22/05

# Lecture $\boxed{3}$

→ Most common material used in molding are epoxy based materials.

(first thing to try

$\boxed{\#}$ Epoxies are a large class of organic materials which have good and reliable curing dynamics.
↳ These epoxies are blended with oil/wax to facilitate better flow.

(80% wt $SiO_2$)

⇒ In most cases they are filled with Silicon Oxide particles in order to decrease thermal expansion and improve high temperature performance.

⇒ Epoxies can be refrigerated upto 24 months

| | |
|---|---|
| Additives | Silicone, wax |
| Filler | 80% wt $SiO_2$ |
| Ionic content (soluble in water)<br>Cl is villian to Aluminium<br>$Cl + Al \rightarrow$ Al Hydrochloride which reacts with $H_2O$ | $\boxed{< 50 \text{ ppm } Cl^-}$<br>(Chlorine is in all epoxies and will leak) |
| **Processing** | |
| Shelf life at °C (B staged) | 24 months at 5°C |
| Temperature range of molding | 170 - 185°C |
| define throughput — Soak time in molding form | lower better 60 - 180 s (contact rigidity) |
| ( but not this one Post mold curing time t and temperature (post hardening) | (4-5 hr at 175°C |

Cured Product

at which viscous liquid ↑ TG
solid ↓

| | |
|---|---|
| → Glass transition temp TG | 140 to 170°C |
| → Coeff expansion below TG | 8 to 15 * $10^{-6}$/K ~ ppm/K |
| → Coeff expansion above TG | 35 to 70 * $10^{-6}$/K |
| → Elastic modulus in bending | 14.5 GPa |
| → Water absorption @ 100°C / 24h | 0.1 - 0.5 % |
| → Inflammability (UL94) d = 1.6 mm | V-0 |
| → Thermal conductivity $\lambda$ | 0.65 W/m-K (↓ = better) |
| → Permittivity $\varepsilon_r$ | 4.0 |
| → Dissipation factor $\tan\delta$ | 0.008 imp for high freq electro |

10 cm/K
1 cm/K

NOTE: Housing temperature must be strictly below glass transition temperature.

- Volume change due to temperature or due to water absorption → causes delimination problems
- water may get into the

## Epoxy Chemistry

→ part of polymer chemistry

Used to build binder material in paints, molding and part fixation. eg : 2K glue UHU+ sofortfest

From (MSDS) material safety data sheet the chemical composition can be derieved.

Binder - epoxy terminated bisphenol A polymer.
Harder - aromatic & tertiary amines.

| Binder Component A | Hardener Component B |
|---|---|

# Properties of Epoxy Polymers

→ They are tightly crosslinked therefore almost insoluble in all organic solvents.

→ Have low shrinkage during curing which makes them ideal for sensitive electronic components.

→ Cured epoxy polymers are thermosets → not meltable and they decompose on heating.

* There are exceptions to the rules but these materials need to be cured with tailored process.

→ Due to nature of curing mechanism epoxy polymers show a significant no. of alcohol groups remaining after curing.
free OH groups

↳ this allows to functionalize them after curing

→ But it also makes the materials susceptible to swelling in aqueous conditions.

→ Epoxy polymers are tolerant to blending - as curing chemistry is robust.

→ Allowing for a no of compounds to be blended with the polymer.

## APPLICATION OF EPOXY'S : Blends & Compounds

They are extremely tolerant to blending and mixing of compounds such as metallic or ceramic particles.

carbon fibre

→ It's convenient to couple epoxy's to surfaces
↪ ideal matrix materials.

→ Fibre reinforced materials [light weight alternative to bulk metal]
Eg: automotive, aerospace industry

→ Carbon fibre reinforced polymers will be the new high strength materials for chassis and car components. Fiber + Epoxy ~~material~~. matrices

Epoxy based fiber compound materials

Fibers or textiles are applied onto a form and held in place, the textile is then coated with liquid epoxy pre polymer which cures in place.

→ Pressing and heating accelerates the process commonly used for light weight chassis of race cars.

## CURING OF EPOXY MONOMERS / POLYMERS

Method 1: Epoxy homopolymerization happens via
→ cationic ring opening polymerization
→ anionic ring opening polymerization.

Leads to low molecular weight polymers.
The process requires catalytic amount of initiators. (High Chain Transfers)

Method 2:

For epoxy curing is by coreaction in a 1:1 molar ratio with suitable curing agents or curing reagents.

→ commonly used are primary amines which attack the epoxy ring

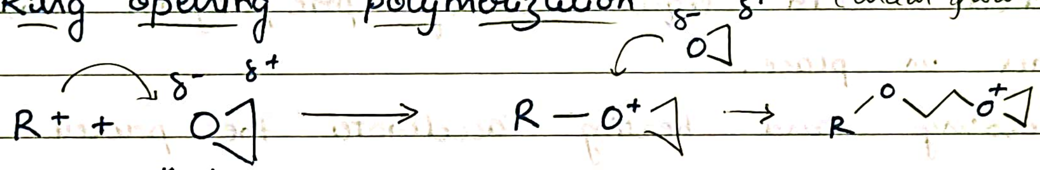
→ In parallel the electronegative oxygen on the ring attracts free Hydrogen.

→ results in secondary amine which again attacks another epoxy ring

→ resulting tertiary amine is still nucleophile but not reactive anymore

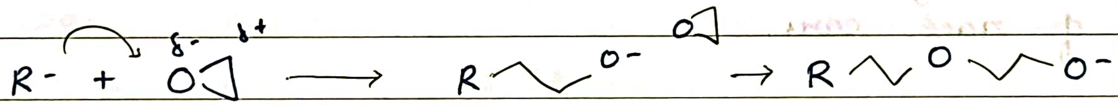
Ring opening polymerization (chain growth) Heterogeneous

Cation



cation ethylene oxide cyclic cation

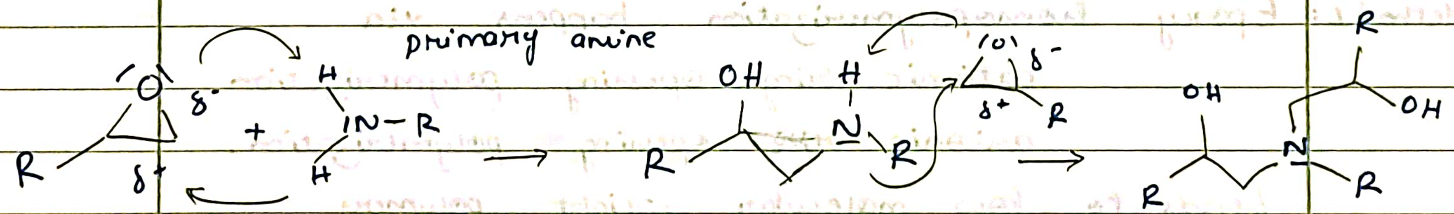
Anion



anion linear anion

Curing by Amines (step growth) Homogeneous.

primary amine



Depending on reaction epoxy curing can be

→ Step growth polymerization

→ Chain growth polymerization

## Amine Curing Agents

A) Aliphatic amines : (smells rotten)

- very reactive curing agents
- usually create a lot of heat during curing (maybe a problem)
- Strong skin irritants (sometimes toxic)

Eg: Tri ethelene triame, di ethelene triami
↳ cadomalene (generated on cadvers)

B) Aromatic amines : (expensive)

- Reactivity not sufficient to cure at room temp.
- Secondary aromatic amines are far less reactive and usually do not form bonds.
- heating is usually required.

Eg: diamino diphenyl methane, 1,4 benzenediamine

C) Polymeric Amines :

- Prepolymers created by reacting excess amines with understoichiometric amounts of epoxy.
- Results in amine functional prepolymers which are liquid and high molecular weight
  ↳ reduced volatility & convenient handling

⇒ polyamides are also convenient curing reagents.
(eg:

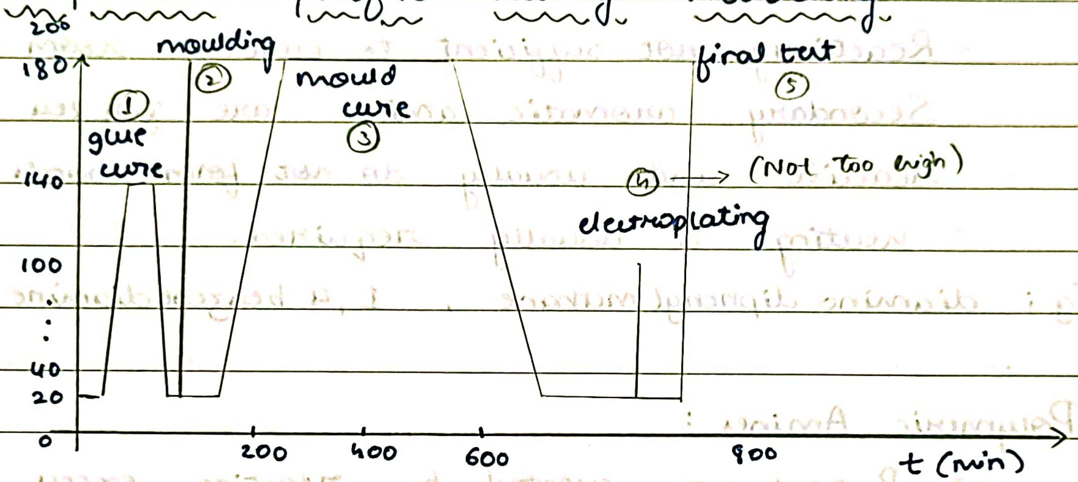
## Common Epoxy Casting Resin Materials

Usually high molecular weight oligo-epoxy monomers/oligomers which are premixed with an amine (aromatic diamine) curing reagent and a catalyst.

Eporides are tolerant to high filler degrees thus they can be highly filled - most common filler is $SiO_2$ [improved heat resistance, smaller thermal expansion coefficient].

Eg: epoxidized novalac, Tris-hydroxyphenol glycidylether

Temperature Profile during Hardening




During assembly the chip is exposed to high temperatures a couple times.

1 → during hardening of fixation glue
2 → during moulding (i.e mold material injection)
3 → during mold curing (which happens outside the mold)
5 → during final tests in QC.

Q: Semiconductors also feel the heat but we always keep temp < 200°c for Si (if exceeded we lose Si doping).

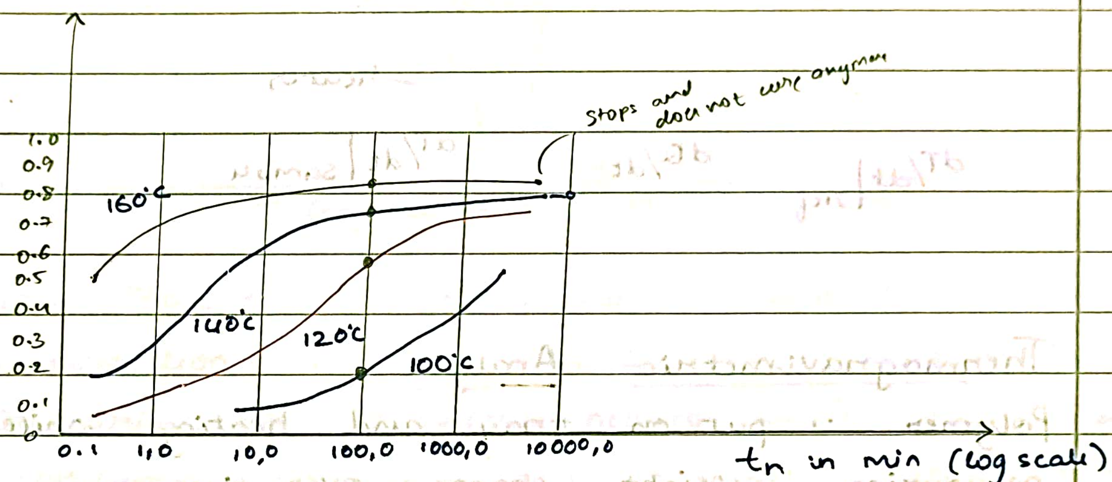
# Hardening Kinetics as measured via DSC

→ Hardening of epoxy is assessed by "Differential Scanning Calorimetry" → measures heat flux

→ Hardening degrees in the range of 80-90% are usually achieved

→ speed of hardening is temperature dependent

→ post hardening is often necessary.



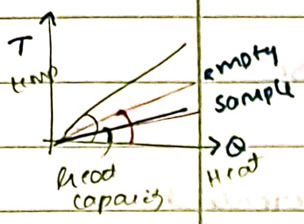

※ Epoxy's harden at room temperature too

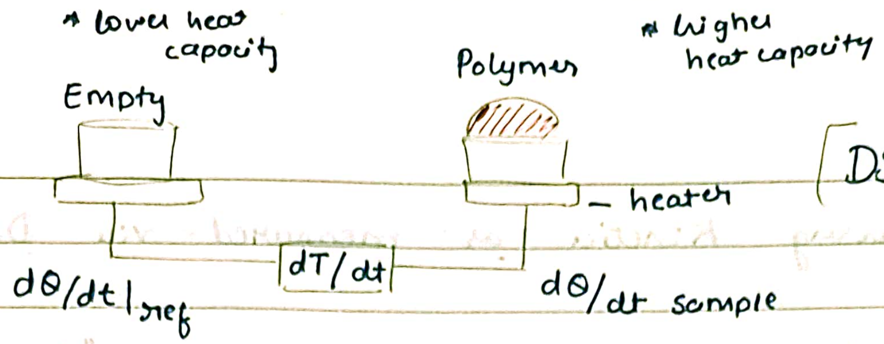
## DSC, DTA and TGA

### Differential Scanning Calorimetry

→ Polymer block is put on a tray alongside an empty tray into temperature controlled chamber.

→ Both are heated at same rate eg 10°C/min while measuring heat flux in both samples.



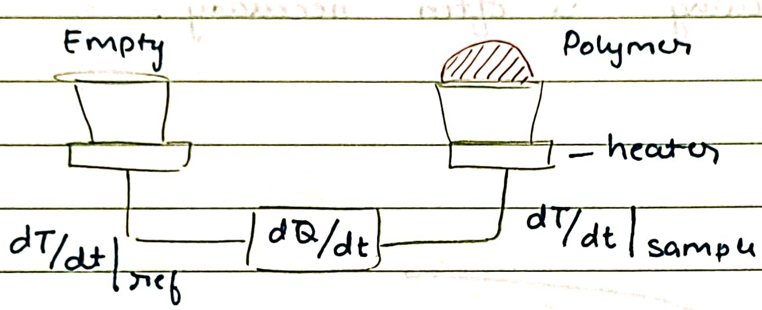




[DSC]

## Differential Thermal Analysis

→ Polymer is placed same way as DSC

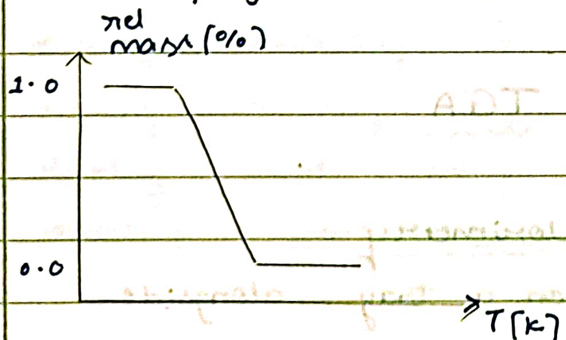
→ Both samples are provided same heat flux while measuring temperature change.

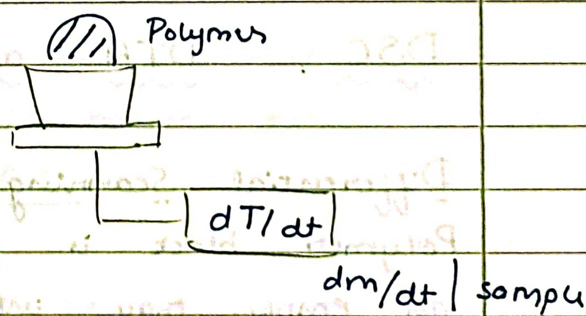



## Thermogravimetric Analysis

→ Polymer is put on tray and heating while measuring weight change over time.

→ allows detection of volatile compounds and polymer composition.

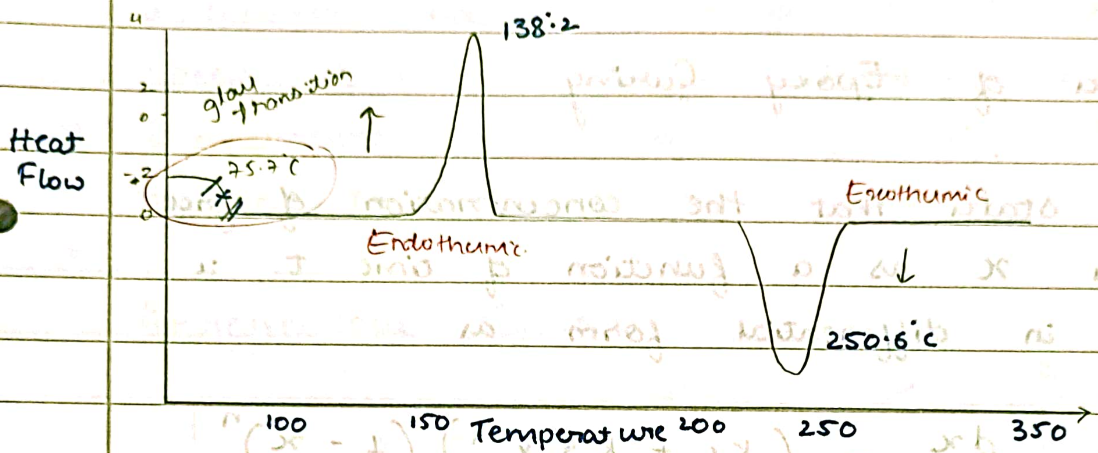


# Thermal Characterization of Polymers

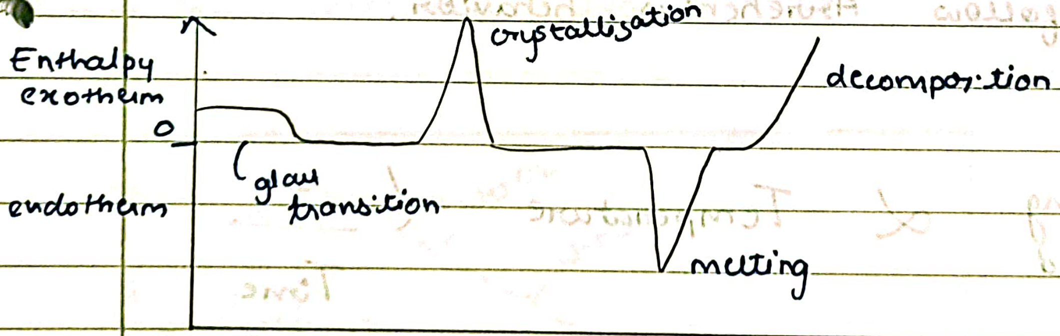
## DSC

Allows detecting thermal transitions within a polymer. Thermal Transitions are structural re-arrangements in the polymer.




DSC of PET

→ Glass transition, recrystallization, melting and decomposition can be seen as either endothermic (requiring heat & → higher heating rate) or exothermic (releasing heat → lower heating rate)




Heat Capacity : $C_p = \dfrac{\frac{q}{t}}{\frac{\Delta T}{t}} = \dfrac{q}{\Delta T}$

$= \dfrac{\text{Amount of energy req.}}{\text{temperature change}}$

* Similar results can be obtained by DTA

Thermogravimetric Analysis
Used to assess polymer composition for cross linked polymers and thermosets allows for determination of composition.

# Kinetics of Epoxy Curing

Model states that the concentration of free epoxies $x$ as a function of time $t$ is given in differential form as

* First Order Kinetics

Curing Speed $$\boxed{\frac{dx}{dt} = (\underbrace{K_1}_{\text{reaction}} + \underbrace{K_2}_{\text{constant}} x^m)(1-x)^n}$$

→ m and n are constants independent of temp 'T'
→ $K_1$ and $K_2$ are temp. dependent rate constants which follow Arrehenius behavior.

$$\text{Curing Speed} \propto \text{Temperature} \propto \frac{1}{\text{Time}}$$

• We will never get 100% cured epoxy

## Influence of temperature

⇒ Many processes are temperature dependent

eg: Oxidation of Silicon to Silicon dioxide

⇒ these reactions usually speed up with temp.

but they require activation energy

a common case is the rough estimate that the speed of a reaction will roughly double if

⇒ temperature is increased by 10K →

referred to as Van't Hoff equation.

⇒

## Arrhenius Equation

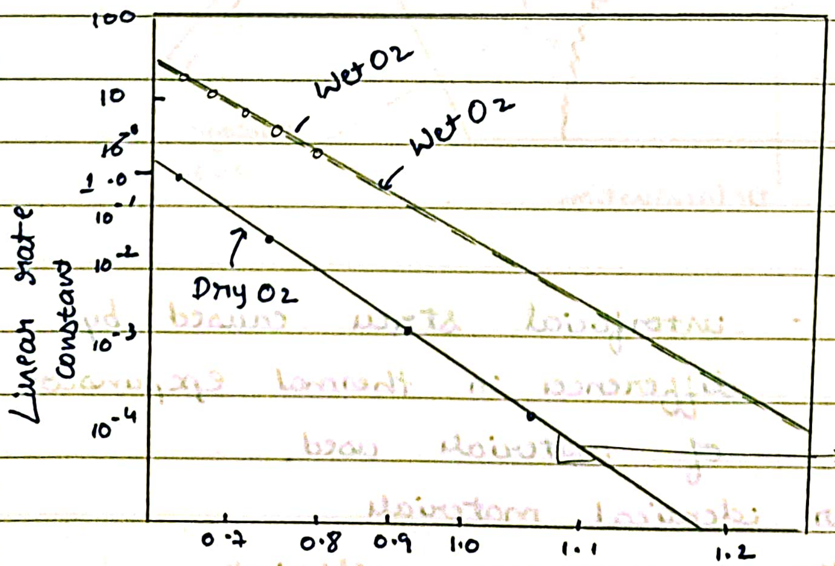
$$\left\{ K = K_0 e^{-\Delta H / RT} \right\} \Longleftarrow \ln\frac{k}{k_0} = -\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

K - rate constant of the reaction at temp T

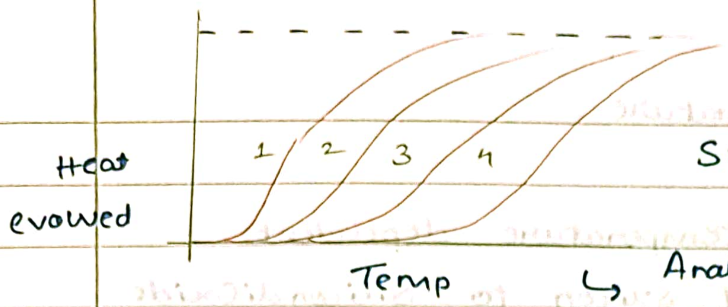
$K_0$ - rate constant at temperature $T_0$

$\Delta H$ - activation energy

R - Universal Gas Constant




→ activation energy is slope times Rate R

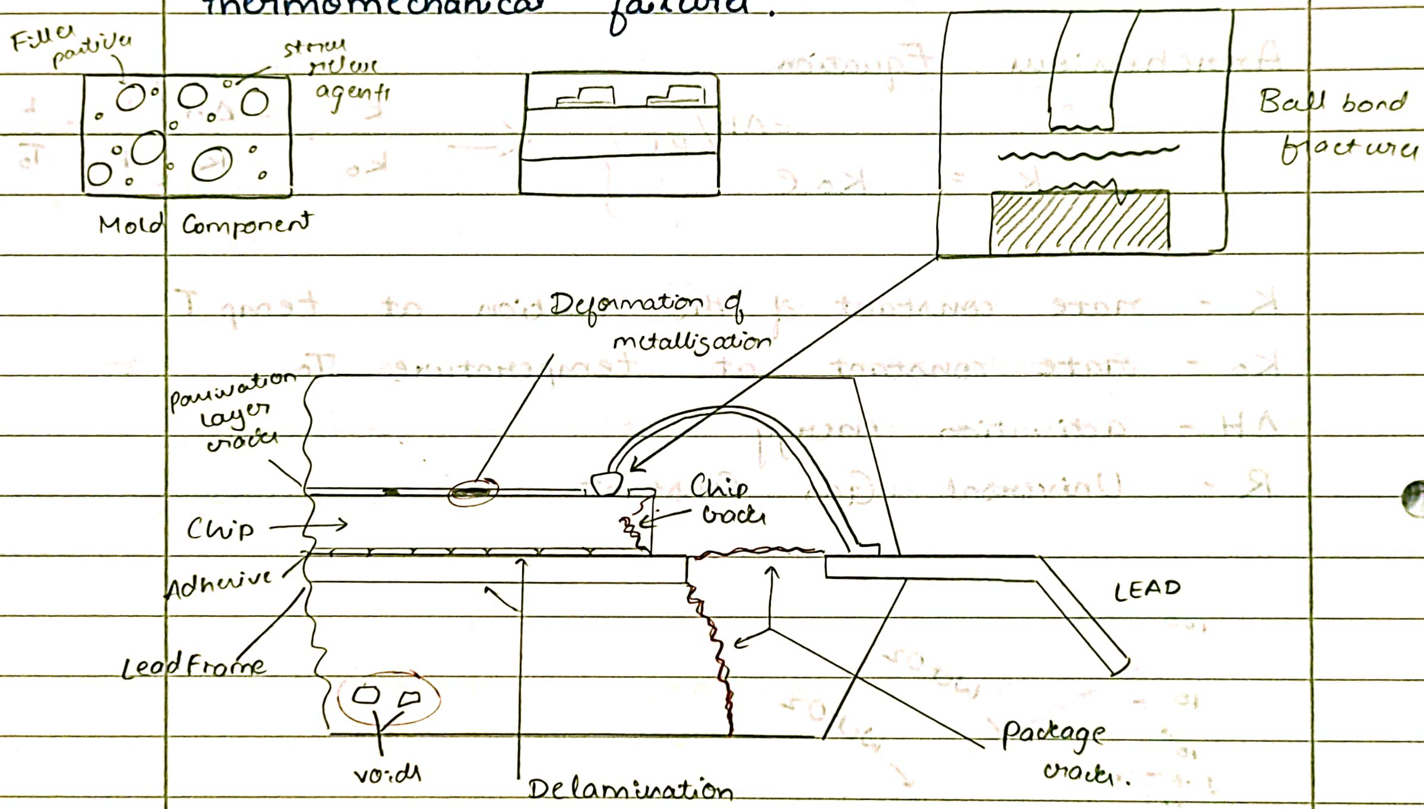



S: 4 > 3 > 2 > 1

↳ Analytical heat released during epoxy curing

## Typical Failure mechanisms in Packages

Many of the typical bulk problems as well as interconnection problems are due to thermomechanical failures.




Major Cause - interfacial stress caused by differences in thermal expansion of materials used.

To Fix → use near identical materials

→ adjust thermal expansion coefficients