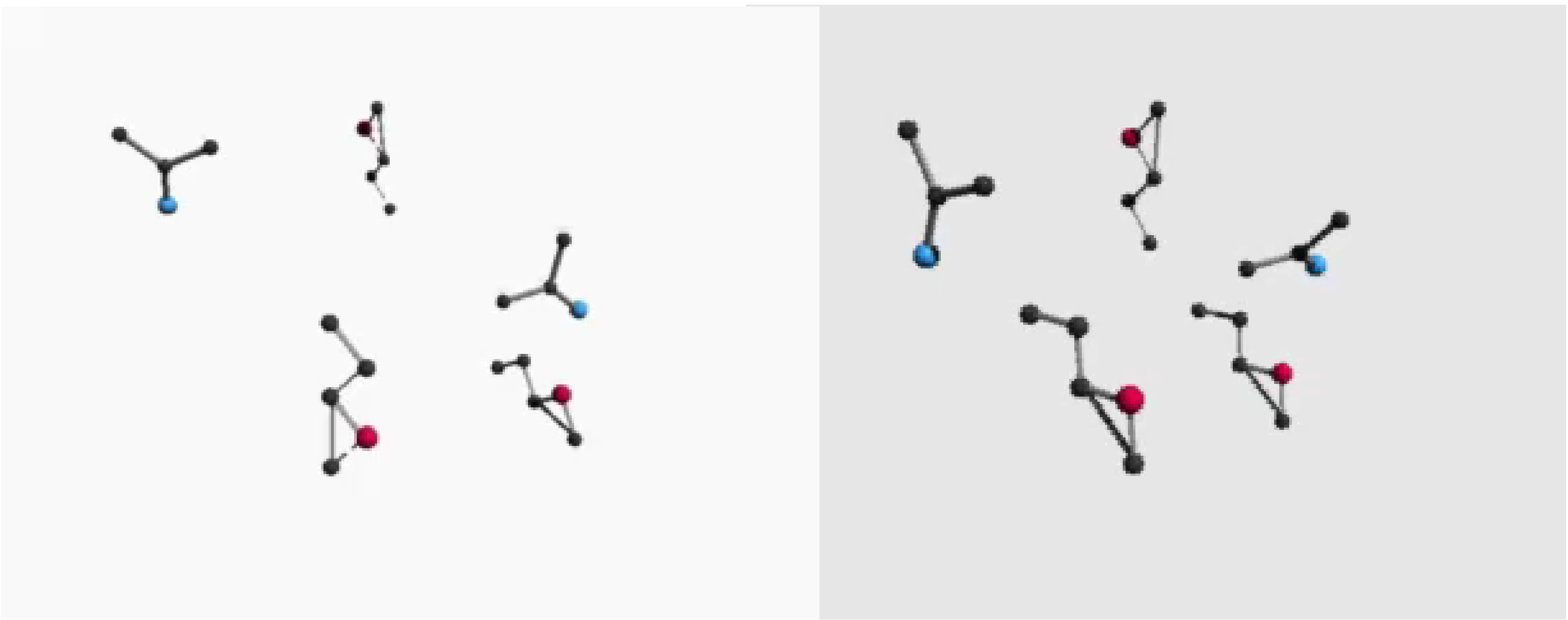


Dipole Moment = 0 D

Polarizability = 2.6 Å

Microwaves Increase Polymer Mobility

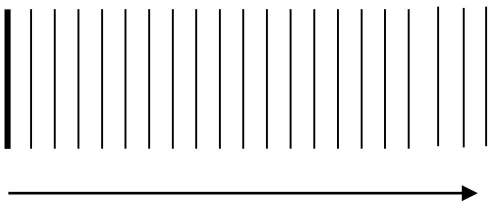
Convection **SHAKES** progressively Microwave **SPINS** volumetrically



- Molecules are spinning; cure reactions continue; adhesion increases

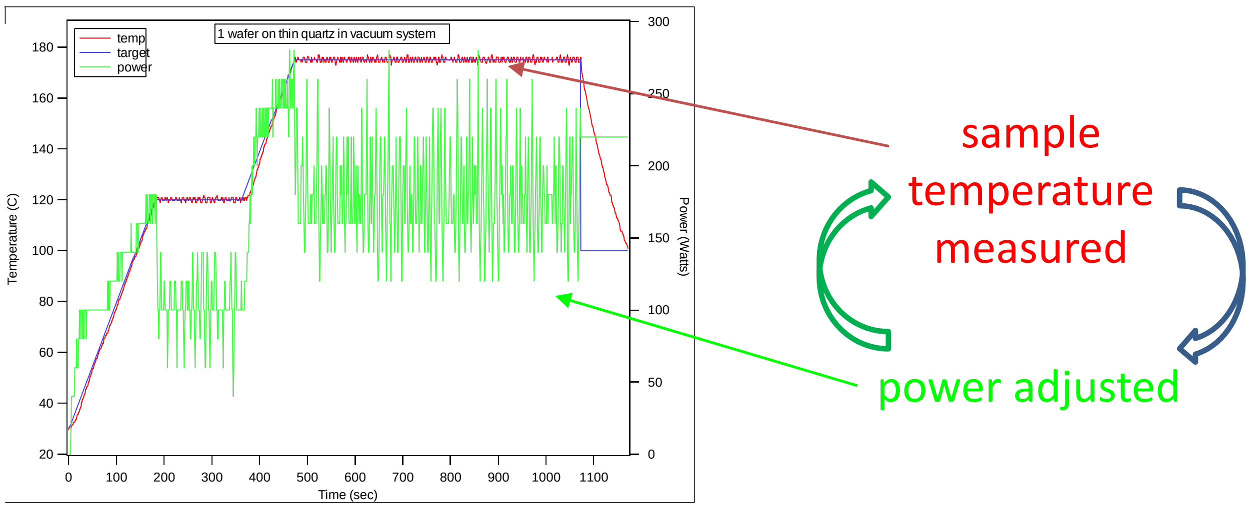
Variable Frequency Microwaves (ORNL 1992)

- Multiple scanned frequencies
  - 4096 frequencies, each 260 Hz wide, for only 25 µs each

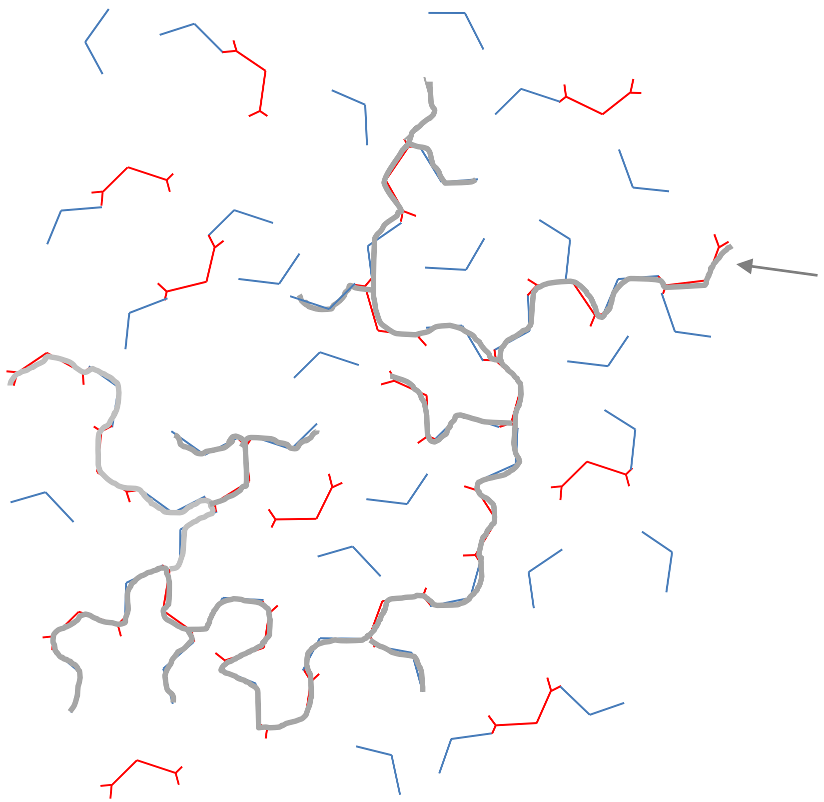


C-band: 5.85-7.0 GHz

- Large, highly uniform field and no metal arcing
- Digital closed-feedback loop for flexible energy control

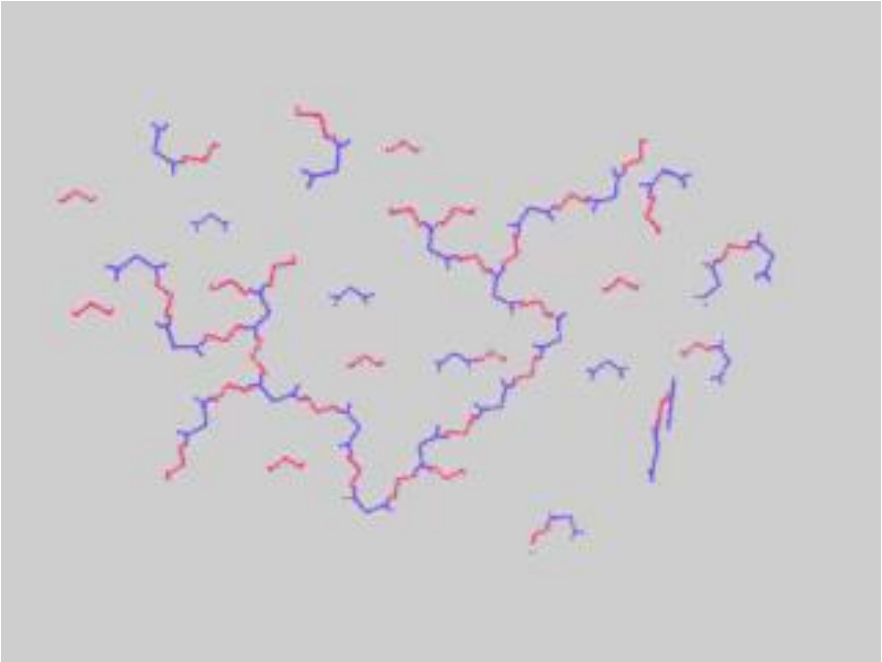


Low Temp?   Back to the Rigid Gel Network



"infinite polymer"

Mobility of Backbone with Microwave Rotation



- <u>Gel state mobility </u>allows the cure reaction to continue at low temperature

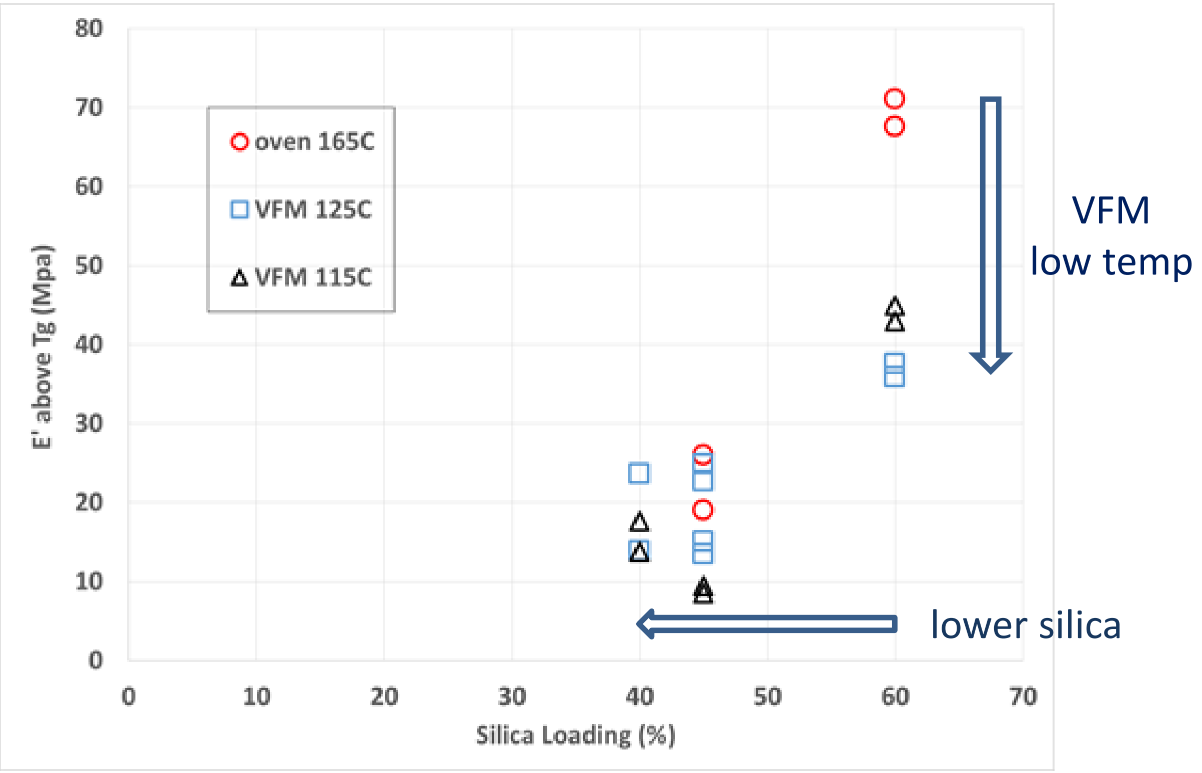
Low Temperature VFM Cure = Low Stress

- Low temperature cure of epoxies (~50°C lower than oven)
  - Full extent of cure, full adhesion, and maximum Tg∞
  - Cure well below Tg∞ temperature **without forming a glass**
  - Similar cure times or faster
- Lower warpage FC-UF and higher package reliability (IBM - 2013)
  - Lowered thermal stress between CTE mis-matched materials (i.e. silicon/BT)
  - Lowered shrinkage stress in the epoxy joint
  - Lowered modulus and crosslink density (!)
- Lower warpage package-on-package assembly (TSMC US 8,846,448)
  - Found void removal improved (as did IBM – 2015)

- How does this affect UF formulations?
  - What about the silica added to lower CTE (increase modulus)?
  - What about the elastomers added to lower modulus?
- What about encapsulants, molding epoxies, and structural parts?

Effects of Silica Loading?

- Namics U8410 underfill
  - With 60%, 45%, and 40% silica filler loading
  - Storage modulus (E’) measured by DMA at 50°C above Tg (tanδ)

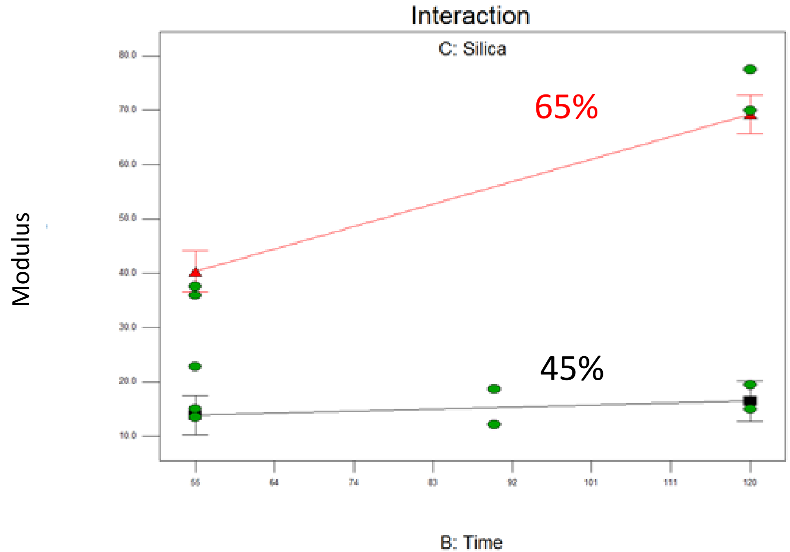


  - Lowered silica loading reduced modulus (as expected)
  - Low temperature VFM cure also lowered modulus

More Details from DOE

- 21 trials with replications and center points

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



- Large effect of silica loading %
  - Silica used to be added for high modulus
  - Now it is added to reduce CTE
- Cure time only matters for 65% loading
  - Lower heat capacity for silica than epoxy?
- No effect of temperature – dropping modulus seems to plateau
- Very low modulus (15 MPa vs. 70 MPa)

Elastomer Additive Has No Effect on Modulus

- For the 60% silica loaded underfill:

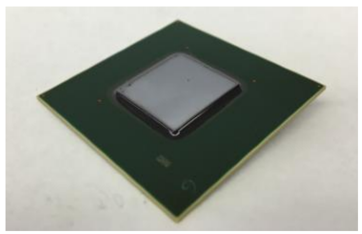
	Elastomer	Cure (°C)	Time	E' (>Tg∞)
Oven cure	Y	165 °C	120 min	71 MPa
VFM cure	Y	115 °C	55 min	40 MPa
VFM cure	N	115 °C	55 min	35 MPa

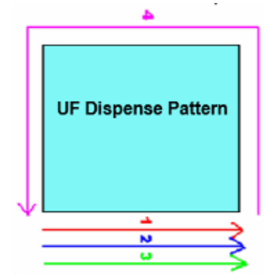
- Once again, there is no benefit to adding elastomer

- Issues with the under-filling process are relieved with:
  - Lower levels of silica loading – faster under-fill dispense
  - Elastomer additives no longer needed

Does Lower Stress Produce Lower Warpage/Bow?

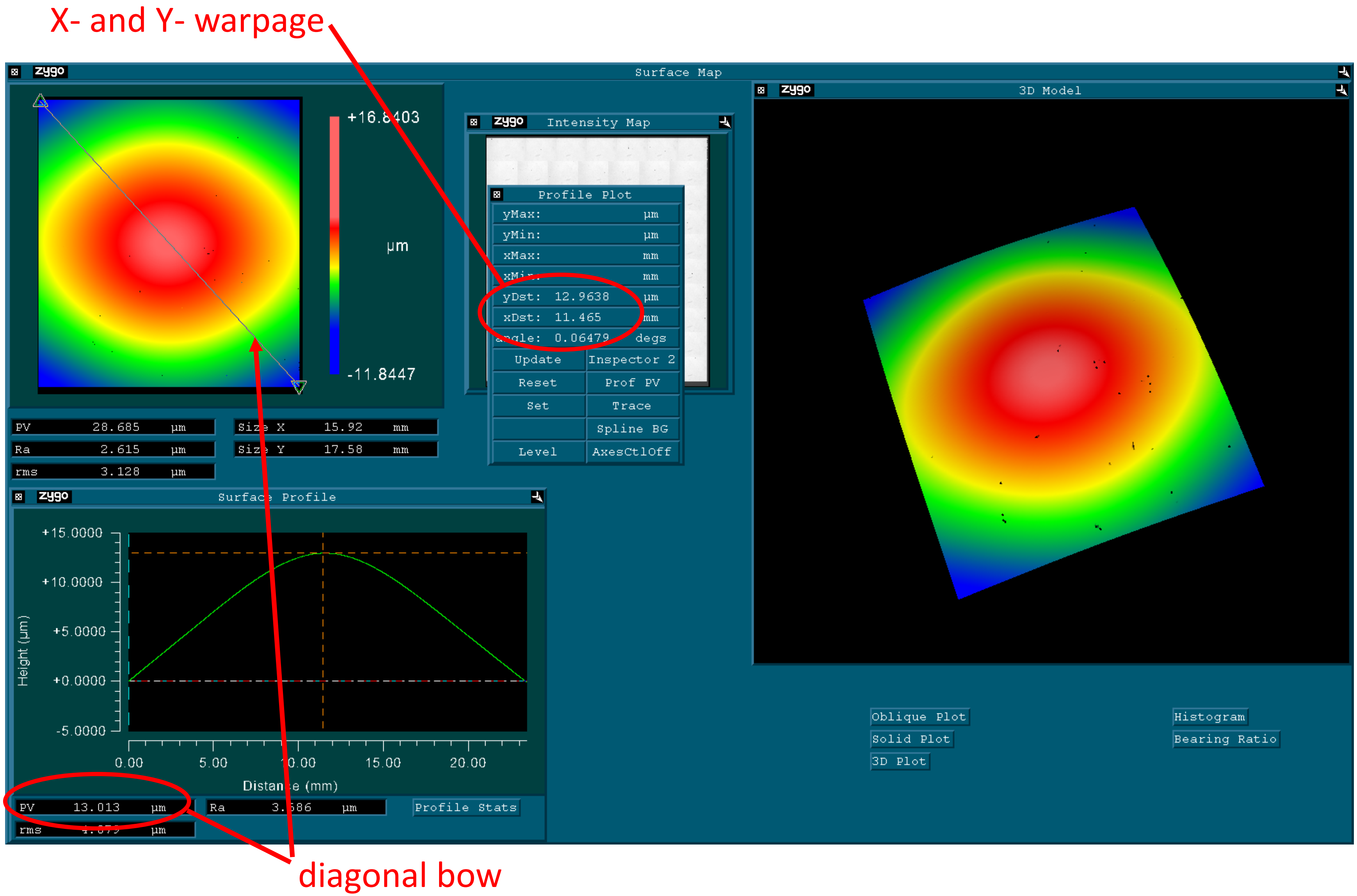
- Materials:
  - U8410-268 with lowered silica loadings and removal of elastomer additive
  - 17mm x 17mm dice on 40mm x 40mm substrate with 1,444 I/O
- Methods:
  - Manual UF dispense with constant air pressure on 100°C hotplate





  - Warpage and bow (3D) measured by optical interferometry (+/- 0.1 μm)
  - Curing by ThermoScientific convection oven and Lambda Microcure 2100
  - VFM samples cured at 115°C for 55 minutes with 0.2 deg/s ramp rate
  - Oven samples cured at 165°C for 60 minutes (standard POR)
  - Extent of oven and VFM cure processes established in SMTAI paper above
    - Equivalent Tg∞ (115°) cure to standard oven POR samples

Measurement of Die Bow



Bow Data Before and After UF

- Three samples each for VFM cure; two samples each for oven cure

	bow PreUF	silica (%)	elastomer	bow UF	Difference	Ave Diff
1	13.0	60	Y	64.368	51.4	45.26
2	13.3	60	Y	69.117	55.8	
3	12.8	60	Y	39.363	26.6	
4	13.1	60	N	65.92	52.8	
5	12.9	60	N	60.289	47.4	
6	12.8	60	N	59.169	46.4	
7	13.3	45	Y	57.161	43.9	
8	12.5	45	Y	52.646	40.1	
9	12.9	45	Y	53.324	40.4	
10	12.0	40	Y	59.644	47.6	
11	12.5	40	Y	57.688	45.2	
12	12.7	40	Y	58.117	45.5	
13	12.8	60	Y	90.969	78.1	80.40
14	13.0	60	Y	95.091	82.1	
15	13.2	60	N	97.295	84.0	
16	11.7	60	N	94.697	83.0	
17	13.4	45	Y	90.977	77.6	
18	12.3	45	Y	90.771	78.5	
19	12.2	40	Y	92.146	79.9	
20	12.0	40	Y	91.928	79.9	
ave =	12.7					44%

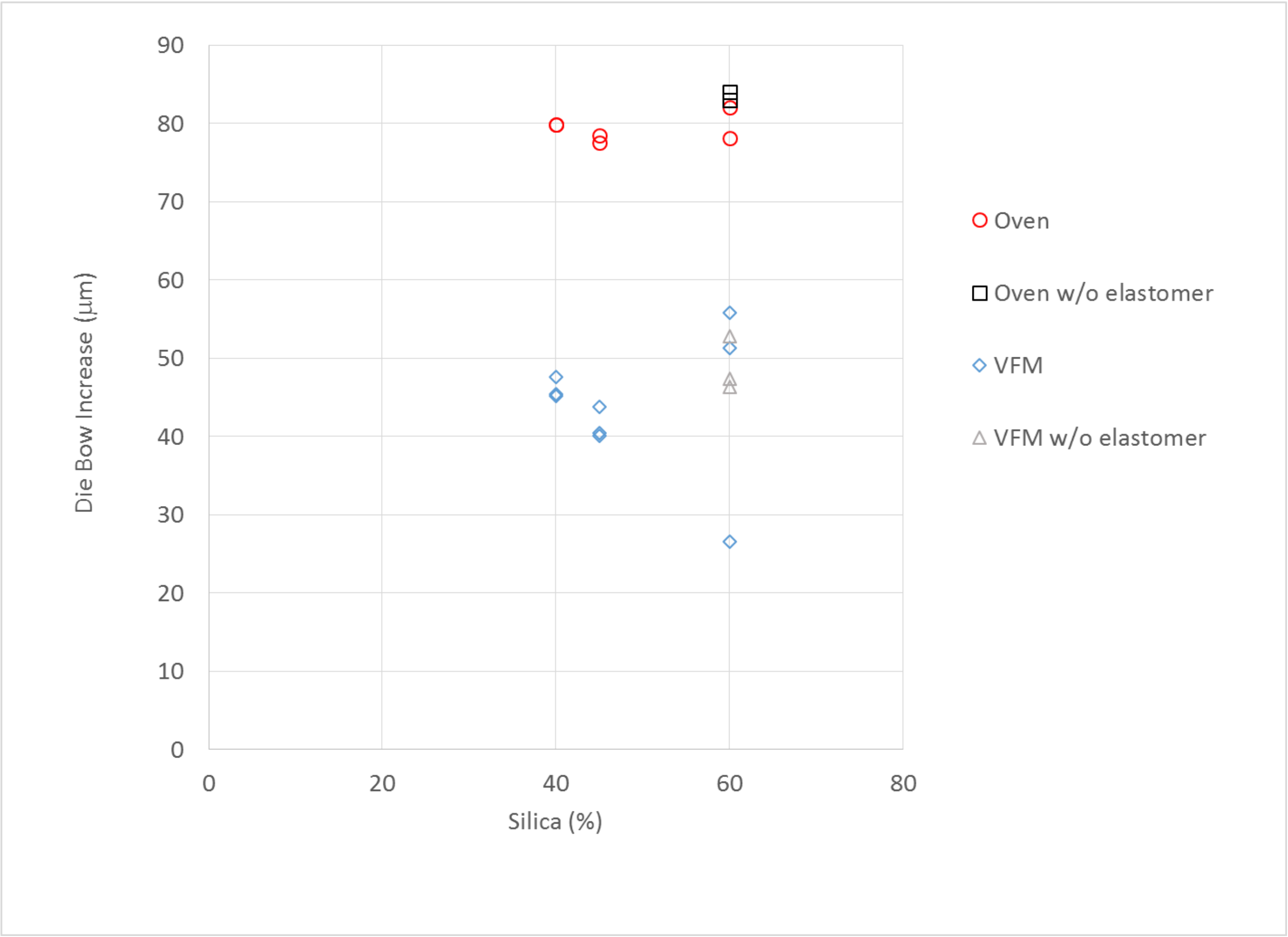
VFM (rows 1–12)

oven (rows 13–20)

44% **lower bow with VFM**

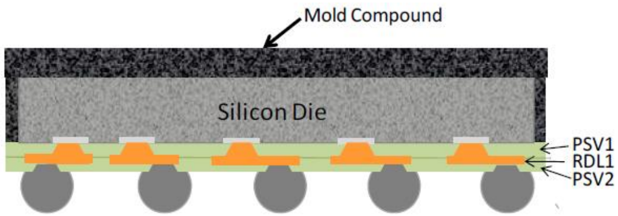
Temperature is Primary Effect on Bow

- VFM cure at 115° vs. oven cure at 165°C



Fan-out Wafer Level Packaging

- Epoxies are molded around silicon dice face down on adhesive tape
- Epoxy thickness and much of the wafer is ground back to leave thin wafer
- Dielectric and metal layer(s) are used to connect dice and to fan-out pads



STATS ChipPAC eWLCS

- There are typically two steps in epoxy molding; mold and post-mold cure
  - The mold process is lower temperature for just a few minutes (glass)
  - The PMC is higher temperature for an hour or more
  - How are the molding and PMC adding stress in a large wafer or panel shape?

Epoxy Wafer PMC Experiments

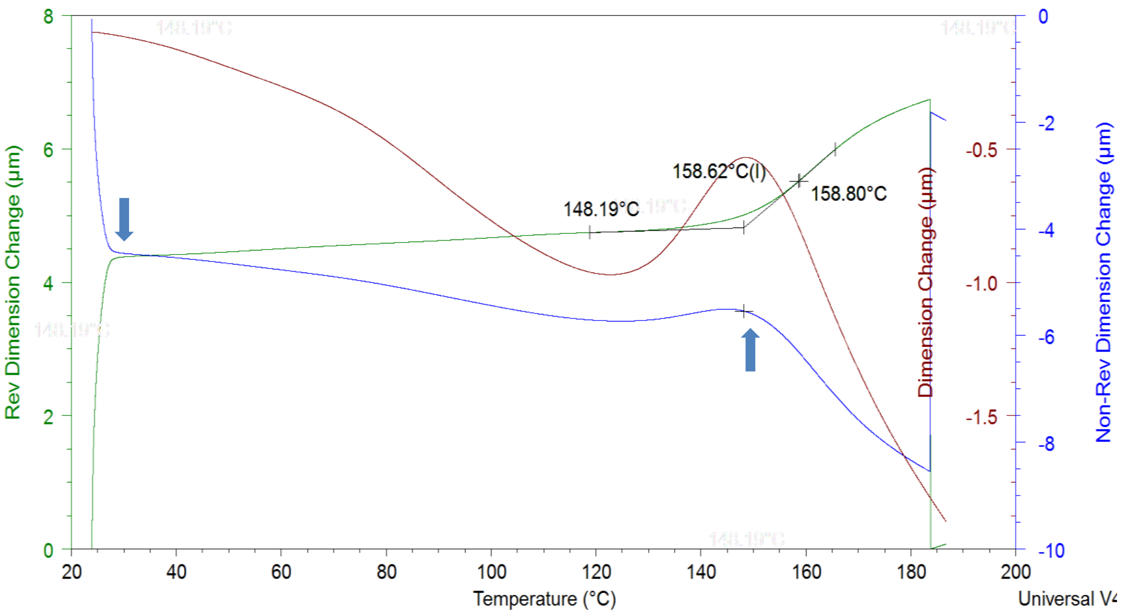
- 300 mm epoxy wafers (Applied Materials) molded at 125°C for 8 minutes
- Results from both 150°C oven PMC and 115°C VFM PMC:
  - Wafer warpage measured clockwise around a wafer on an optical bench

Location Clock Dial O'clock	Wafer 1 Before Cure Lift in mm	Wafer 1 After 115C; 30 min VFM Cure Lift in mm	Wafer 2 Before Cure Lift in mm	Wafer 2 After 115C; 60 min VFM Cure 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

  - This mold cure produced nearly full cure (based on $Tg\infty$ values)
  - PMC with VFM still seemed to reduce warpage in the wafer by >3 mm.

Shrinkage Stress Measured by modulated-TMA

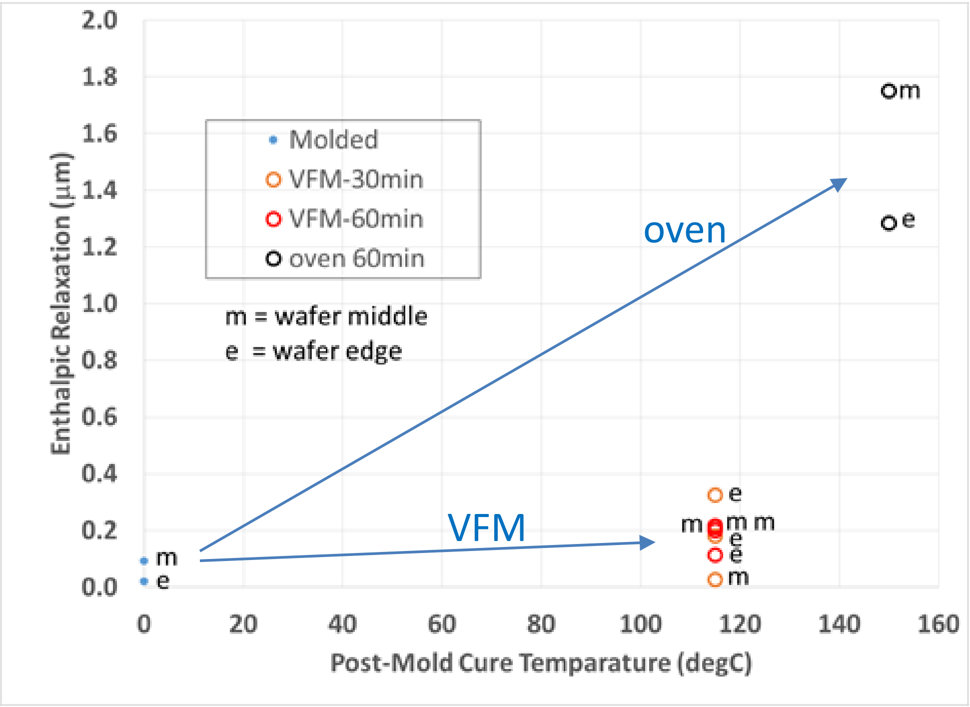
- Samples from the molded and PMC epoxy wafers taken at the middle and edges
- The non-reversible enthalpy of relaxation shrinkage (blue)



  - One-time final increase in shrinkage of the polymer network
  - Most thermosets display this shrinkage on heating after cure

Oven vs. VFM Shrinkage Stress from PMC

- Lower temperature PMC (with VFM) reduces final heat shrinkage



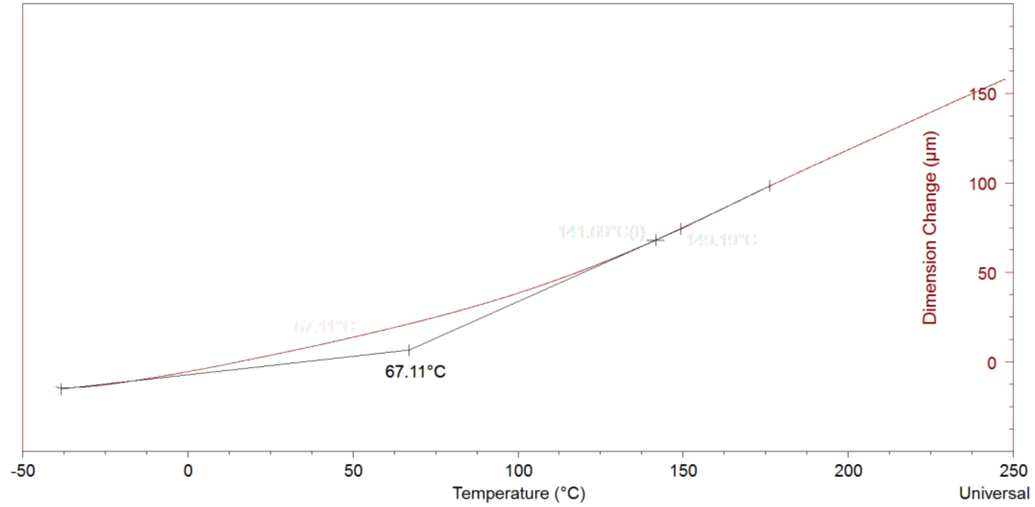
  - Lower temperature <u>oven</u> PMC would create uncured glass

- These wafers were oven molded. Would VFM molding reduce wafer warpage even more? This is under study.

Low Temperature Curing without VFM?

- An example of low temperature supplier cure profiles:
  - Standard: 110°C for 90 seconds
  - Alternate: 80°C for 5 minutes
  - Data sheet Tg = <u>114°C</u> (from TMA)

  - **Oven cure 80°C for 5 minutes: Tg = <u>67°C</u> (from TMA)**



  - It's an unstable glass.

Epoxy Stress Summary

- Both <u>thermal stress </u>between dissimilar materials, and <u>chemical shrinkage stress</u>, are reduced by lowering cure temperatures with VFM
  - Molecular rotation with microwave energy enhances chain rotations even after gelation which continues curing and adhesion processes
  - Lower modulus and lower crosslink density reduces stress with VFM
  - Lowered cure temperatures in standard ovens cannot be used because of inadequate cure and conversion to glasses
- Lower warpage in real FC and PoP device packages
- Silica filler loading can be reduced with low temperature VFM curing
- Elastomer additives can be eliminated with low temperature VFM curing
- 300 mm epoxy wafers have lower warpage and shrinkage stress with VFM post-mold cure

Acknowledgements:

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