Thermal Resistant Polymers for Microelectronic Applications

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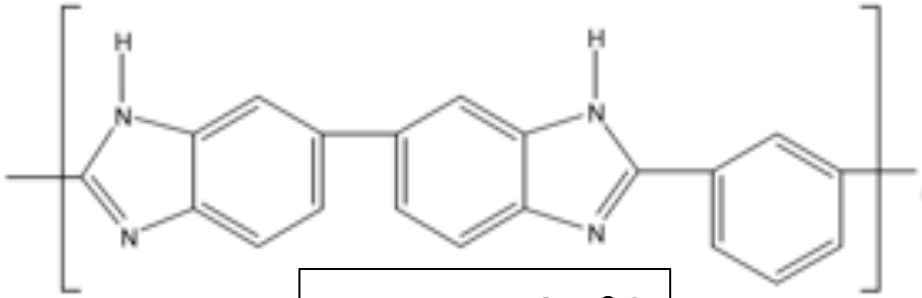
Agenda

1. Matching Properties w/Applications
2. Polymers Review
3. Design & Approach
4. Summary

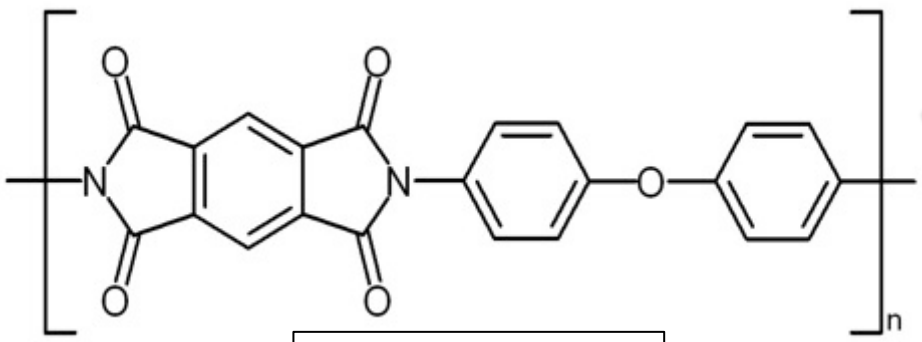
1 Matching Properties w/Applications

- High Tg = thermal resistance
- Low TGA at elevated temperature
- Low CTE for system matching
- Oxidative resistance
- Low color development
- Abrasion resistance used in aerospace
- Broad coating possibilities

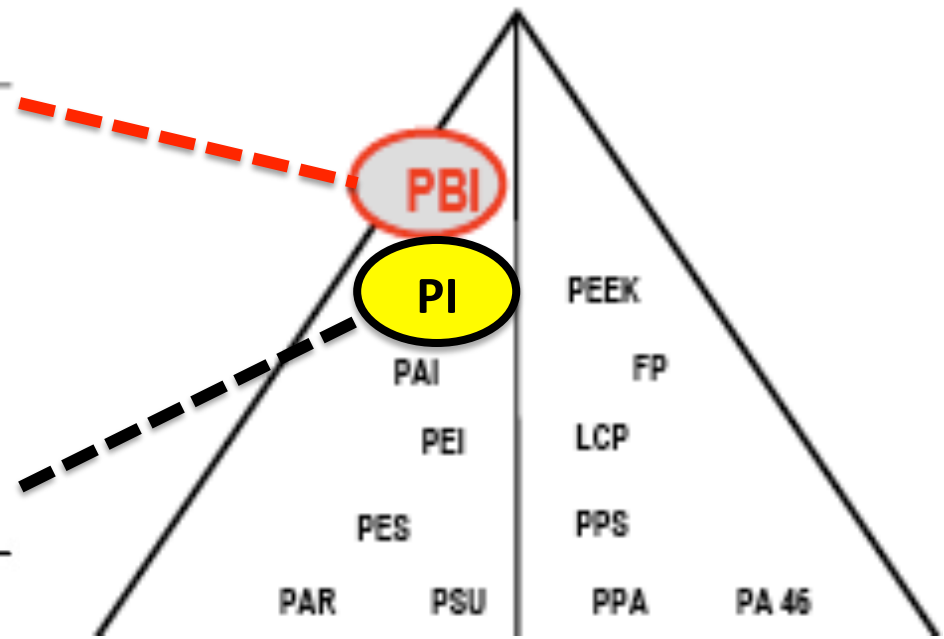
Engineering Polymers



PBI Tg = 427 °C



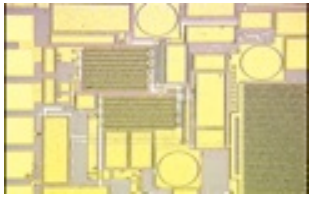
PI Tg = 370 °C



Fire Fighting & Protection

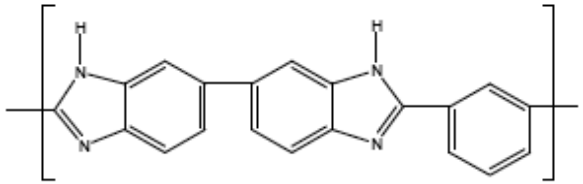
Automotive

Injection Molding



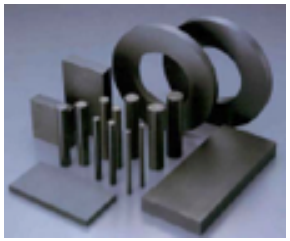
Electronics & Semiconductor

Polybenzimidazole (PBI)

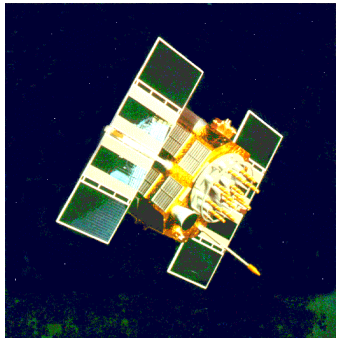


Aviation

Thermal Resistance
for Multiple Applications



Compression Molding



Aerospace

Metal Working

Transparent Display

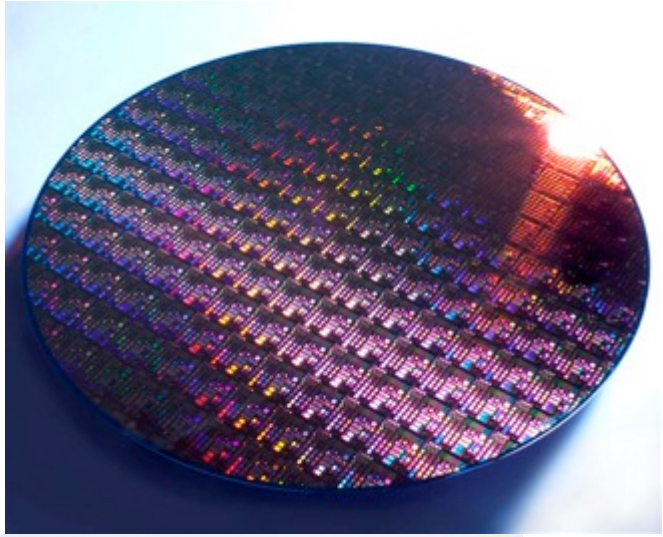
- Rising interests exists for transparent displays that allow user to see multiple objects
- Transparent display can be integrated to vehicle windshields, domestic glass, display units for retail and related

Transparent Display

US Patent: US 8314902 B2

Transparent Coating for other applications

Aerospace



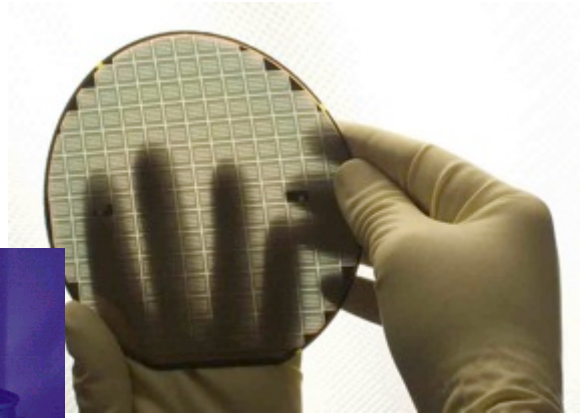
Electronics

Optical Filters

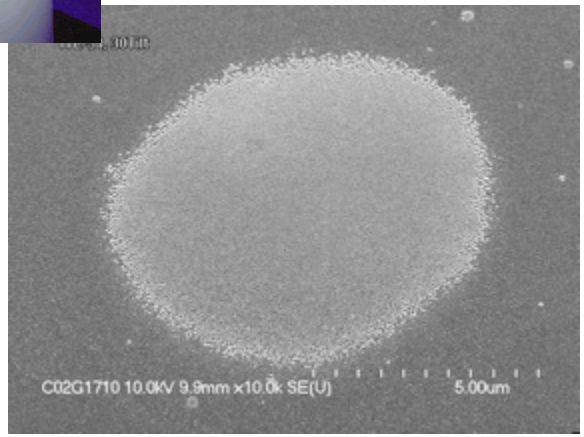
Thermal Induced Irregularities

Fab Tooling

Chemicals



Handling



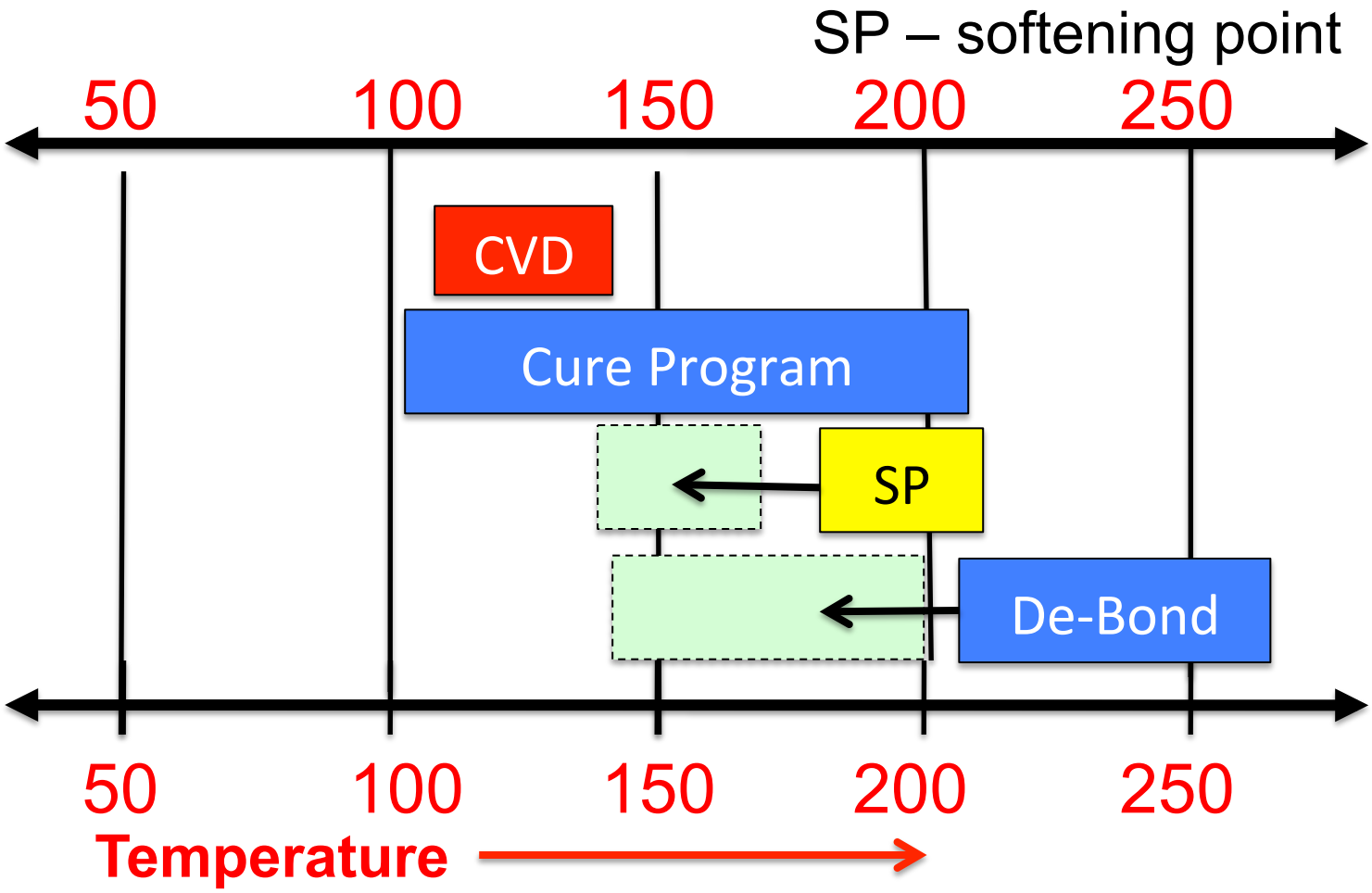
Contamination

Low Outgas Product for CVD

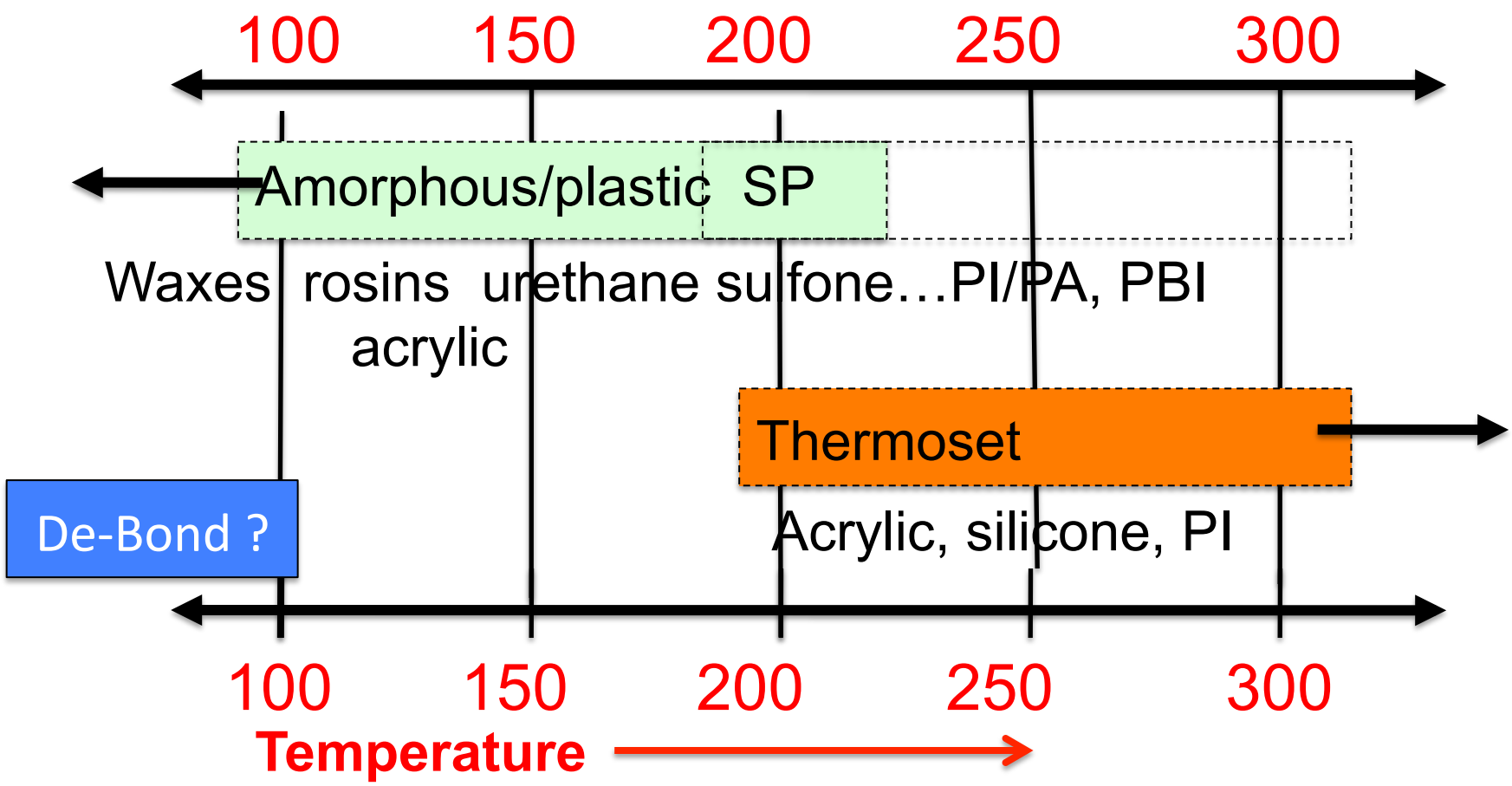
Targets for successful CVD processing:

- Low permeability coating
- High Tg
- If amorphous, high softening/melting point
- Softening/melt pt is > process temp
- Design cure program as > process temp

Process Overlay



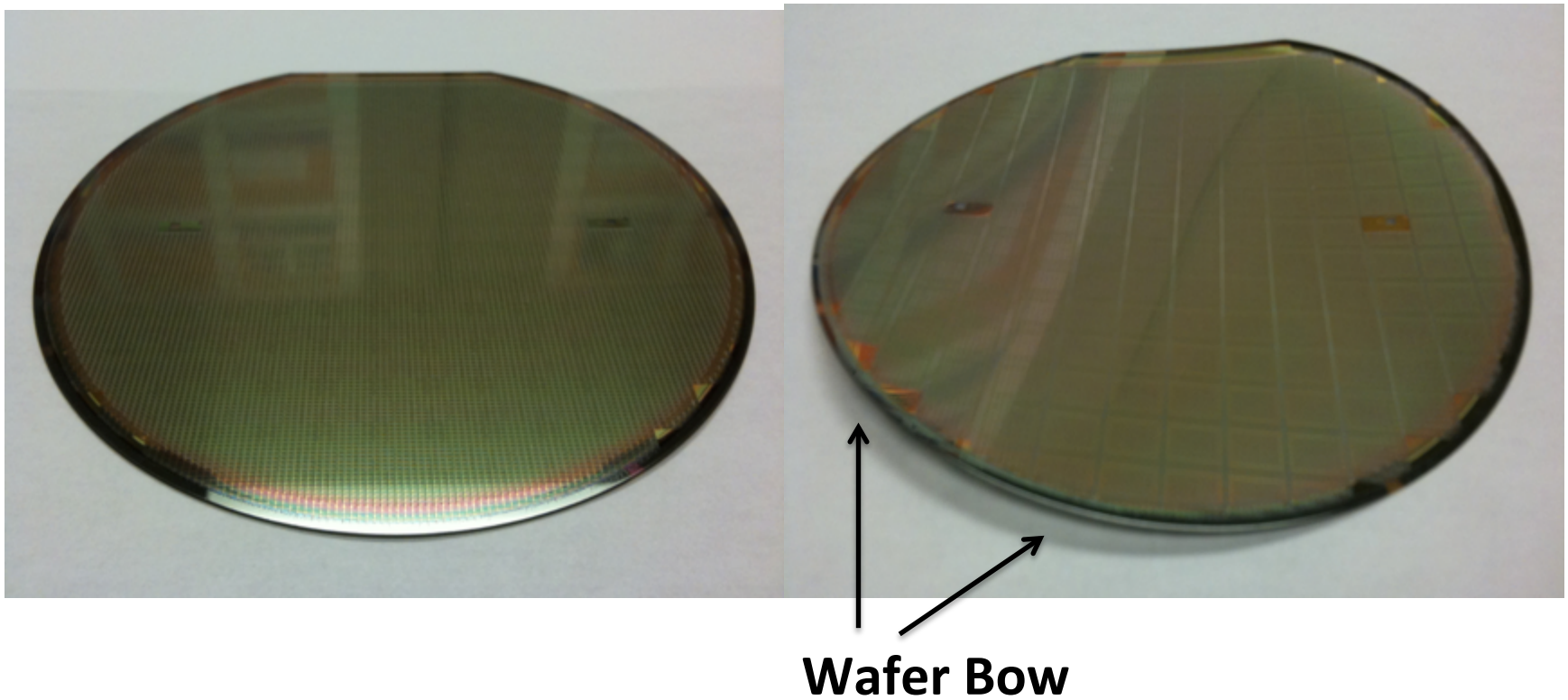
Materials Overlay



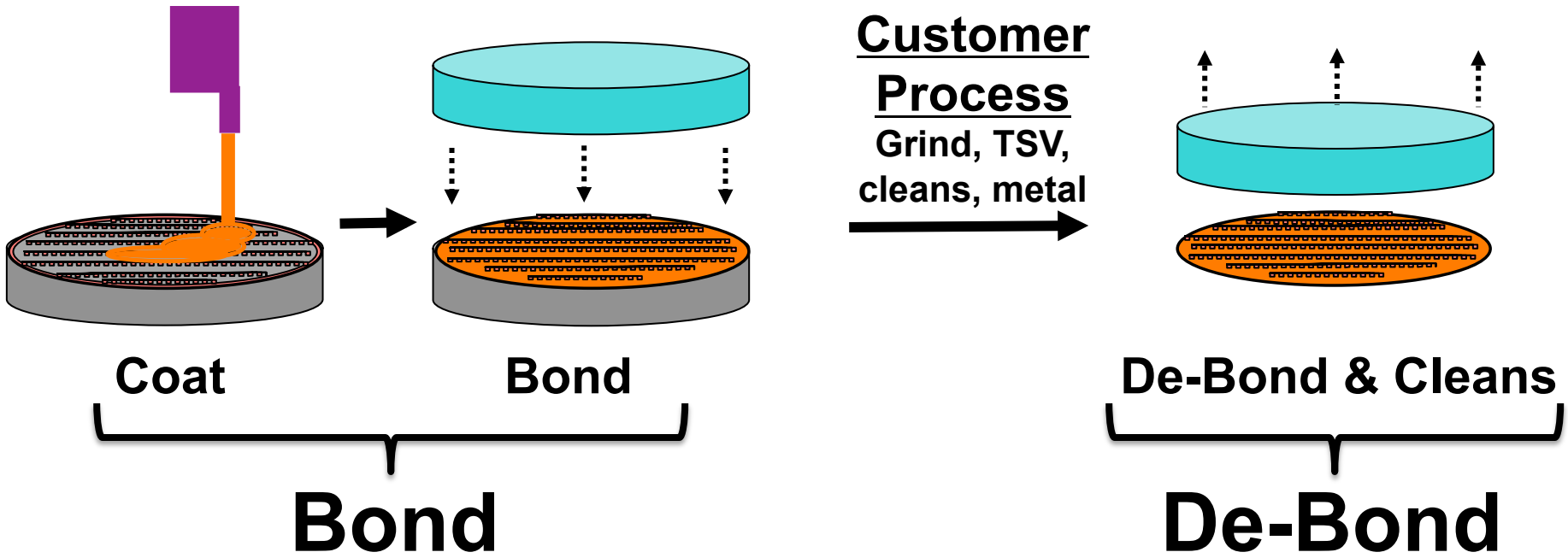
Stress Introduction

Bowing observed from stress of thinning and/or coating

Full thickness ~ 700um **Thinned ~ 100um**

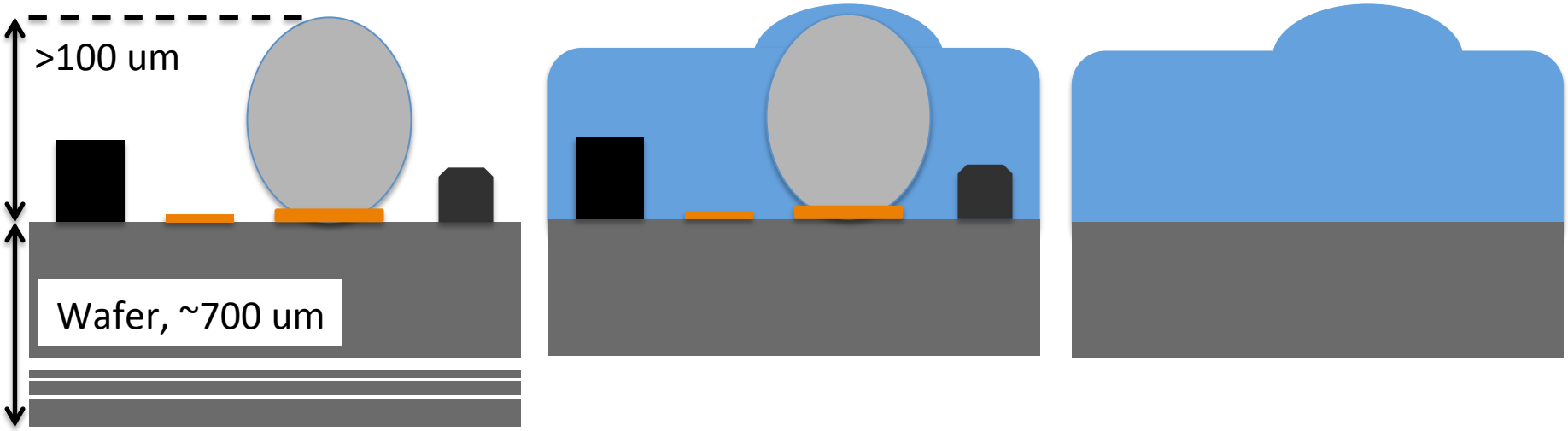


Temporary Bonding Process



Two ACTIVE steps occur with Temporary Bonding Technologies.
The "BOND" step is similar between popular practices.
Primary differences occur during "DE-BOND".

Planarization Layer

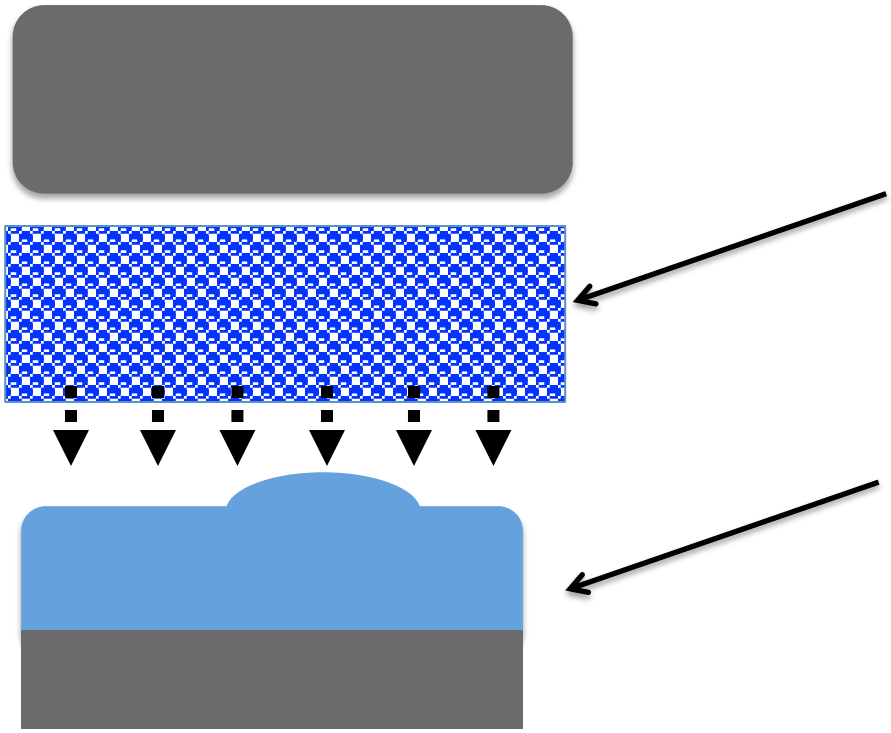


Wafer with Topography (able to planarize >100um)

Planarization Coating

Film Attachment

Adhesive Bond



B – Adhesive w/capillary penetrant

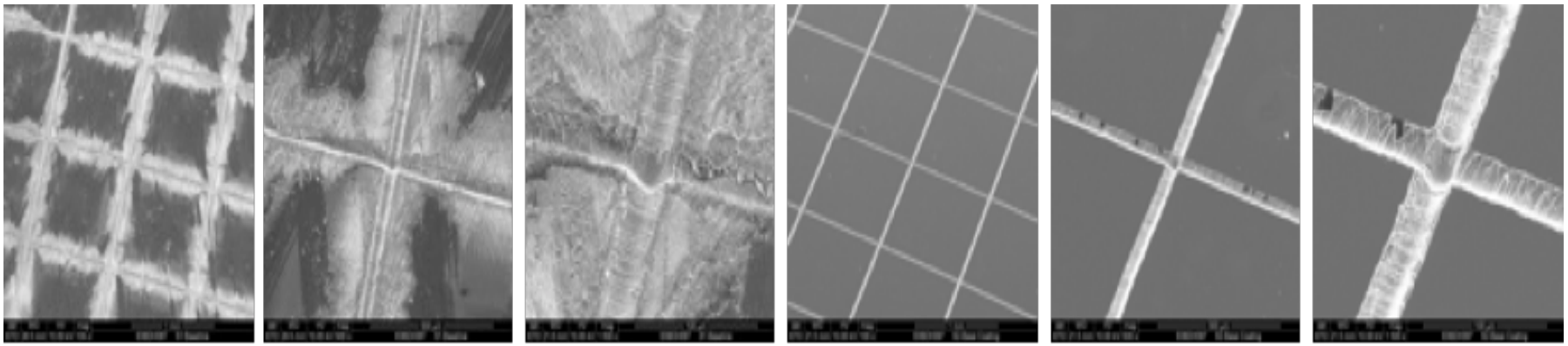
A – Planarizing Coating

Film Attachment

Wafer Bonding Chemistries

Firm	Chemistry	DeBond Method	Batch or SW	Cleans
BSI	Rubber	Chemical, slide, peel	SW	Non-polar solvent
3M	Acrylic	Ablate/peel	SW	Polar solvent
TMAT & Dow Corning	Silicone	Peel	SW	Non-polar solvent
DuPont	Polyimide	Ablate/peel	SW	Polar solvent
TOK	Urethane	Chemical	Batch	Polar solvent
Daetec	Rosin Acid	Chemical	Batch	Detergent

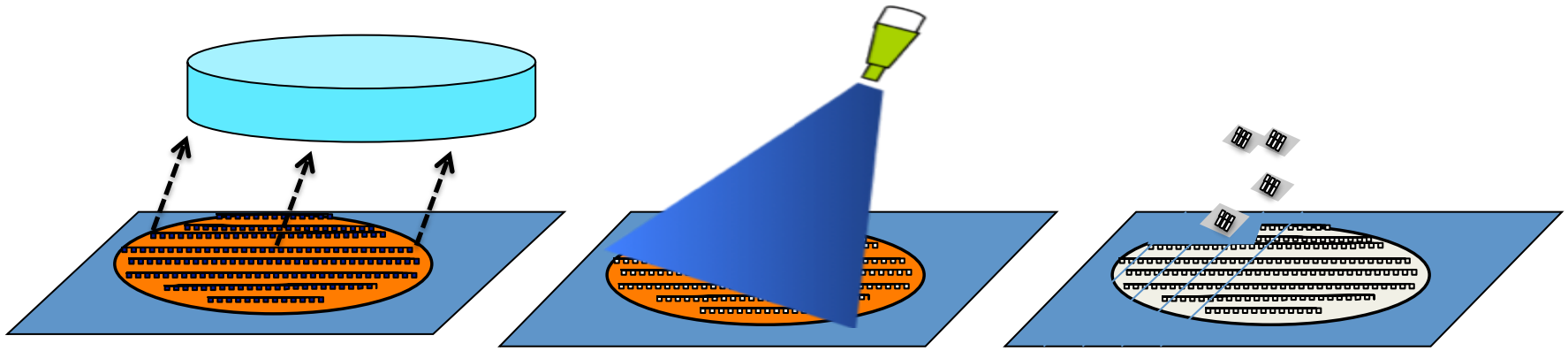
Washable Laser Coatings



Before - No Coating

Coating & Cleans

Roadmap to Dicing



Film Attachment Carrier Demount

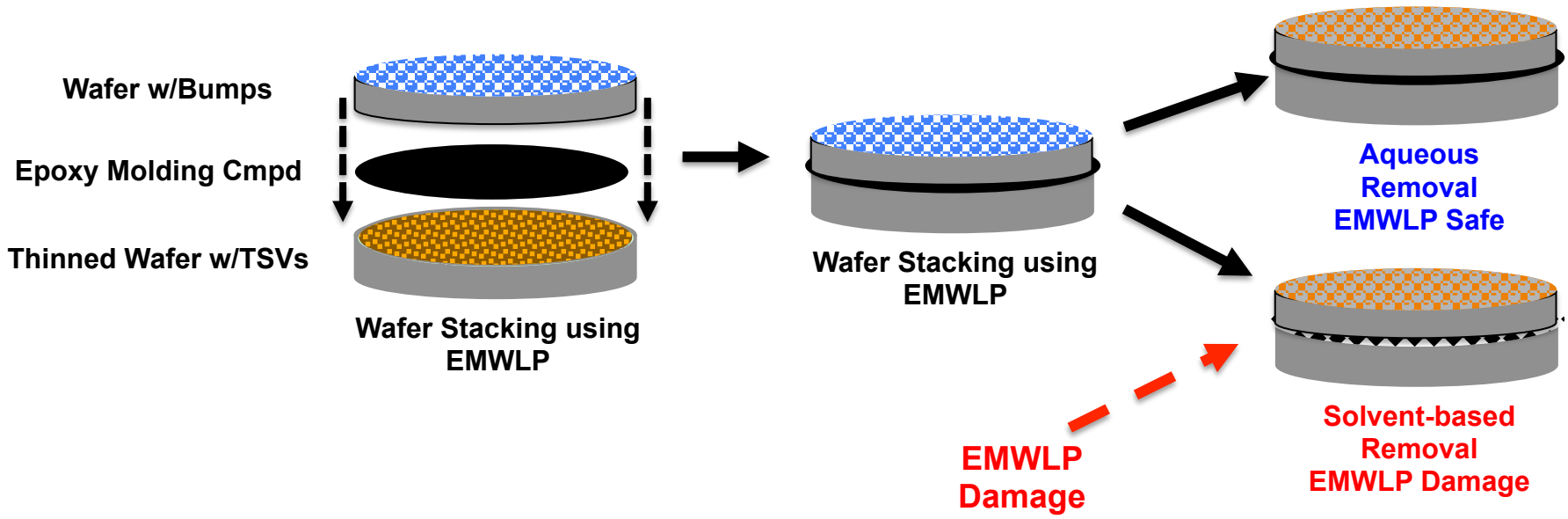
Wafer Cleans Safe for Tape

Dicing

cleans compatible to tape or vice-versa

Wafer Stacking

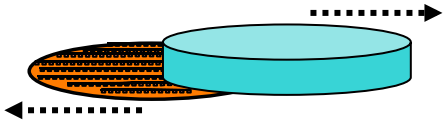
- 3D wafer level stacking using epoxy molding
- Embedded Micro Wafer Level Pkg (EMWLP)



High Throughput Process

Single wafer vs Batch

1) SW

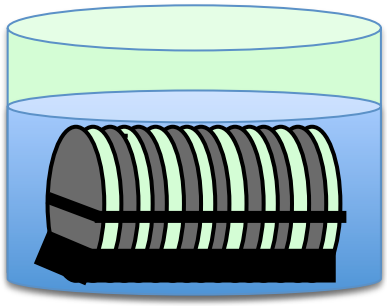


Slide/Debond + Clean

~12 wph

SW Debond & Cleans

2) AQ



Batch Demount & Cleans

Batch Debond & Cleans (Wet Bench)

100-400 wph

Benefits & Cost

- Product costs 10-75% of commercial
- COO <10% due to batch processing

COO Defined (SEMI E35)

$$COO = \frac{F\$+R\$+Y\$}{L \times T \times Y \times U} = \frac{Costs}{Product}$$

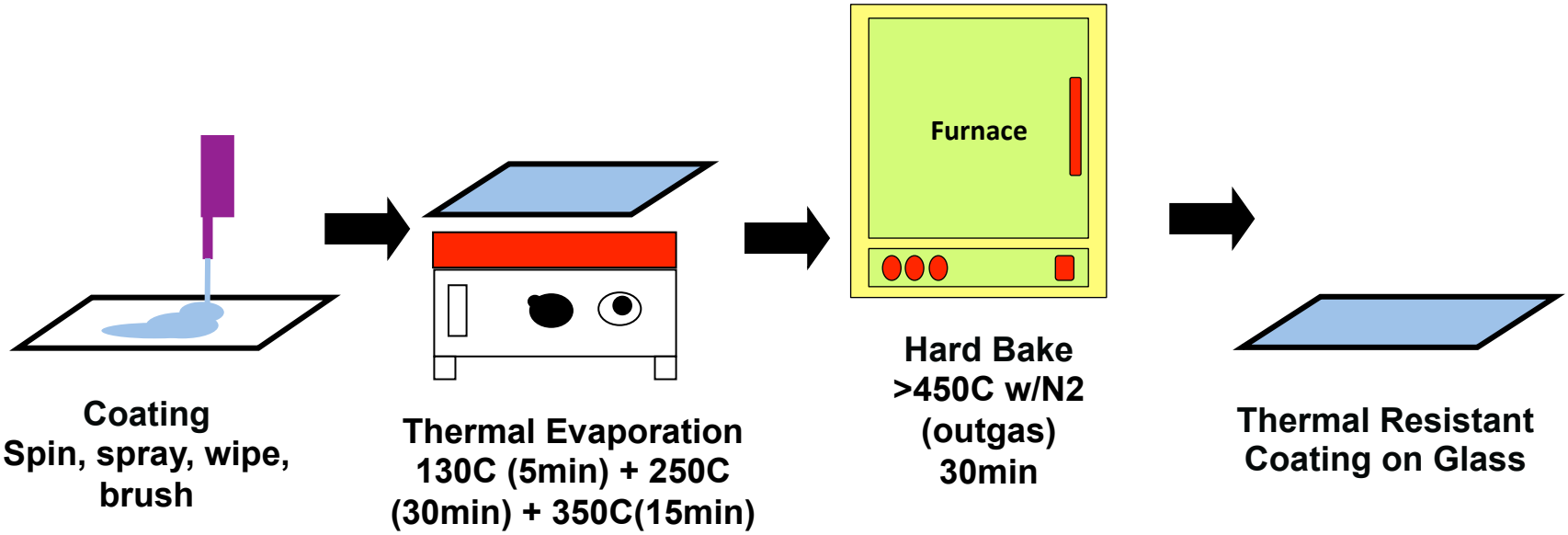
Item	Definition
F$	Fixed Costs
R$	Recurring Costs
Y$	Yield Cost (scrap)
L	Equipment Life
T	Throughput
Y	Composite Yield
U	Utilization

$$\frac{COO_2}{COO_1} = \frac{\text{AQ DB/Cleans}}{\text{Rubber DB/Cleans}}$$

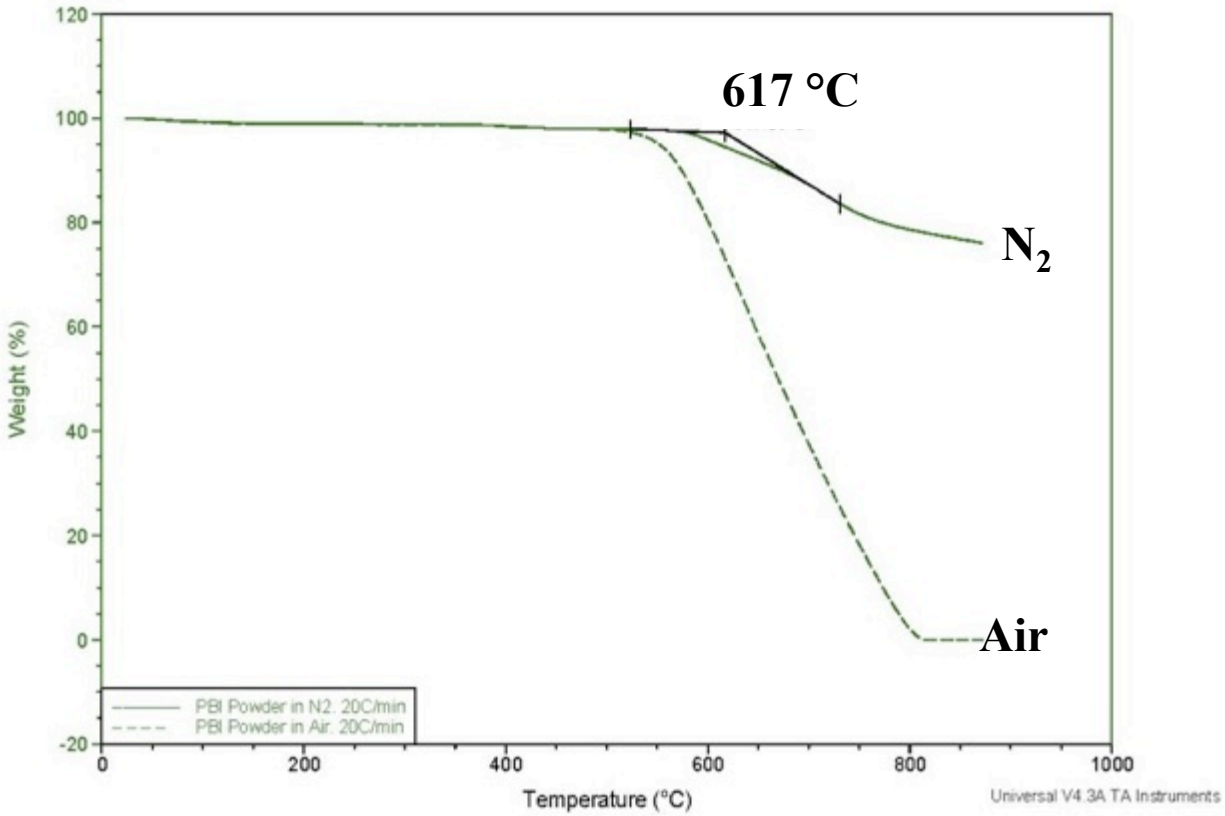
2 Polymers Review

- Few engineering polymers can exhibit thermal resistance to 500C
- Even fewer are transparent
- Fewer still are flexible to allow removal by peeling
- Commercially available do not meet these objectives, are expensive

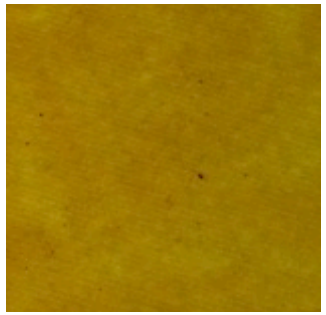
Coating Processing



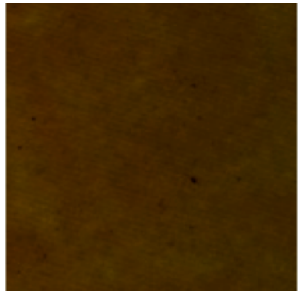
PBI TGA Scan



PBI is non-Transparent

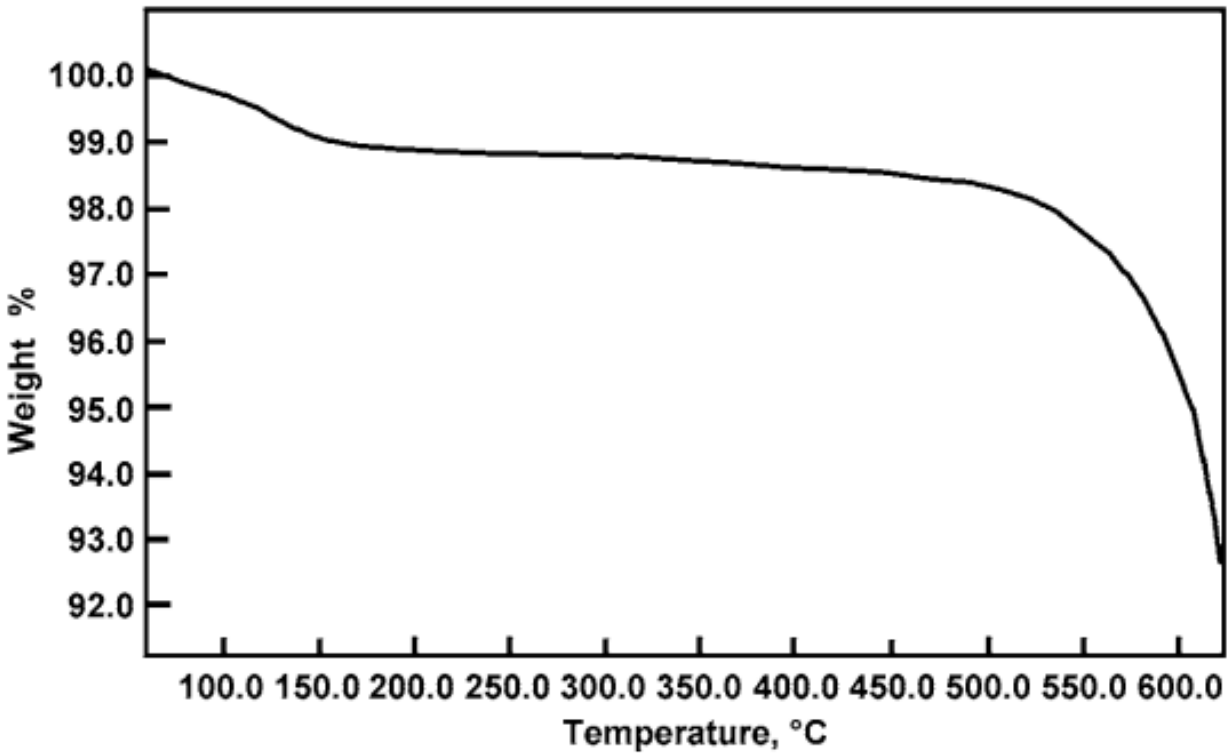


Exposed to 350C



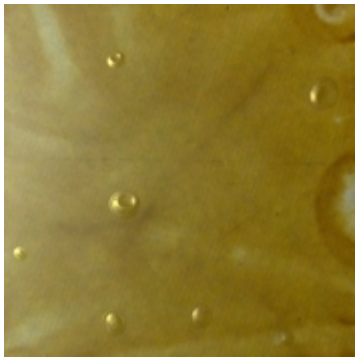
Exposed to 500C

PI TGA Scan



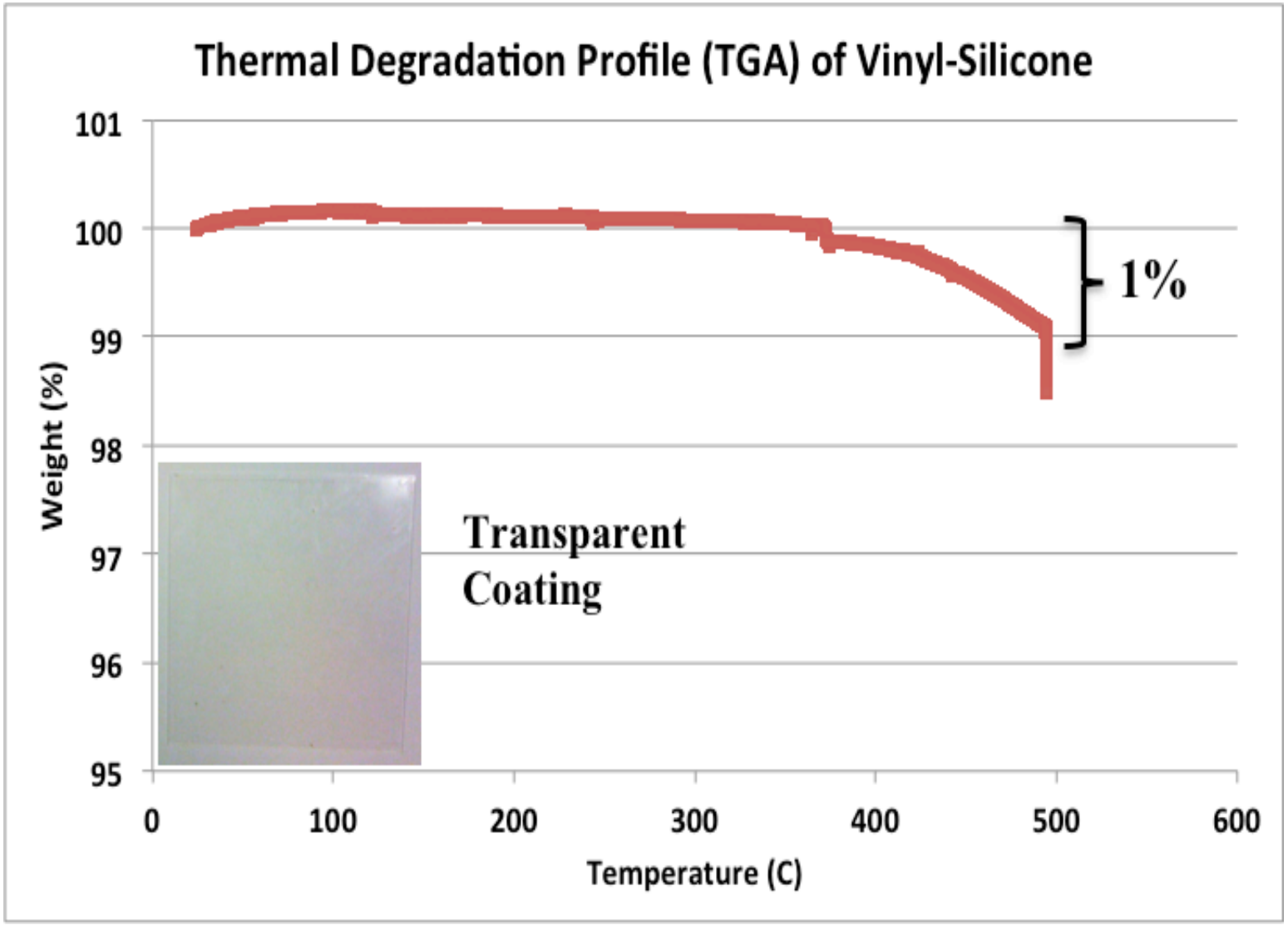
PI loses Transparency with temperature

Exposed to 350C



Exposed to 500C

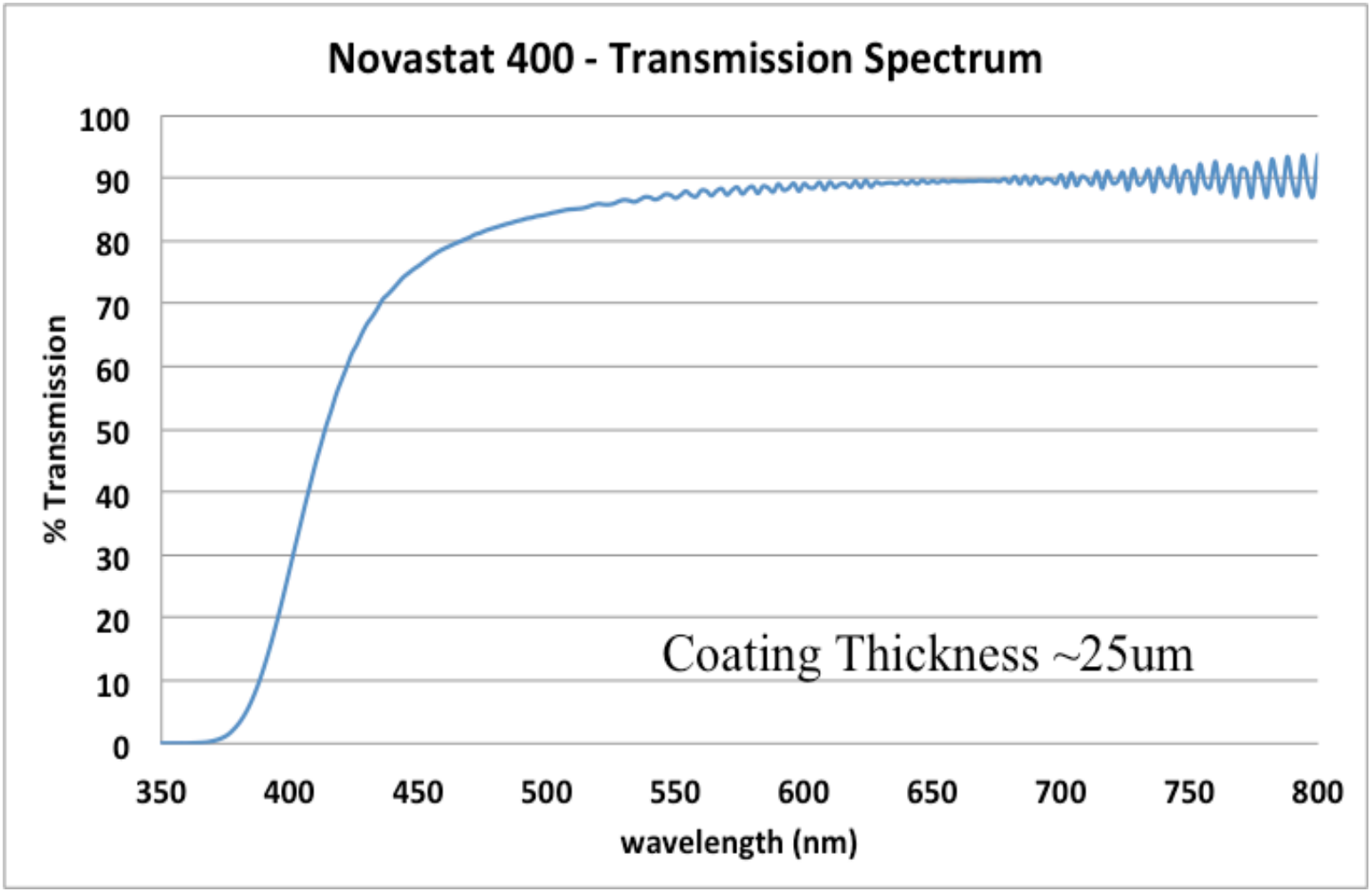
Silicone TGA Scan



Daetec PI Review

- Daetec has evaluated many PI chemistries from suppliers in Asia, EU, and North America.
- Some exhibit promising transparency at medium temperature (i.e. 350C) and low thickness (i.e. <10um)
- As temperature increases, transparency loss occurs

PI Transparency

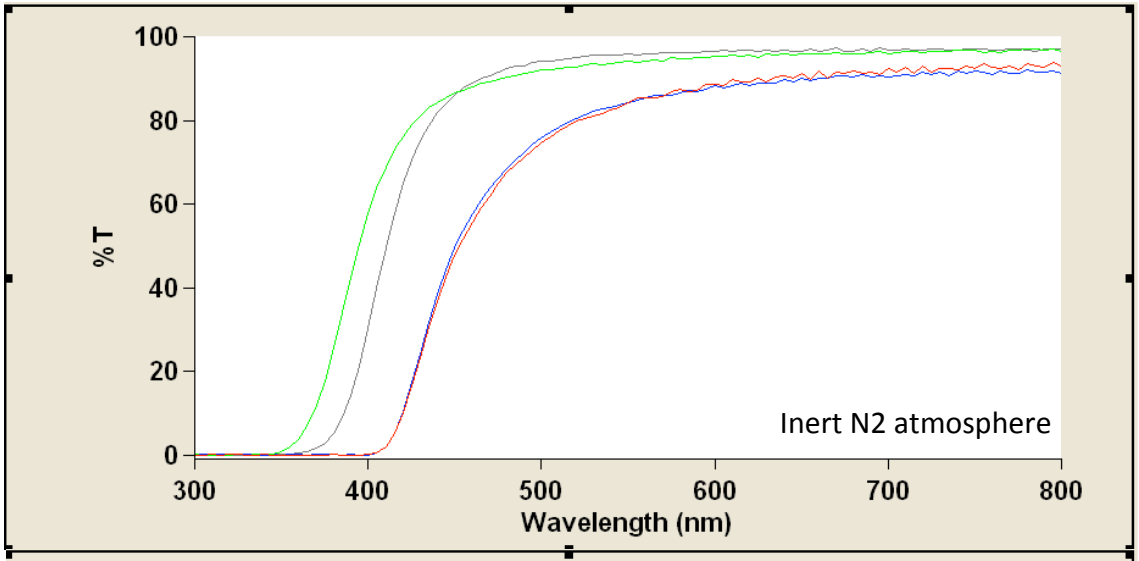


PI Transparency Loss w/Temperature

PI Samples 1-4

350C

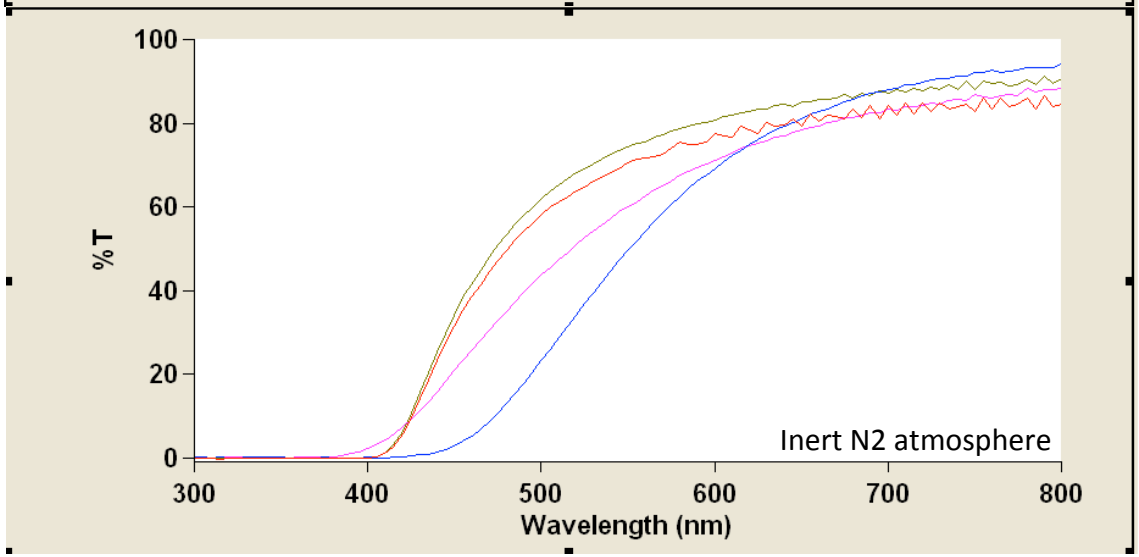
Moderate Transparency with 2 samples



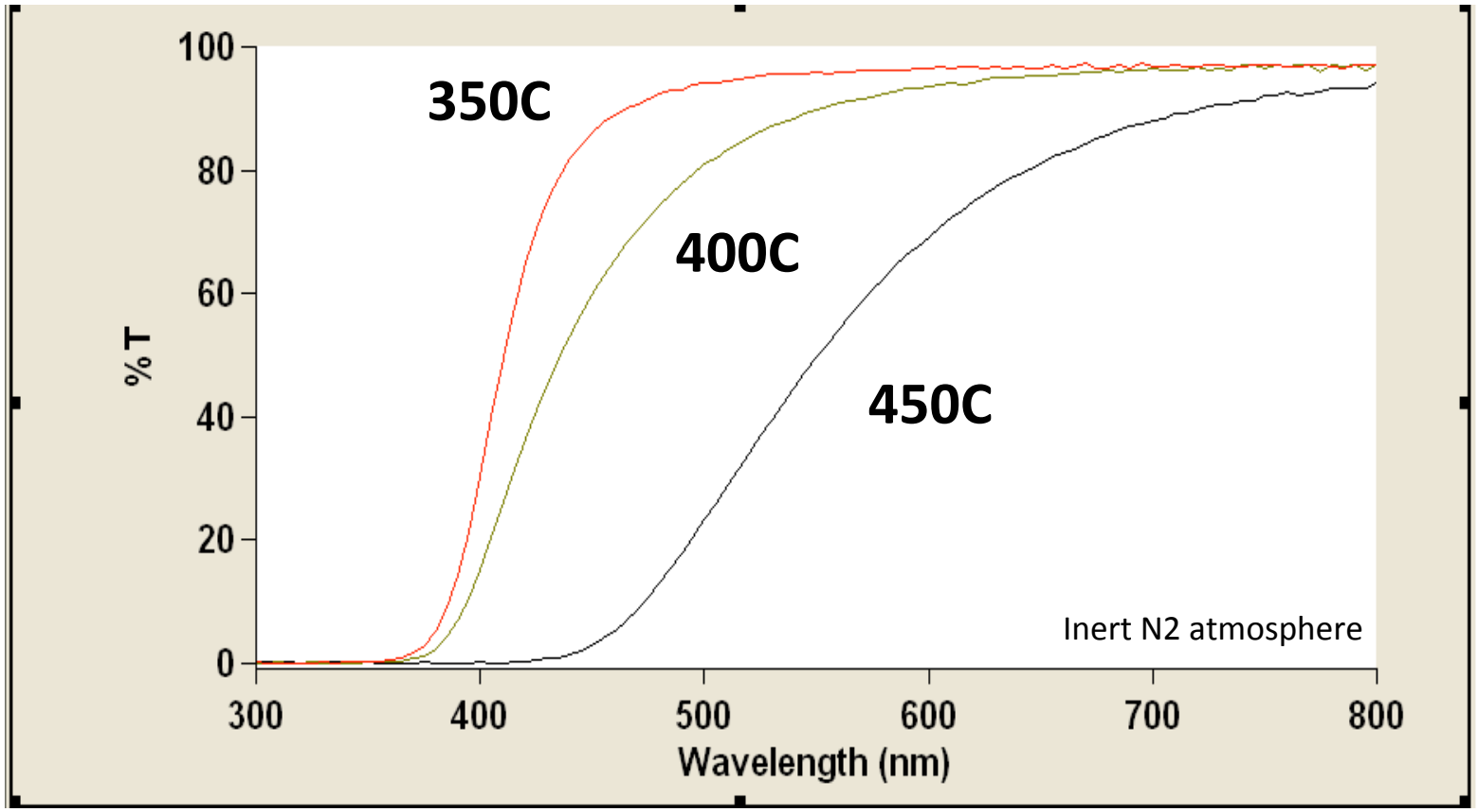
PI Samples 1-4

450C

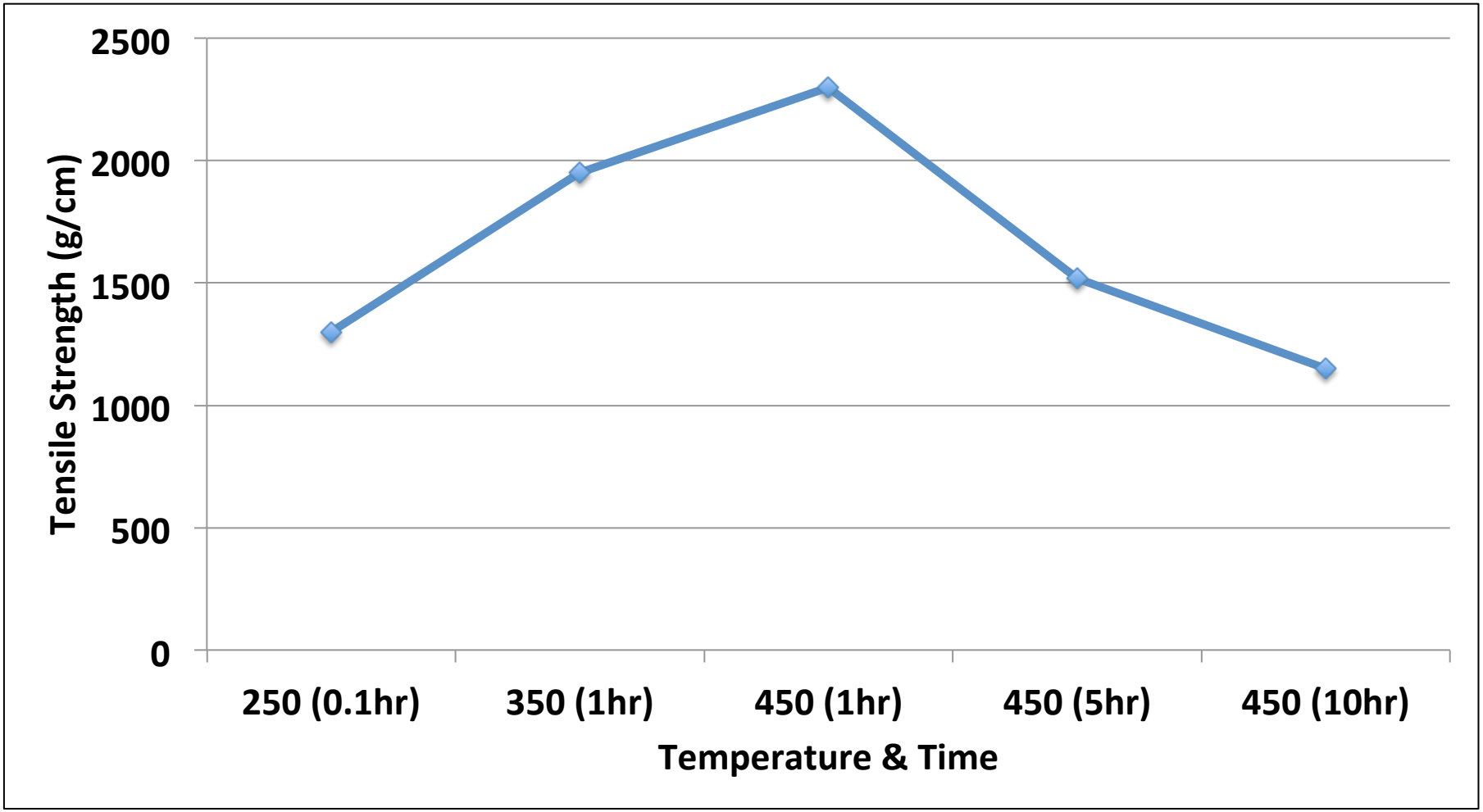
Transparency Loss With <u>ALL</u> samples

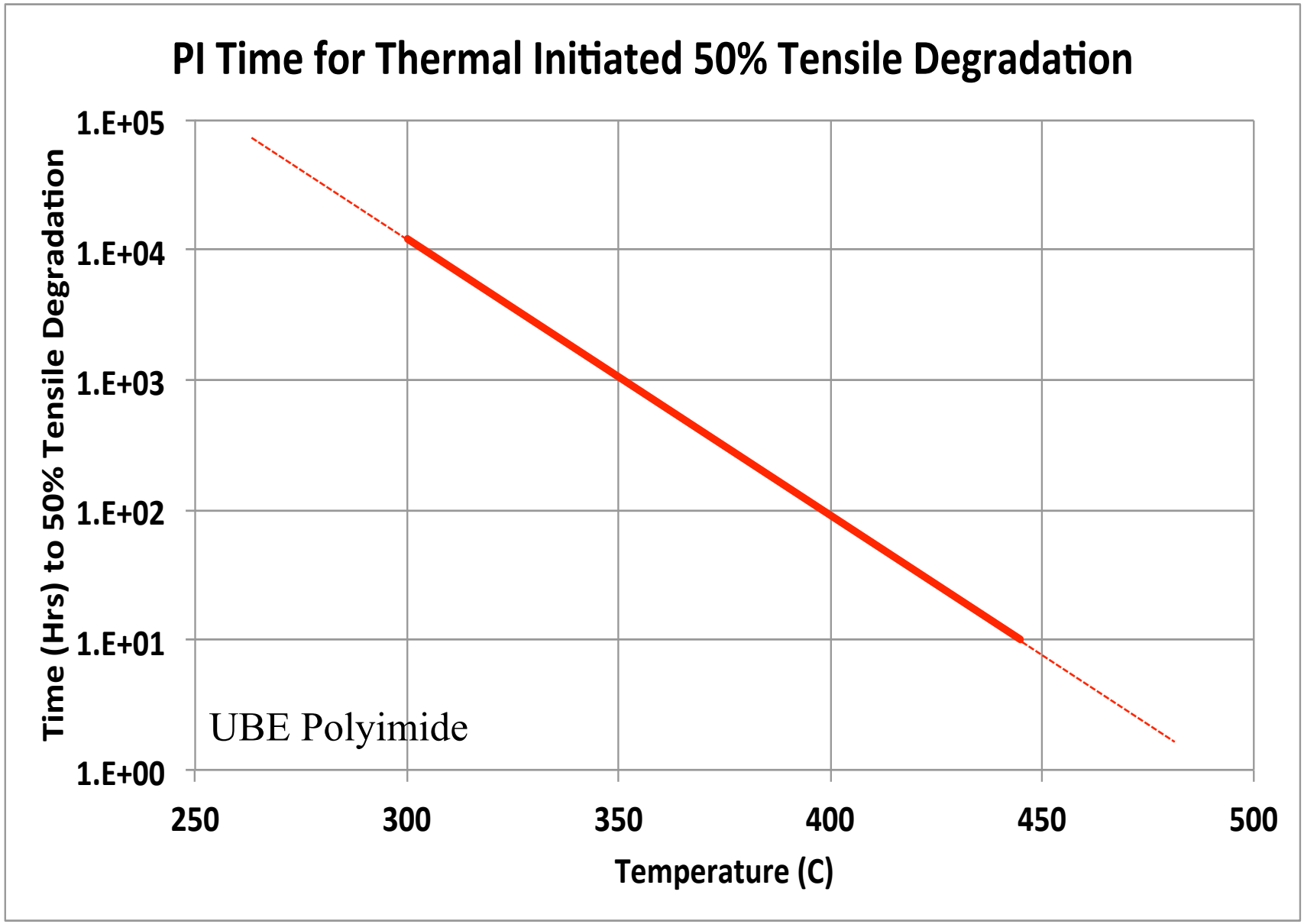


Typical PI Transparency Thermal Trend



PI Tensile Loss vs Thermal



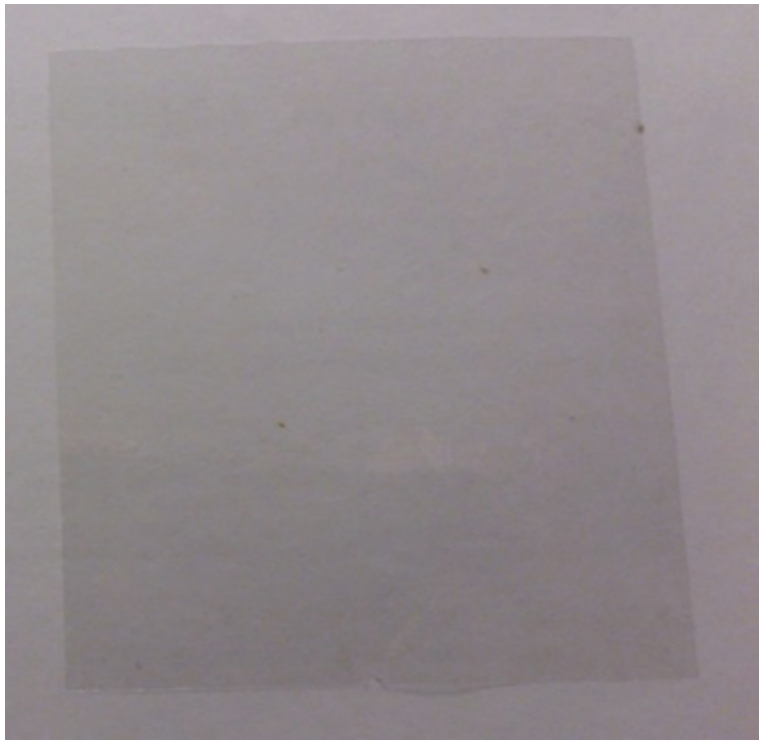

PI Time for Thermal Initiated 50% Tensile Degradation
Time (Hrs) to 50% Tensile Degradation
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
250
300
350
400
450
500
Temperature (C)
UBE Polyimide

Another Direction- Silicone Polymer

- High thermal resistance up to 600°C
- Flexible silicone polymer available to produce film
- Silicone is transparent at high temperature, with %T >95% at 500°C
- High tensile strength could be achieved by fillers add-in

Silicone film at 400°C

- Silicone can be made into flexible film and can be exposed to high temperature

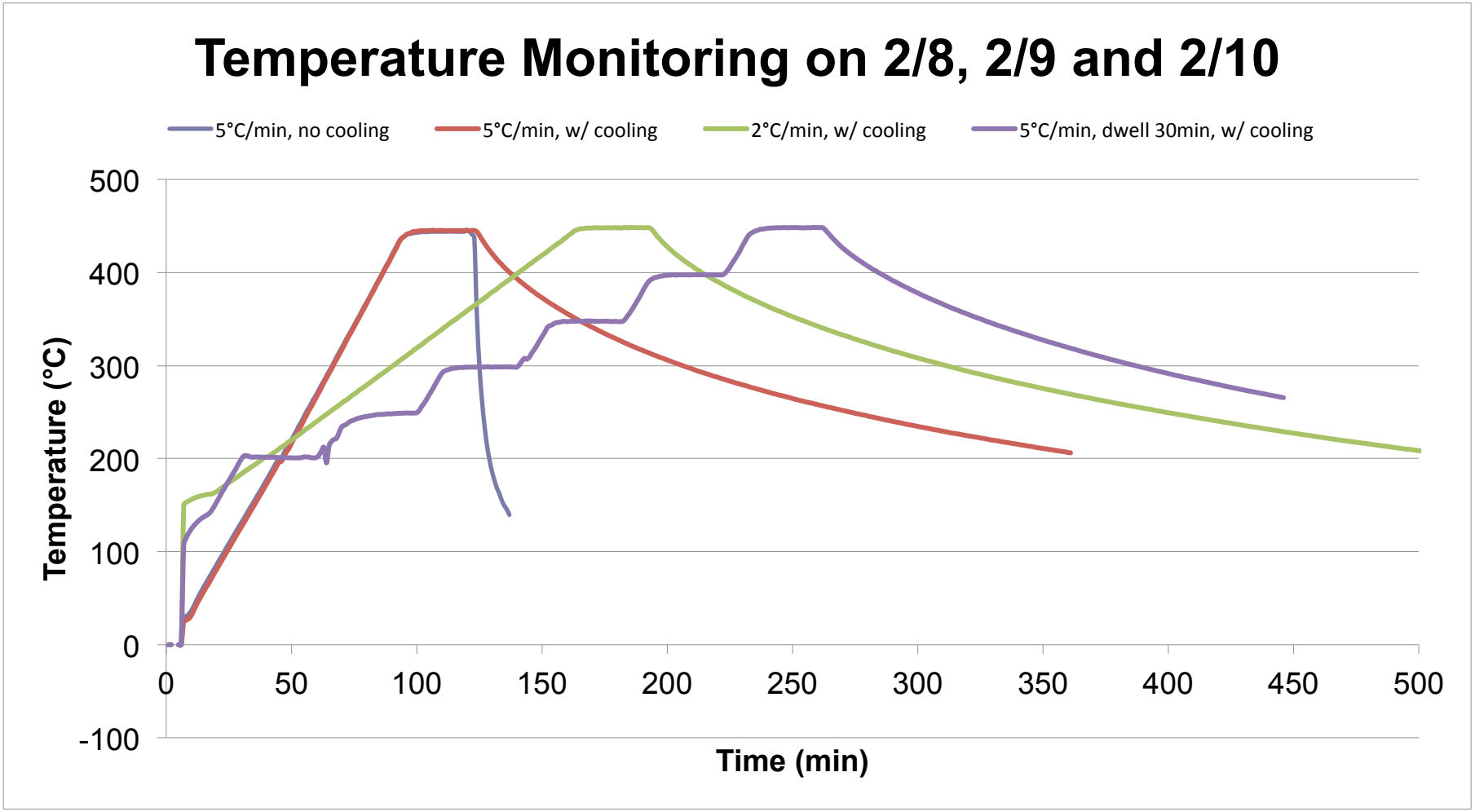


Thermal Exposure to 450°C

- This experiment is to explore the curing temperature of silicone
- Cooling reduce thermal shock of the coating creating a smooth surface

	Ramp rate	Cooling?	Total time in furnace
1	5C/min, dwelling at 50C interval	Yes	7.5hr
2	2C/min	Yes	7.5hr
3	5C/min	Yes	6hr
4	5C/min	No	2.5hr

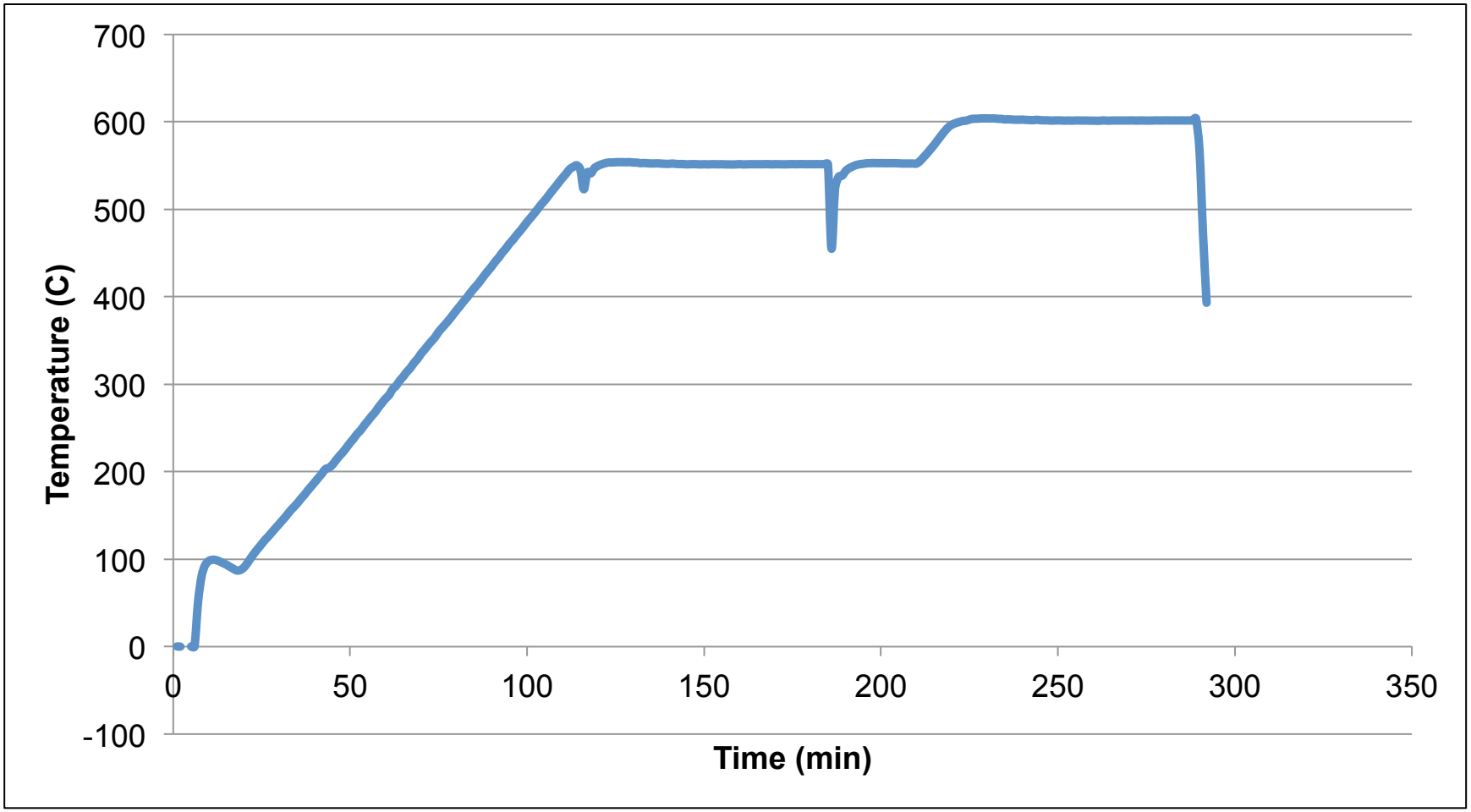
Different Thermal Exposure to 450C



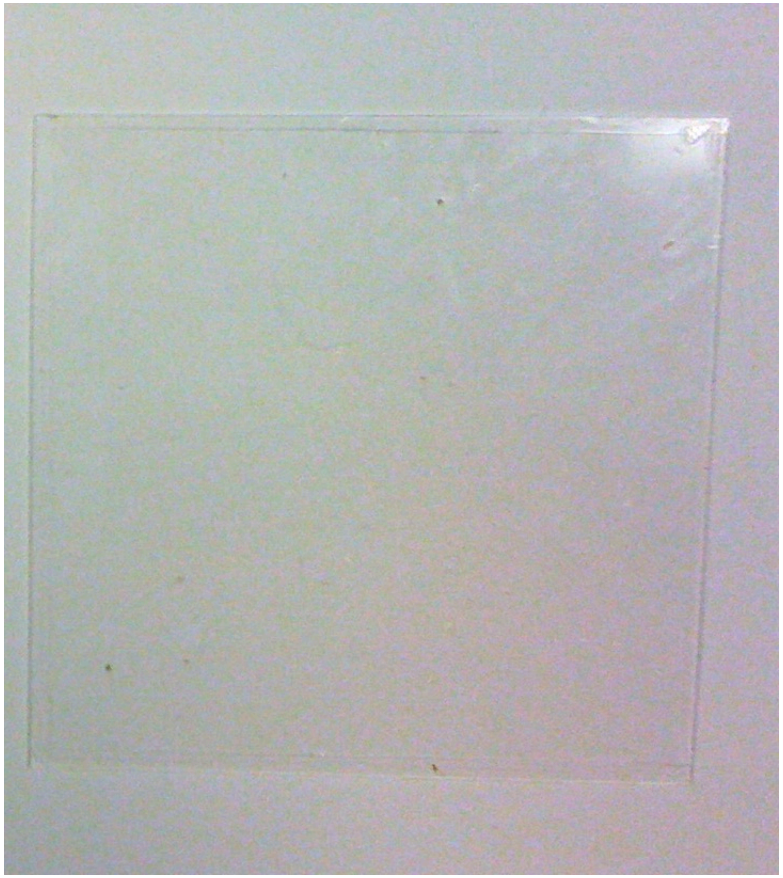
Different Thermal Exposure to 450C

- Decreasing the ramp rate is not helpful
- Silicone coating maintains clarity and smoothness after thermal shock at 450C
- A shorter baking time in the furnace (including cooling) is recommended

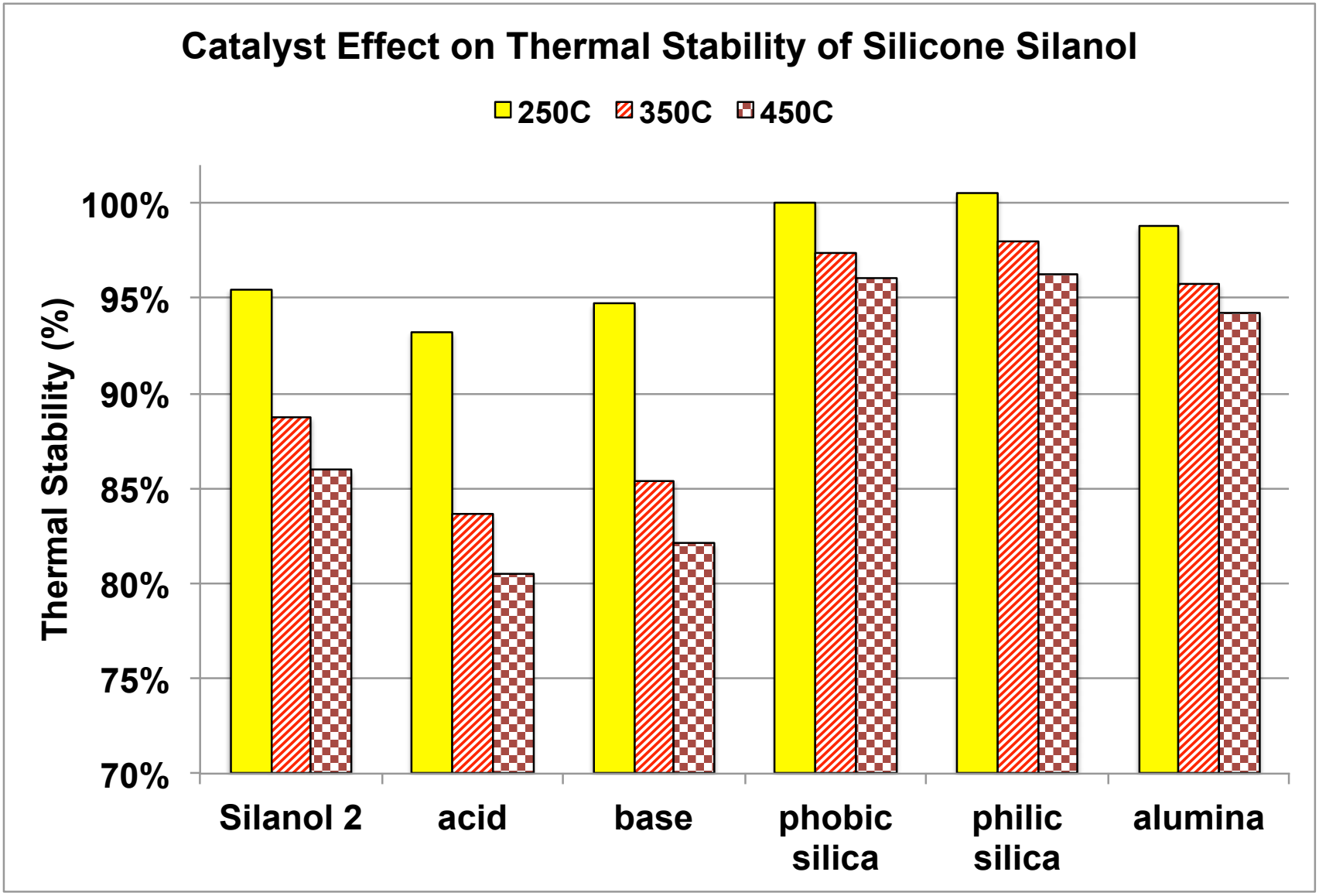
Coating/Film Exposed to 600C



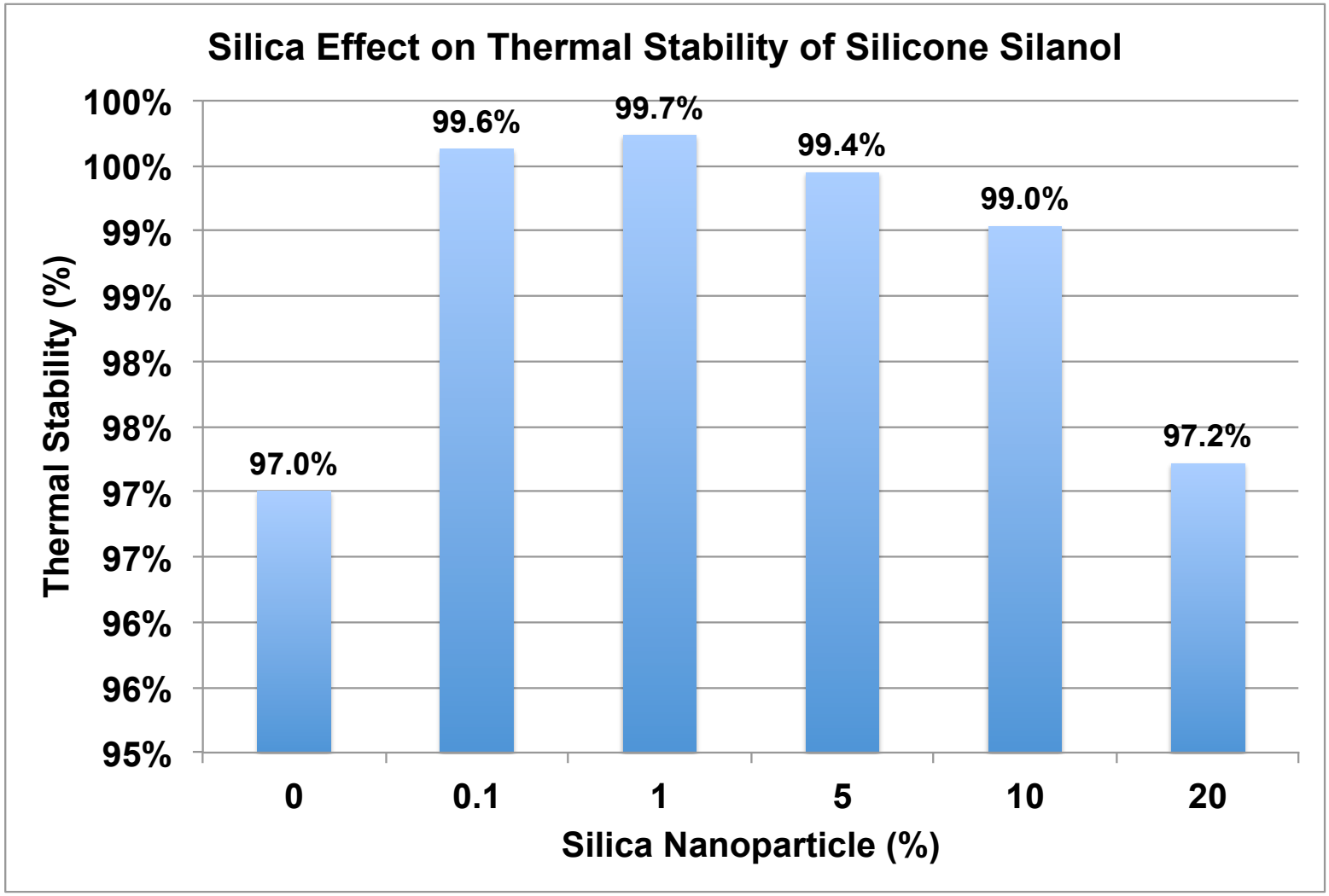
Coating Exposed to 600C



- ~5microns on glass
- Without primer


Catalyst Effect on Thermal Stability of Silicone Silanol
250C
350C
450C
Thermal Stability (%)
100%
95%
90%
85%
80%
75%
70%
Silanol 2
acid
base
phobic silica
philic silica
alumina

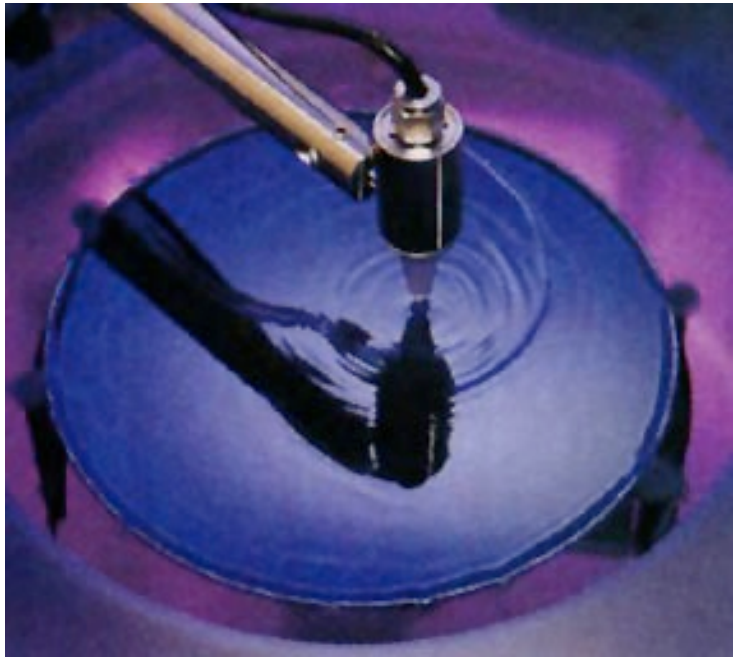
Silicone 400C Thermal Resistance



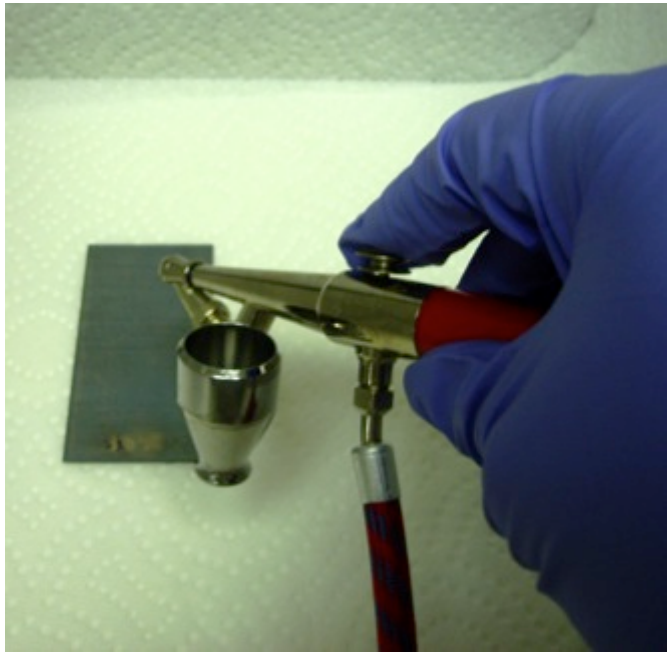
3 Design & Approach

- Thermal resistant coating is applied to glass
- Primer may be used for adhesion and release
- Cured coating may be processed to a film
- Film can be removed by peeling operation

Coating Application Options

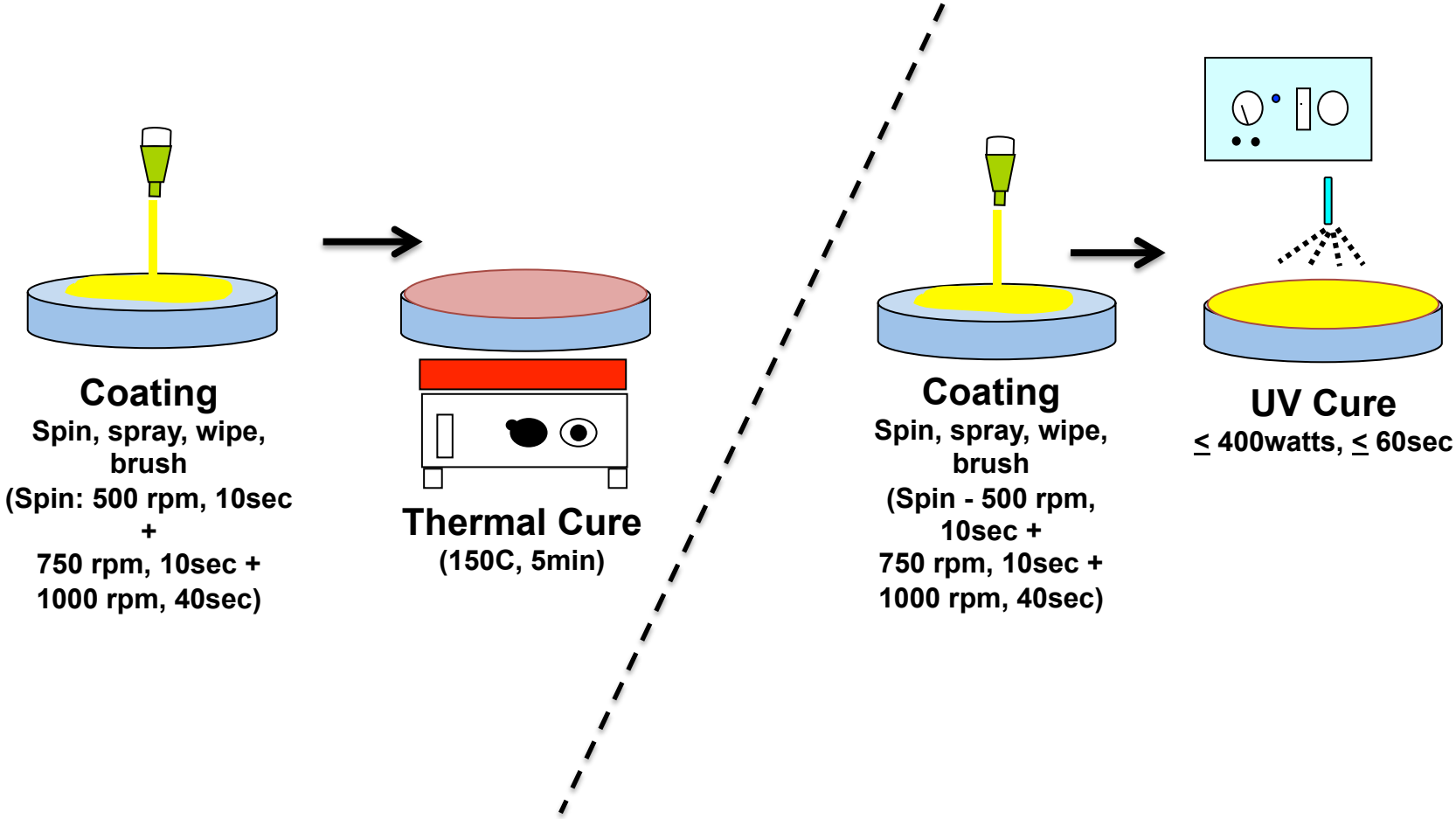


Spin-Coating



Spray-Coating

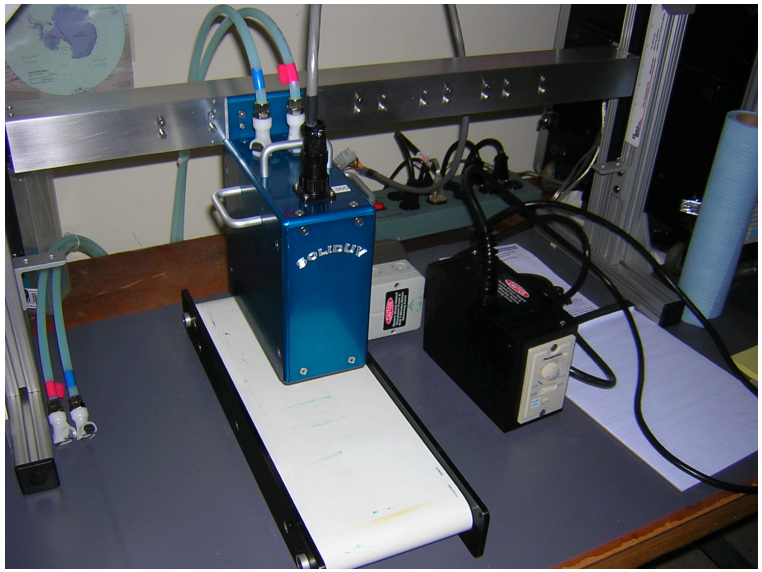
Evaporative vs UV



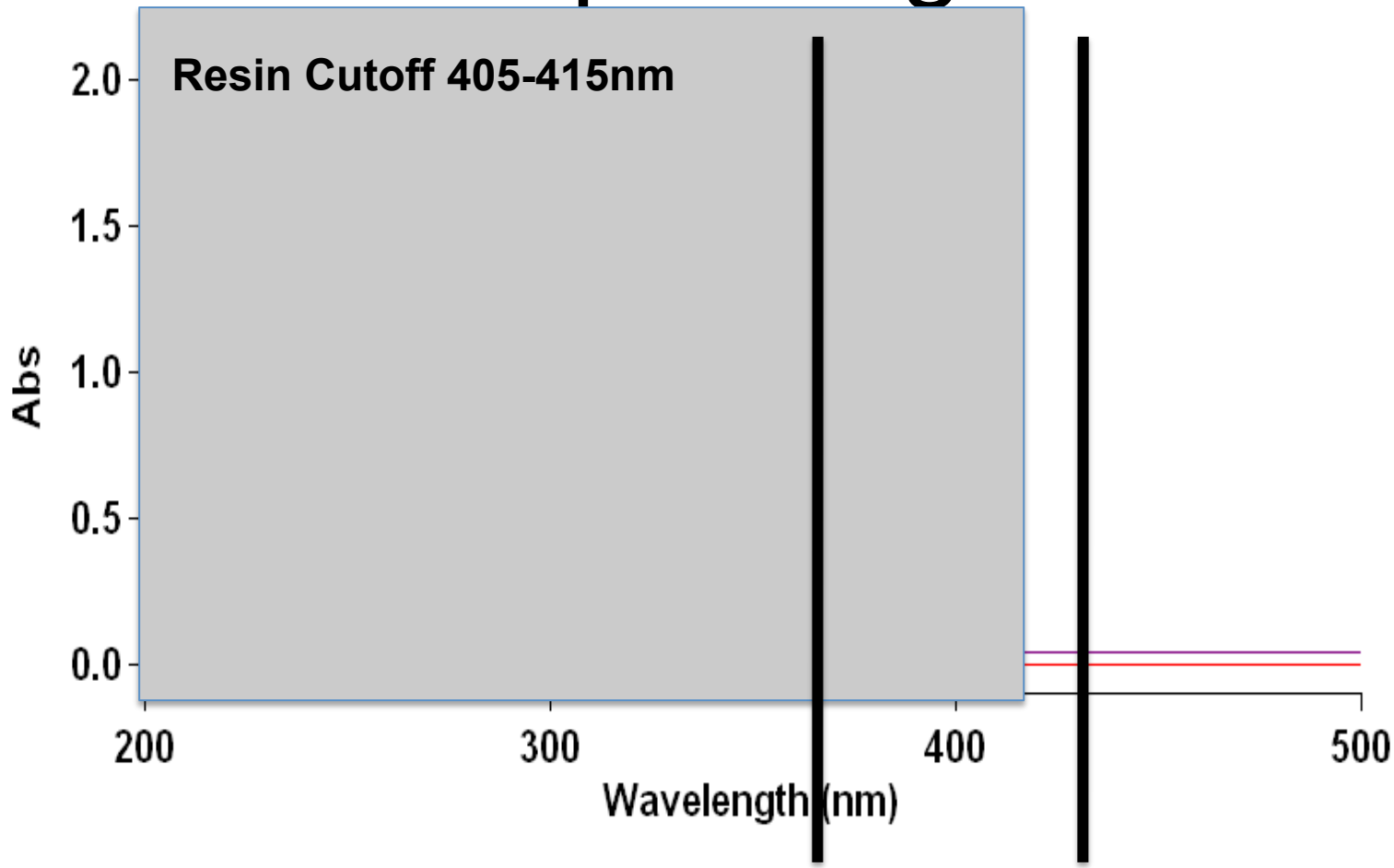
UV Equipment

Conveyor – Hg Lamp

Stationary - LED



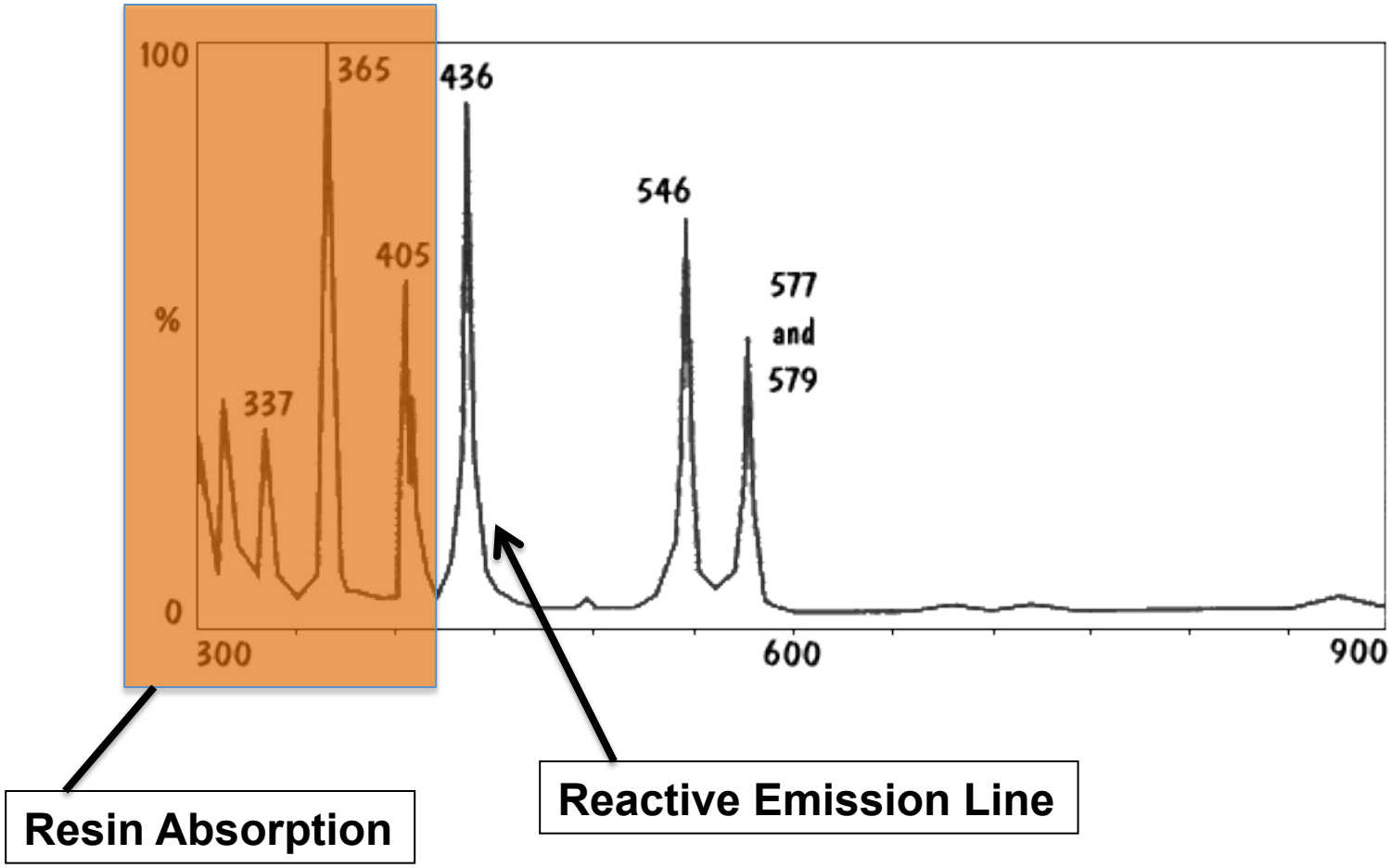
Define UV Operating Window



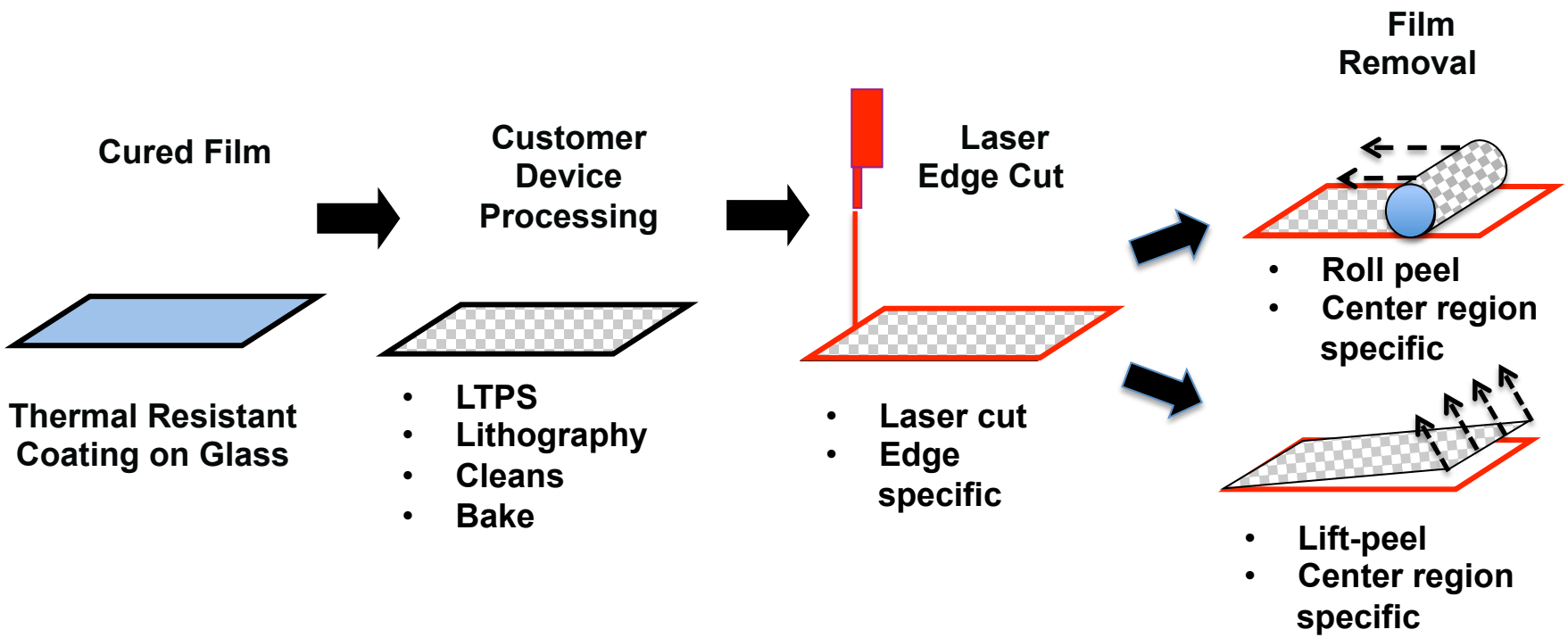
I-line 365nm

G-line 436nm

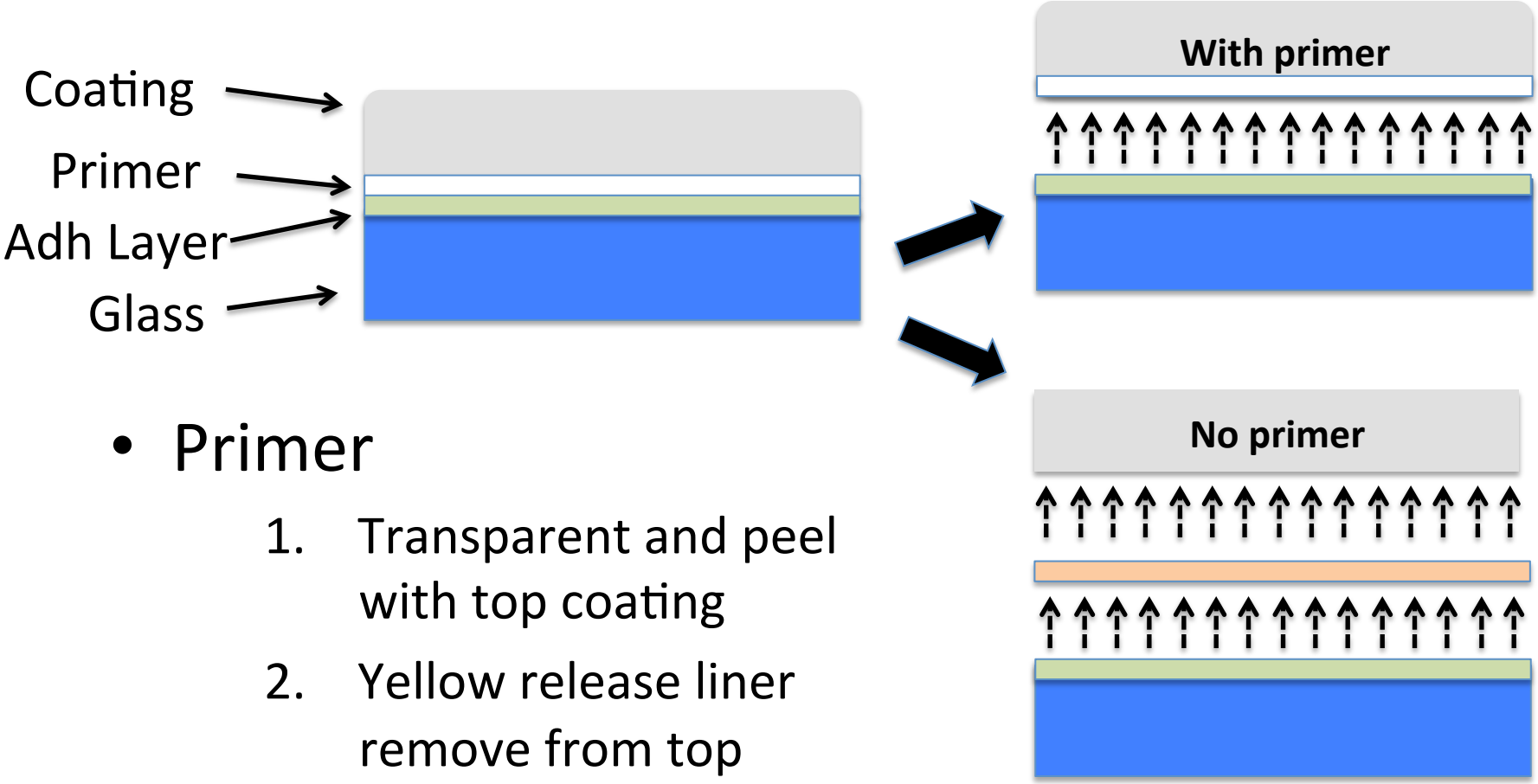
Identify Available Reactive Lines



Coating Processed to a Film



Development – Primer



- Primer
  1. Transparent and peel with top coating
  2. Yellow release liner remove from top coating

Limited Adhesion

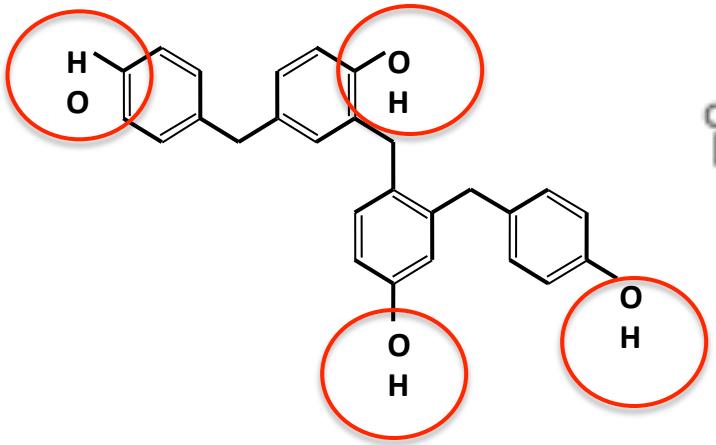
- Large MW molecules with limited functionality for surface chemical bonding
- Some are highly permeable to moisture (PI); limited barrier quality exists
- As moisture passes, changes occur in morphology and stress, causing adhesion to fail
- Improved coating adhesion is achieved by using primers

Desired Adhesion Chemistries

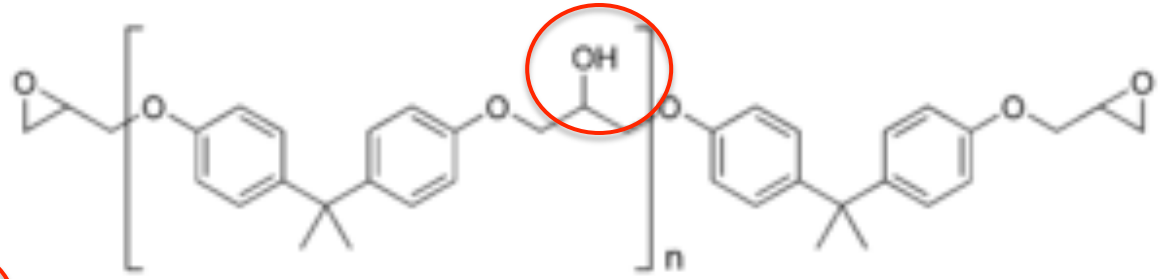
Material	OH functionality	6-member ring	Crosslink?
PBI	No	Yes	No
PVB	Yes	Yes	Yes
Epoxy	Yes	Yes	Yes
Novolac	Yes	Yes	Yes

- OH functionality: improve adhesion to hydrophilic surfaces.
- 6-member ring: entangle with PBI molecule.
- Crosslink: “lock” system in place during cure process.

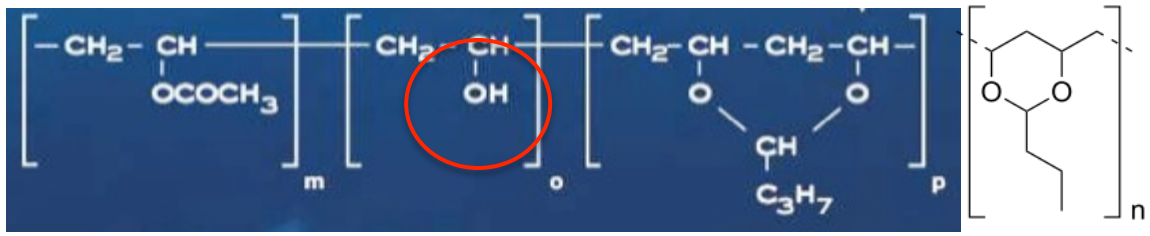
Primer Chemistries for Adhesion



Novolac



Epoxy



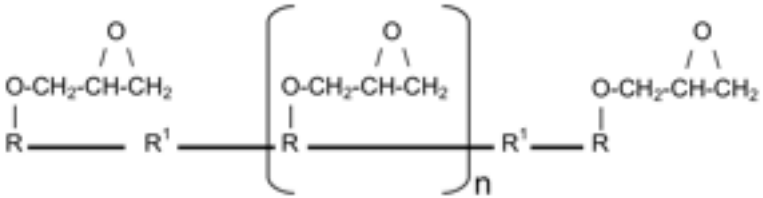
Polyvinyl butyral

Primer Coating & Crosslinking Model

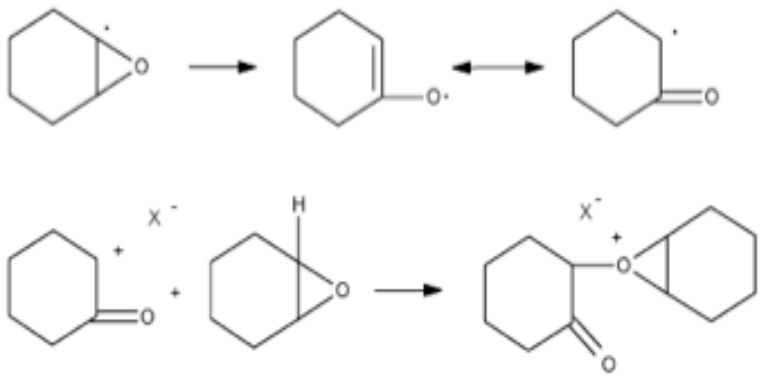
Primer Applied
Spin, dip, brush, wipe

Soft Bake, 100-250C
≤ 10min

Epoxy Primer



Thermal/Alkali Catalyzed Cross-linking



Curing Process

Primer

- Apply primer
- Bake as follows:
  - 100C ≤ 10min
  - 250C ≤ 10min

Engineering Coating

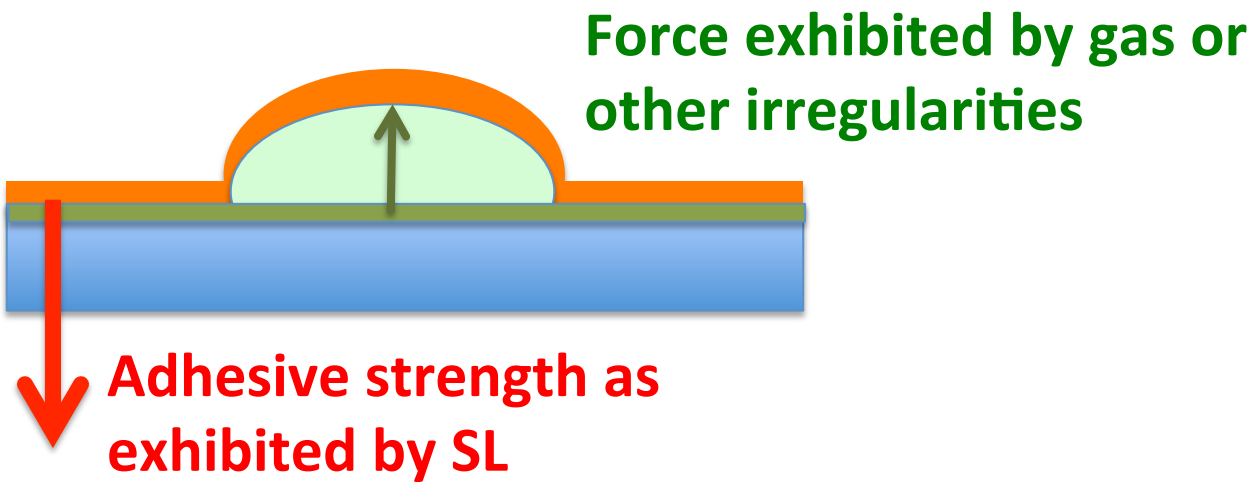
- Apply Coating
- Bake as follows:
  - 100C ≤ 10min
  - 250C ≤ 10min
  - 380C ≤ 10min

Thermal Induced Irregularities

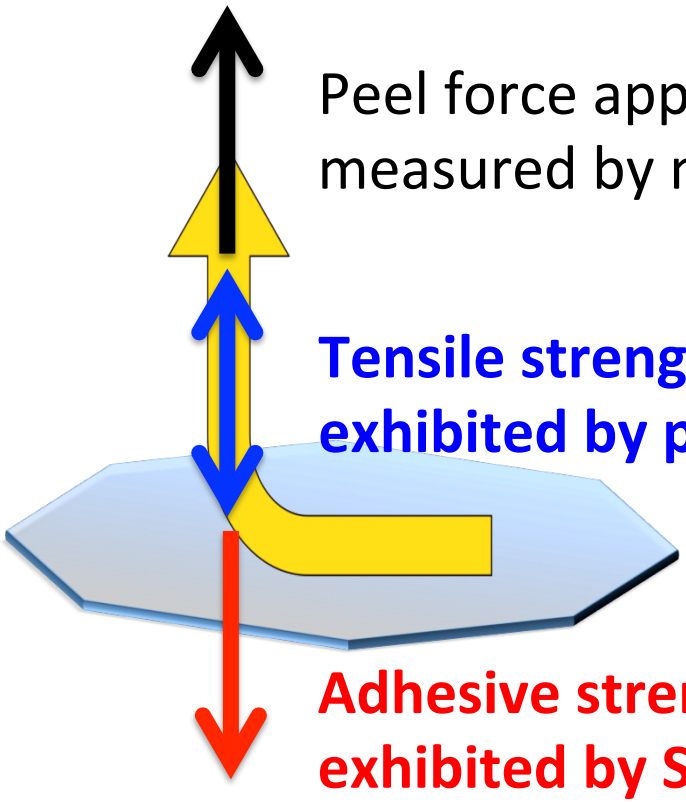
- Particles, dust, etc.
- Moisture (post cure SL rxn)
- Polymer degradation (PI & SL)
- Process chemical impact (IPA, DIW, acids/ bases, etc.)

Bubble Model

Bubble forms when force of irregularity > adhesive



Bond & Peel Model



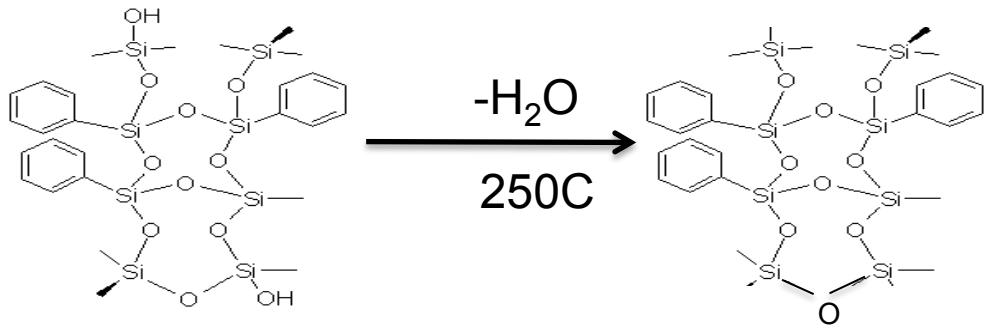
Peel force applied by and measured by meter

Tensile strength as exhibited by polymer

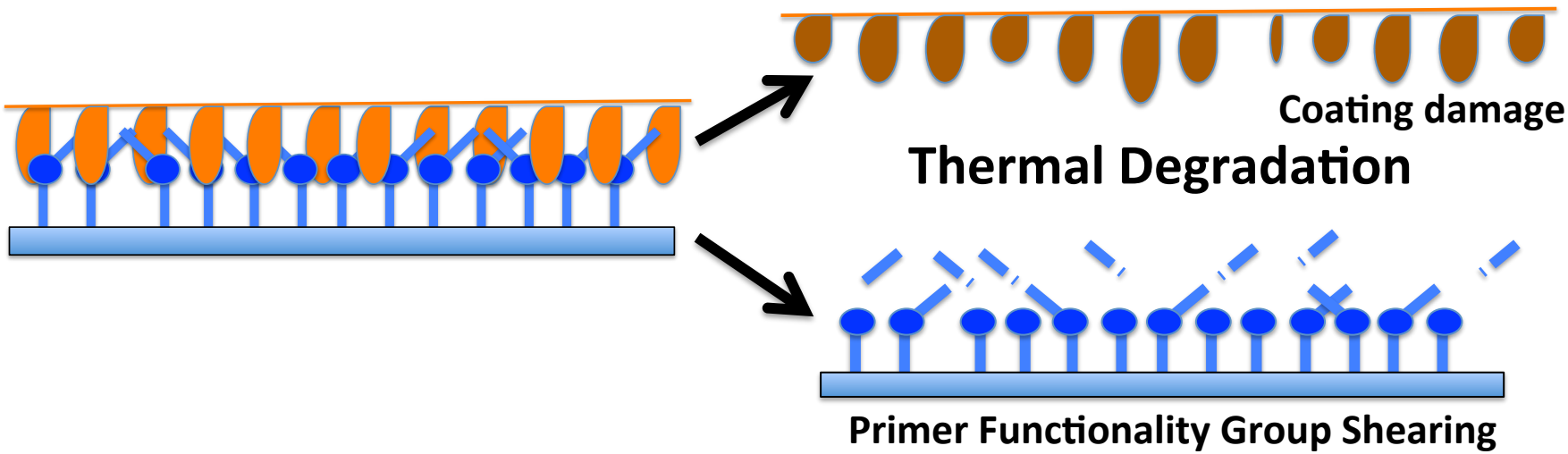
Adhesive strength as exhibited by SL

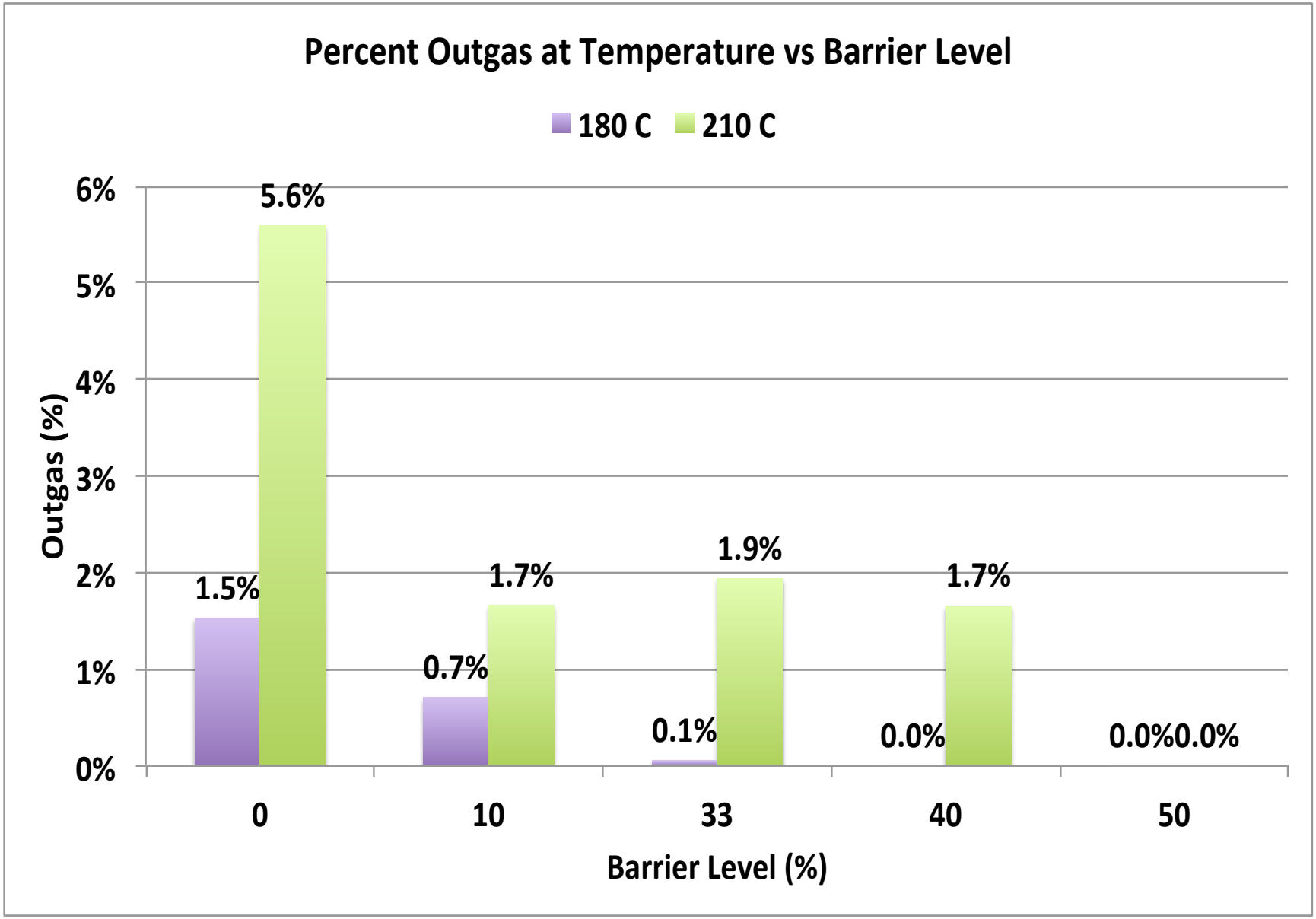
Model of thin substrate peeling with adhesive minimizing bubble formation

Thermal Induced Irregularities



Silicone Cure Moisture Generation




Percent Outgas at Temperature vs Barrier Level
180 C
210 C
6%
5%
4%
3%
2%
1%
0%
Outgas (%)
5.6%
1.5%
1.7%
0.7%
1.9%
0.1%
1.7%
0.0%
0.0%0.0%
0
10
33
40
50
Barrier Level (%)

4 Summary

- Thermal resistant polymers exist for microelectronic applications
- Properties include thermal stability, low outgas, application accepted by fabs
- Products at 400C, up to 600C are needed
- Peelable products are needed for display
- Daetec has developed >400C silicone based products for display and semiconductor

Contact for More Information

- DAETEC provides development, consulting, and technical training/support to solve manufacturing problems and introduce new options of doing business.
- Diversified Applications Engineering Technologies (DAETEC)

  Camarillo, CA (USA) (805) 484-5546

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