How Does Controlling Only One Process Principle of Adhesives and Coatings Avoid Material Failure Mechanisms

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Common Failure Mechanisms

- Yield and product failures can seem to have many causes
  - Is prevention possible?

- Cracking
  - Within a material

- Delamination
  - At interfaces (loss of adhesion)

- Movement
  - Part shifting or tilting

- Stability
  - Movement at later stages of production or product life

- Warpage
  - Curvature from CTE differences in joints

- Stress
  - Non-uniformity of joint and material stresses
Common Industry Misconceptions

- Material properties are listed on technical data sheets
- Material properties can be compared by specification sheets
- Adhesives can have optional cure schedules
- Thermomechanical properties of adhesives depend on the chemistry
- Flip-chip underfills relieve CTE–mismatch stress
- Silica fillers reduce modulus by lowering CTE
- Low temperature curing requires longer cure times
- Cracking within polymers is caused by over-heating
- Pot life and storage life are pretty flexible
**What Do Polymers Look Like?**

- Small molecules combine head-to-tail in a “thermoset”.

- This backbone becomes **rigid** forming a **gel** which needs higher temperatures to complete the cure.
Cured amorphous polymers change from a solid glass to a rubber.

Polymers with higher crosslinking density have higher Tg values.

As the crosslink density increases during cure, the Tg rises.
Reduce Crack Failures?

- Thermosets are very random amorphous networks
  - They all have “defects” – partially connected chains and crosslinks; solutes
  - The fracture surface energy ($G_{ic}$) at which the defect becomes a crack:
    - $G_{ic}$ is inversely proportional to the crosslink length ($M_c^{1/2}$) and the extent of cure

- To reduce the cracking of a polymer, cure it as completely as possible.
Got Delamination?
Reduce Delamination (Adhesion) Failures

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

  ![Chemical Structure]

  - 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)

- To increase adhesion, cured it as completely as possible.
Reduce Movement Failures

- Higher glass transition temperature (Tg) is more thermally stable
  - A polymer above Tg is rubbery and allows parts to move
- Coefficient of thermal expansion CTE (expansion with each degree change)
  - CTE is higher in less of cured resins
  - Polymer expansions and contractions are larger with higher CTE
  - Parts move more with changes in temperature with higher CTE
- Chemical resistance to solvents, acids, and bases increases with higher extent of cure.

- To reduce part movements, tilting, and separating:
  - Increase Tg by complete cure
  - Decrease CTE by complete cure
  - Increase chemical resistance by complete cure
Vitrification Creates Instability Failures

- Cure temperature MUST be > Tg up to the “ultimate” Tg∞
- If cure temperature < Tg∞, vitrification stops the cure
  - only higher temperature will complete the cure reaction
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

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

165°C cure temp = 2100 ppm difference
100°C cure temp = 1125 ppm difference

Fig. 5: A failed part of the control cell after 1000 cycles.
*Courtesy: IBM*
Reduce Shrinkage Stress Failures

- Cure temperature directly proportional to total shrinkage stress
  - Shrinkage begins at gelation point
  - Temperature difference between gelation and room temperature

- **Lower** the cure temperature to lower the shrinkage, warpage, and stress!
  - But not below $T_g^\infty$

Reduce Latent Failures

- Just because it’s hard doesn’t mean it’s fully cured. (vitrified?)
- The “hidden” polymer is usually not as cured as the “exposed” polymer
- Solder reflow processes use high temperatures even for just minutes
- Hundreds of combinations of different materials joined under stress
  - Technology advances are increasing material stresses:
    - Smaller product dimensions with more parts (camera lenses)
    - More silicon (low CTE)
    - Larger silicon dimensions
    - Lower dielectric constants (more brittle HfO_x)
    - More complex packaging (PoP, MCM, FOWLP)
    - Less expensive plastics (lower temperature tolerance)
    - More glass (low CTE) in more complex displays
- Borderline reliability in products that experience thermal excursions
- “Good enough” products become unreliable products
  - We depend on our gadgets and high reliability is now expected!
Measurement of $T_g^\infty$

- The $T_g$ value is the best measure of the extent of cure
  - There will always be some connections that are unable to form ("Twister")

- Determine the "ultimate" ($T_g^\infty$):
  - Increase the temperature of cure and the $T_g$ increases (below it)
  - Finally the $T_g$ stops increasing ($T_g^\infty$) and actually starts decreasing
    (Decreasing $T_g$ means the polymer is decomposing)

- Analysis of polymer thermo-mechanical properties
  
  $T_g$ signal: noise

  - Differential Scanning Calorimetry (DSC): 1.1 : 1
  - Thermo Mechanical Analysis (TMA): 4 : 1
  - Dynamic Mechanical Analysis (DMA): 1,000 : 1
How do you measure Tg?

- **DSC:** measure calories given off during heating
  
  ![DSC diagram](image)

- **TMA:** measures mechanical transitions during heating
  
  ![TMA diagram](image)

- **DMA:** measures mechanical properties during heating
  
  ![DMA diagram](image)

- Other tools, like spectroscopy, are limited by the random complexities of polymers
Good Enough?

- Failure at solder joint less *costly* than failure in dielectric (Cisco, 2006)
  - Choose low modulus UF and accept low Tg \((120^\circ C \rightarrow 90^\circ C)\)
  - Coincident increase in no-lead solder temp increase \(183^\circ C \rightarrow 260^\circ C\)

- Current need for lower temperature processing
  - Use of lower temperature tolerant (*cheap*) plastic materials
  - Use of lower temperature tolerant devices (memories and others)
  - Multicomponent assembly flows aided by lower temperature processes

- Good enough?
  - Product requirement: \(125^\circ C\) Tg adhesive with \(60^\circ C\) cure.
  - Supplier data sheet: \(Tg = 114^\circ C\), cure = \(80^\circ C\) for 5 minutes
  - Actual Tg = \(67^\circ C!\)
  - Fails and poor yield.
Commercial Blends

- Commercial materials are actually complex blends
  - Basic components (“resin” + “hardener”)
  - Second set of basic components
  - Catalyst(s)
  - Elastomer (to reduce modulus)
  - Adhesion promoter(s)
  - Silica filler (to reduce CTE – 20% to 90% by weight)
  - Colorant(s)

- Suppliers have proprietary basic component set competencies
  - Epoxy-amines
  - Epoxy-thiols
  - Elastomers
  - Novolacs
  - Acrylates
  - UV-thermal dual cure
UV Blends

- UV catalyzed adhesives are useful for quick attachment (tacking) of parts.
- Since UV adhesives are not very strong, they are often combined with a thermal component to “finish off” the cure.
- Ultraviolet energy is very high frequency but also very short wavelength.
  - Short wavelength translates to shallow penetration depth (few microns).
- Typical extent of cure ~ 30% for UV component.
  - This leaves 70% of the UV component uncured.
  - The 30% cured portion blocks crosslinking of thermal component.
  - Thermal component cures from surface down also.
  - Adhesion to bottom surface must rely on the thermal component.

- Higher temperatures and times must be used to overcome the complications of the UV curing process and to create adhesion to all surfaces.
Why is Incomplete Cure so Common?

Product History
  New Design
    Mechanical
    Electrical
    Thermal
    Prototype
      Cost
        Reliability
          yield
          UPH
            Volume
              Suppliers
                Suppliers

Materials

Temperature and stress
Thermoplastic Coatings Too

- Most silicon is coated with multiple polymer dielectric layers
  - Stress relief and planarization (softer than metals and glasses)
  - Alpha particle barrier
  - Redistribution layers for interconnects and packaging

- High expectations and high cure conditions
  - Initially high-end military, space, mainframe applications
  - Polyimides (PI) cured at 350°C for 6 hours

- Commercial and personal telecom product cost needs
  - Same robust and stable thermomechanical properties
  - Lower cost and lower process temperatures (160°C) and times (30 min)

- Reality:
  - Compromised properties from new chemistries
  - Progress, but currently a brick wall at 225°C and 4 hours
Quiz

- Fan-Out-Wafer-Level-Packaging
  - Low cost, high volume. Moving from 300mm wafer to large panel format.

- Epoxy coating on back of dice: cure 150°C, Tg = 95°C
- Redistribution dielectric layers: cure 250°C, Tg = 320°C
- Solder reflow: 265°C

- What failure issues would you expect?
Microwave Curing

(an alternate universe?)
Longer Wavelength Microwaves

IR heat generated as vibrations

\[ \lambda = 0.006 \text{ mm} \]

MW heat generated as rotations

\[ \lambda = 50 \text{ mm} \]
Molecular Rotation Depends on Polarizability

Water (H₂O)
- Dipole Moment = 1.86 D
- Polarizability = 1.45 Å

Methane (CH₄)
- Dipole Moment = 0 D
- Polarizability = 2.6 Å
Microwaves Increase Molecular Mobility

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

- Molecules are spinning; cure reactions continue; adhesion increases
Gel state mobility allows the cure reaction to continue at low temperature
The Diffusion of Heat is Different

Heat transfer in a convection oven

Instant energy penetration with microwaves

Gibbs Free Energy: \[ \Delta G = \Delta H - T \Delta S \]

entropy is greatly enhanced by microwaves
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

![Graph showing temperature and power over time](image)

- Sample temperature measured
- Power adjusted

1 wafer on thin quartz in vacuum system
IR Thermal Image: Wafer Processing

Wafer edge
VFM Allows Low Temperature Processing

- As rotational entropy increases, the necessary temperature decreases.

\[ \Delta G = \Delta H - T \Delta S \]

- The boiling points of solvents go down (NMP bp 203°C → 140°C)
- Drying is simplified (water bp 100°C → 40°C)
- Chemical reactions complete at lower temperatures:
  - Epoxy-amine polymerization complete at 100°C instead of 170°C
    - Equivalent \( Tg_\infty = 133°C \), no vitrification, same moduli
- Commercial mixtures show the same full cure at temperatures below \( Tg_\infty \).

- Recall: Cure temperature MUST be higher than the \( Tg_\infty \) for full cure.
Low Temperature Cures with Microwaves

- Full cure measured as $T_{g\infty}$ from DMA and $\Delta H$ from DSC (no glass formed)
## Is Warpage Reduced?

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Did You Know This?

- Energy producing reactions then heat their neighbors

- This “exotherm” is an additional, uncontrolled heat source.

- Sample in “60°C oven” actually reaches 97°C (with higher stress).

![Graph showing energy of activation and exotherm heat of reaction.]

- **Oven heat at 60°C**
- **Sample temperature**
- **ΔH**
- **Power control**
- **VFM**
Lowered Storage Modulus After Full Cure?

- Henkel CUF8830 cured to the same Tg (see tanδ peak red arrows)

- Elastic (storage) modulus is ~ 3X lower above the Tg (rubber regime)
- Cross-link density is lower with VFM (chains between links are 3X longer)
- IBM (iMAPS 2013, IEEE 2015) found same lower modulus
- Lower modulus = lower stress and higher fracture energy (toughness)
  - Stress-strain measurements confirm increased $G_{lc}$
Several studies with consistently lower warpage of VFM cured dielectrics
- This data was for 200 mm wafers
- Two different material suppliers

- Cured to equivalent Tg but VFM cures were ~100°C lower

[Bar charts showing warpage comparison between PI and PBO for Conv and VFM]
Physics of Microwaves

\[ P_{av} = \omega \varepsilon_0 \varepsilon''_{\text{eff}} E_{\text{rms}}^2 V \]

- \( P_{av} \) = Average power dissipated
- \( \omega \) = Angular frequency
- \( \varepsilon''_{\text{eff}} \) = Dielectric loss factor
- \( E_{\text{rms}} \) = Electric field intensity (rms)
- \( V \) = Volume of the load

- Power absorption depends on the material having a high dielectric loss factor and polarizability (angular frequency).
- Higher sample volume increases power absorption!
- Average field intensity squared increases power absorption.
  - Uniformity is crucial to microwave curing
  - Sample heating does not depend on Boltzmann distribution spreading
Lessons

- Many failure modes in electronic assemblies are due to inadequate cure.
- Material properties depend strongly on extent of cure.
- Easy fix is to assure all films, adhesives, and coatings are fully cured.
  - There is a cost:
    - Higher temperature cure (longer cure times usually not helpful).
    - Analysis of extent of cure requires DMA, knowledge, and effort.
- Stress and warpage are directly proportional to cure temperature.
- Easy fix is the cure at lowest temperature still above $T_{g\infty}$.
  - There is a cost:
    - Lower temperature cures take much longer (exponential).
- Alternative fix to both chemistry and temperature issues.
  - VFM curing options:
    - Failures fix: Very fast full curing at full extent of cure.
    - Stress fix: Low temperature curing at reasonable times.
  - Typical adhesive chemistries are very reactive to microwaves.