Properties and Characteristics of HD4100 PSPI Cured at 250°C with Microwaves

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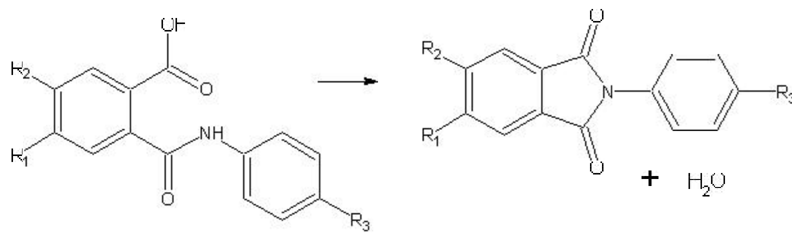
Outline

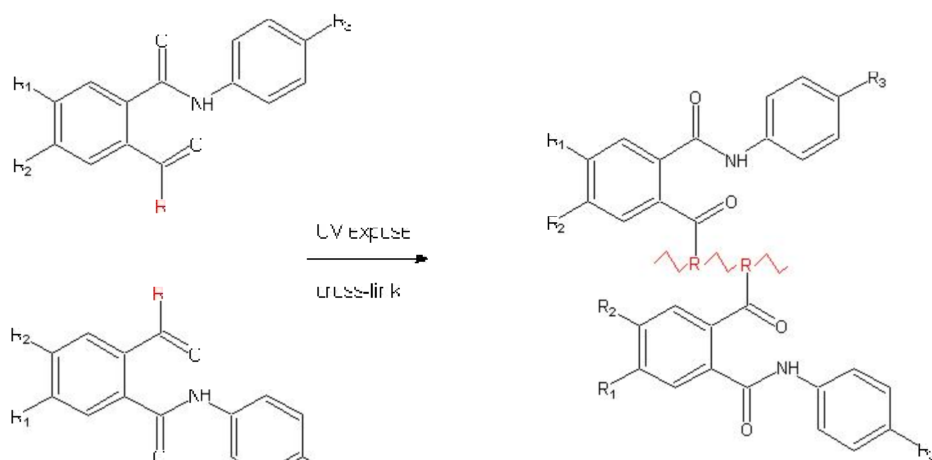
- Background/Chemistry of PSPI curing
- Definitions of “cure” and chemical/thermal stability
- Mechanism of Variable Frequency Microwave curing
- Effects of cure variables on HD4100 film properties
- Optional processes to match film property needs

Chemistry of PSPI Curing

- Imidization reaction is a ring closure
  - Product is a very thermally and chemically stable thermoplastic



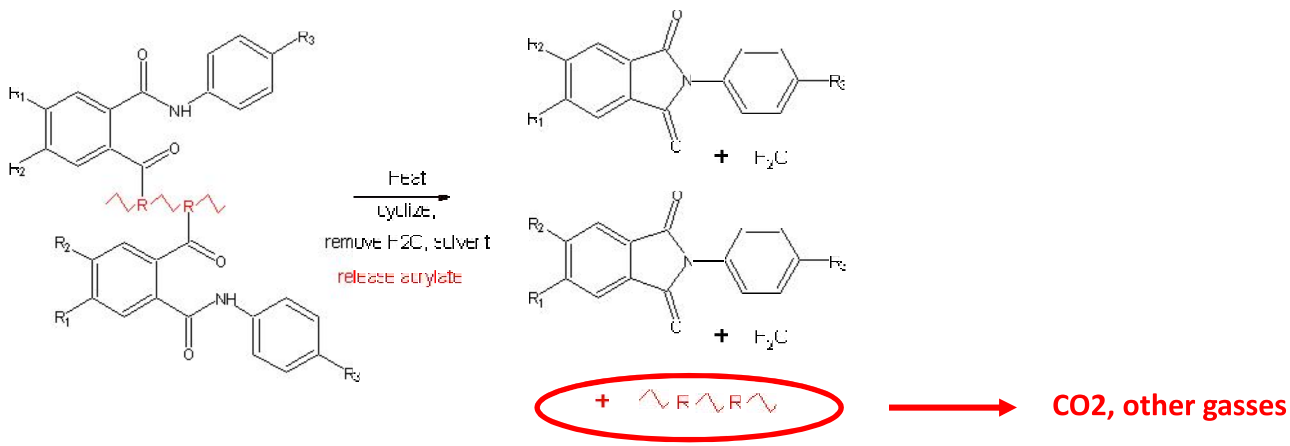
- Photosensitive precursors crosslink on light exposure
  - Crosslinked intermediate is not soluble in developer ("negative acting")



R = acrylate

Chemistry Continued . . .

- Photosensitive precursor releases residue with ring closure
  - Acrylate residue is thermally decomposed to CO_2 and other gasses



  - Removal of residue increases Tg and film shrinkage in out-of-plane axis
- TWO parts of “cure”:
  - imidization : necessary for chemical stability
  - acrylate removal : necessary for high Tg and thermal stability

Microwaves are Low Heat Choice

- **Electromagnetic Spectrum**

Gamma Rays	**Nuclei**
X-Ray	**Inner Electrons**
UV	**Covalent Bond Disruption**
Visible	
IR	**Molecular Vibration**
Microwaves	**Molecular Rotation**
RF	**Charge Flow**

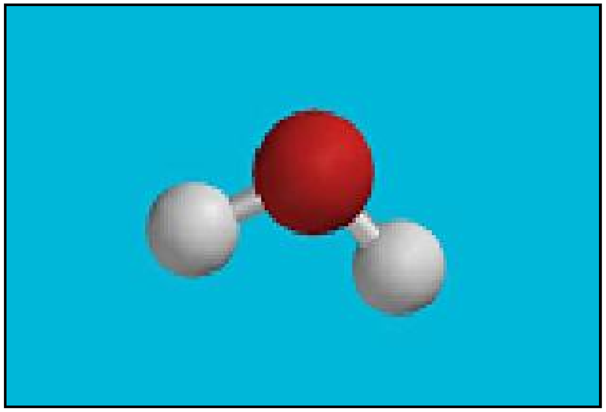
↑ Ionizing Radiation

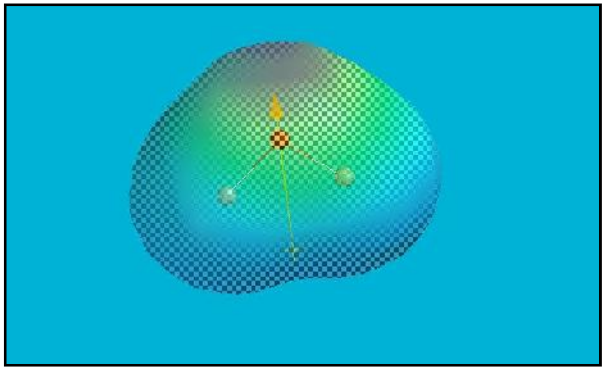
↓ Non-Ionizing Radiation

- **Microwaves stimulate electrons in dipoles causing local rotation**
  - **No polarizability, no heating**

Microwaves Cause Dipole Rotation

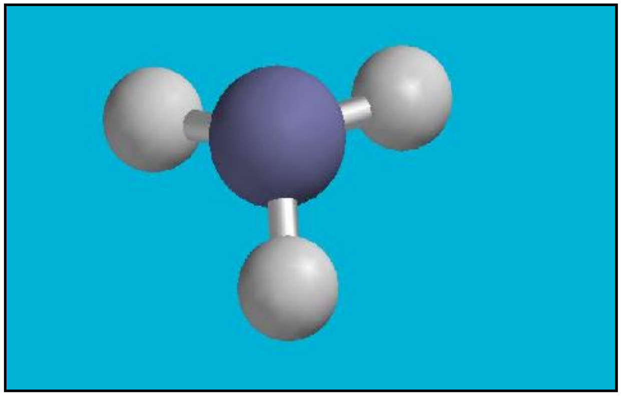
Water (H_2O)

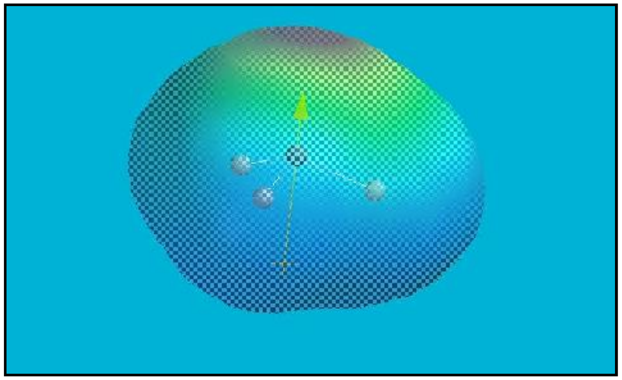




Dipole Moment = 1.861Debye

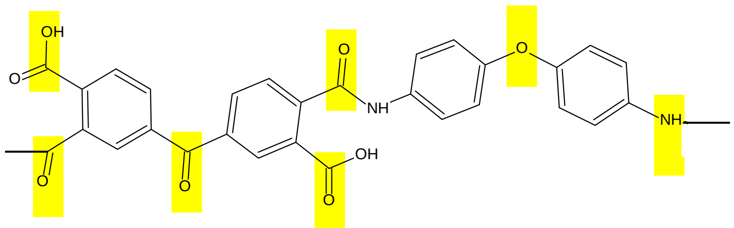
Ammonia (NH_3)



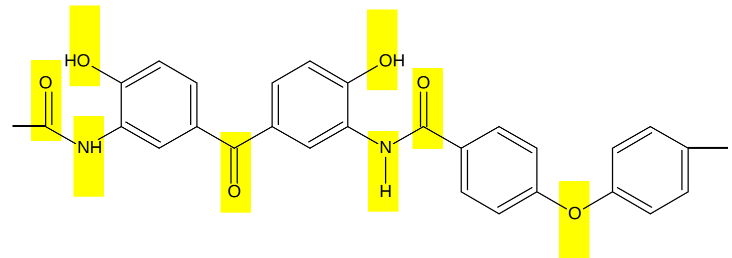


Dipole Moment = 1.5 Debye

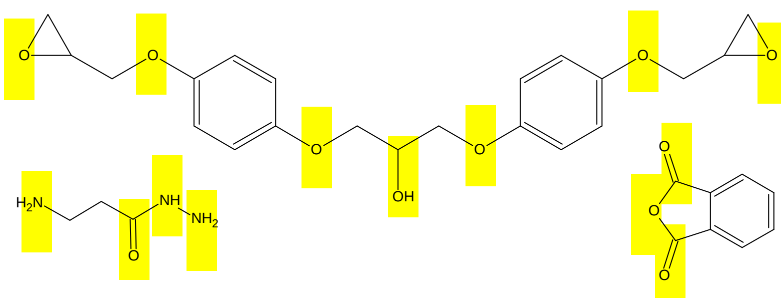
Dipoles in Polymer Resins



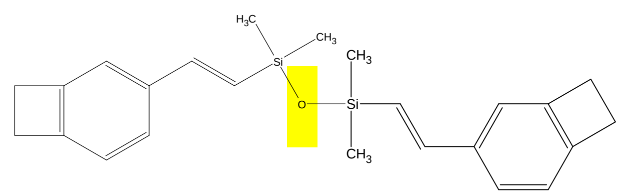
PI



PBO



Epoxies

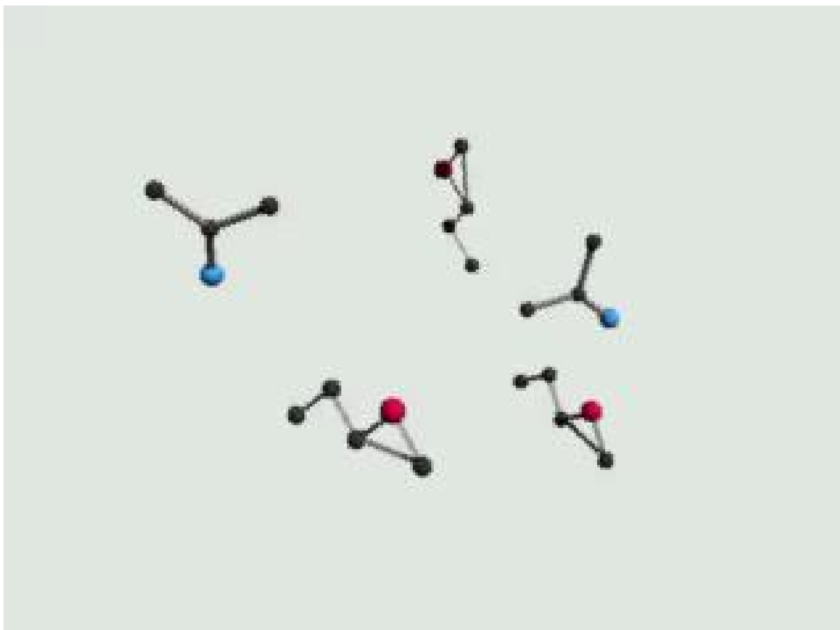


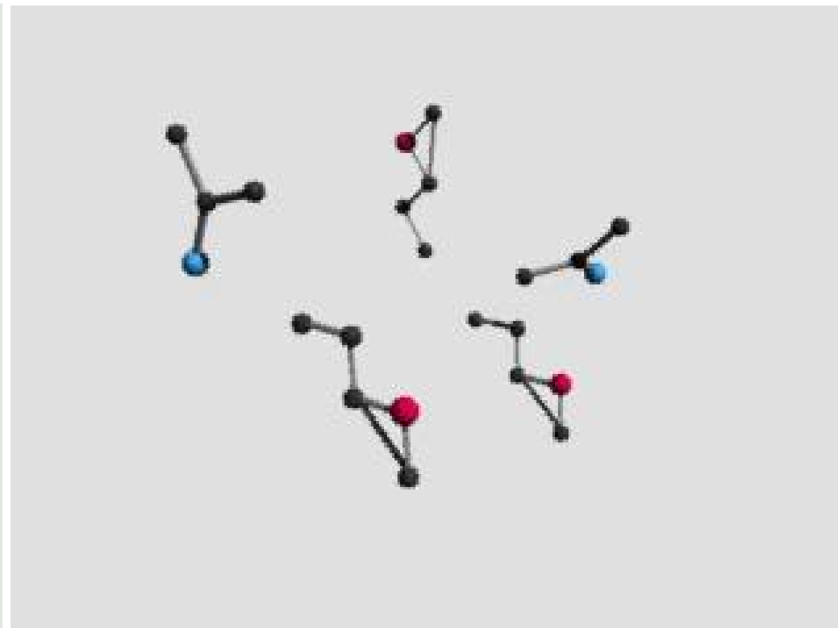
BCB

- Most polymer resins are very responsive to microwaves

Different Heat Mechanism with Microwaves

Convection **shakes** progressively   Microwave **spins** volumetrically

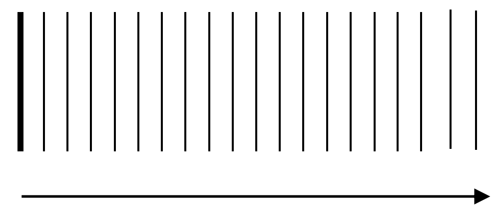


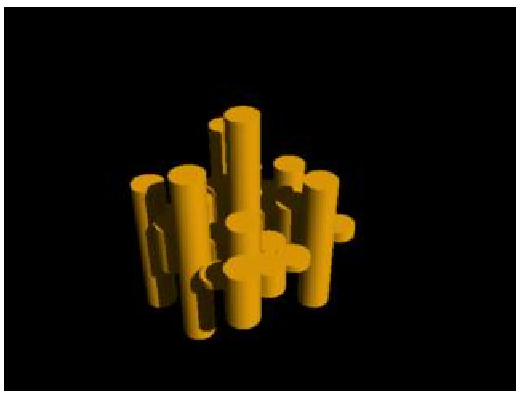


click each to animate

Variable Frequency Microwaves

- 4096 scanned frequencies in 0.1 second
- Each pulse only 25μs long

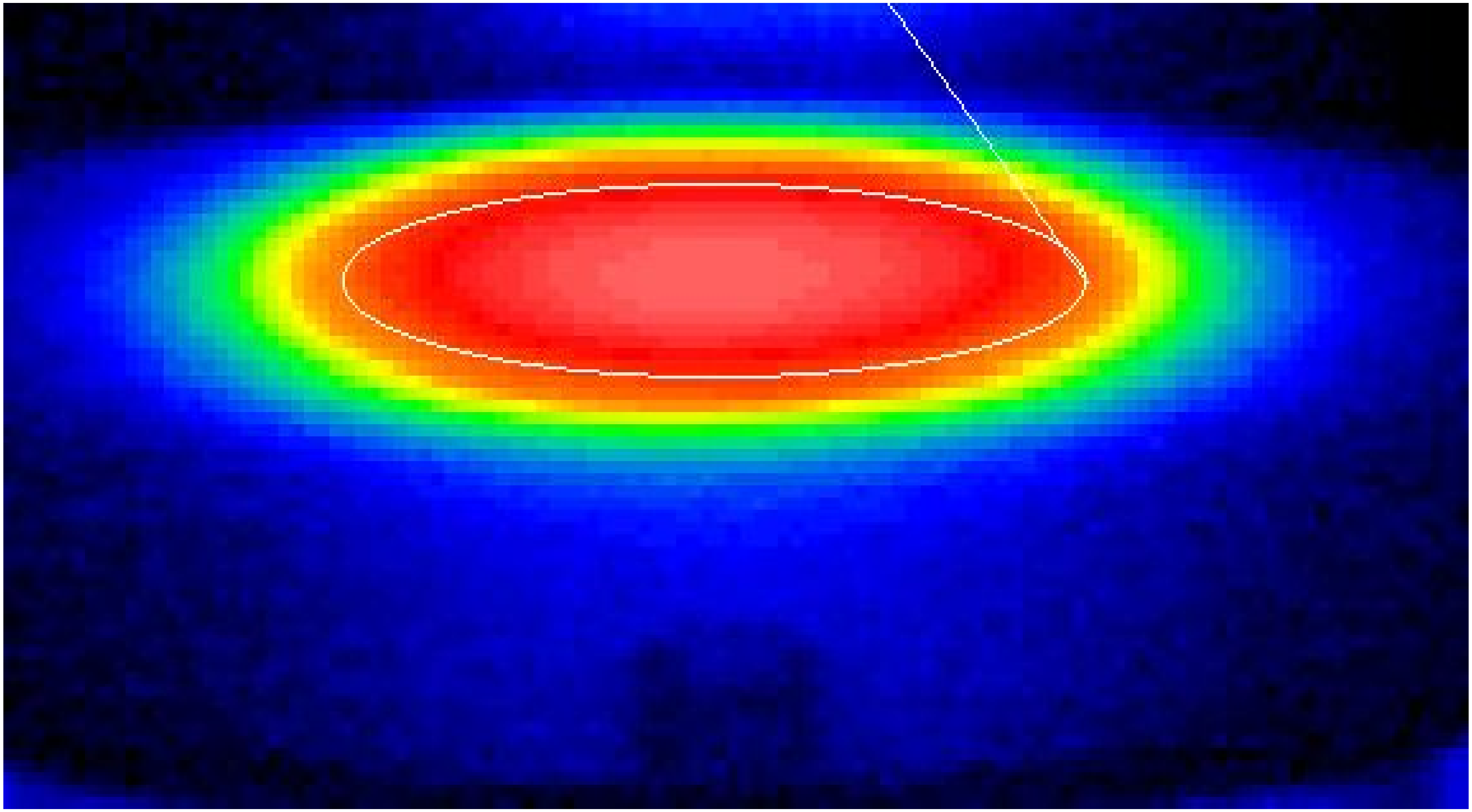




Very uniform heating

No arcing with metals

IR Thermal Image: Wafer Processing



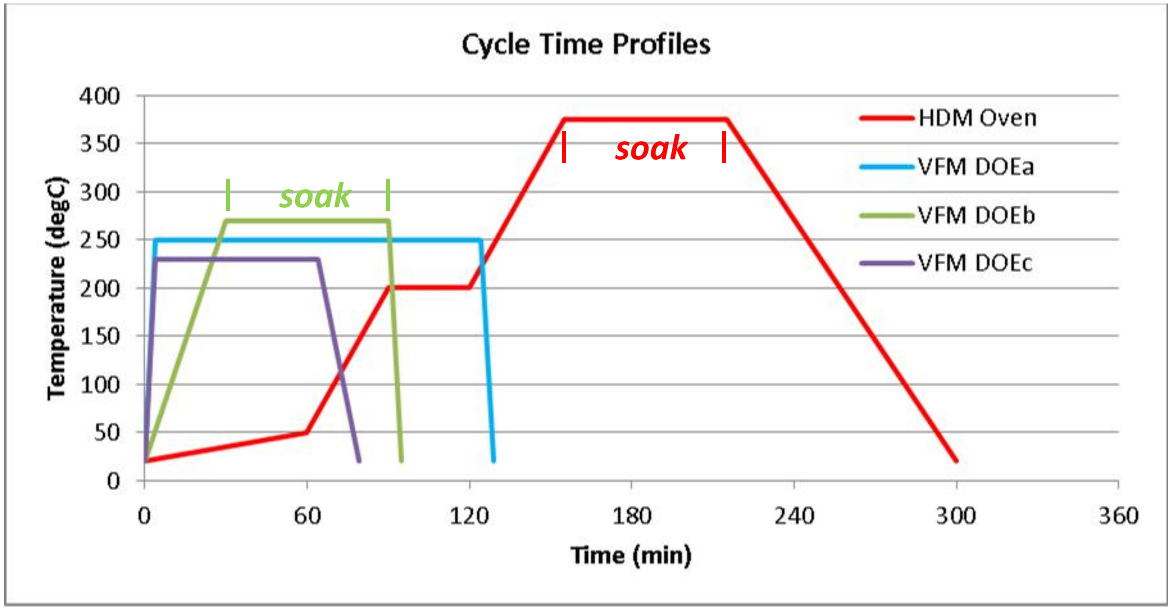
Low Temperature Cure Experimental Designs

- Variables:
  - Soak temperatures: 230°C, 250°C, 270°C
  - Time at soak: 1, 2, 3 hours
  - Ramp rate to soak: 0.2, 0.6, 1.0 °C/sec
  - Cooling ramp rate: 5 °C/min, 25°C/min
  - Atmosphere: 20, 5000, 20000 ppm O_2
- Stress DOE:
  - Sixteen wafers blanket coated with HD4100 to 5-6µm after cure
  - Measure cured film shrinkage, stress, and wafer bow
- Tensile DOE:
  - Eleven wafers with PI2611 release layer and coupon patterned HD4100 (10µm)
  - Measure modulus, break elongation, break strength, Tg, Td1%, Td5%, CTE
- Standard oven cures (reference)
  - Four wafers at 375°C and two wafers at 250°C

All wafers are 200mm diameter

“Soak Time” vs. “Cycle Time”

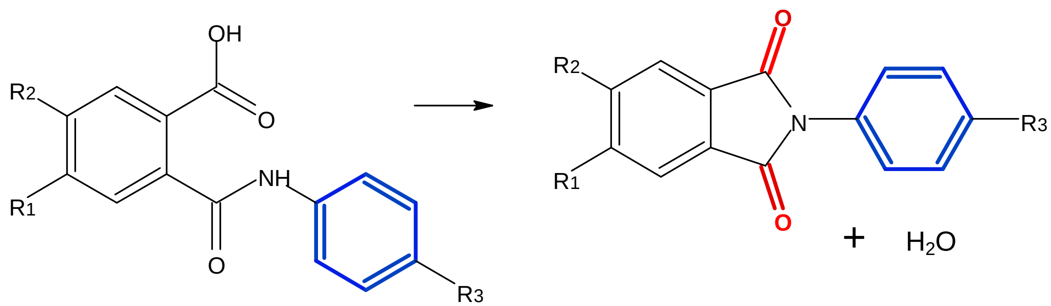
- “Cure time” is given as <u>soak</u> time, not cycle time
  - Standard industry-wide practice
- VFM only heats the sample, not the oven, fixtures, or the air

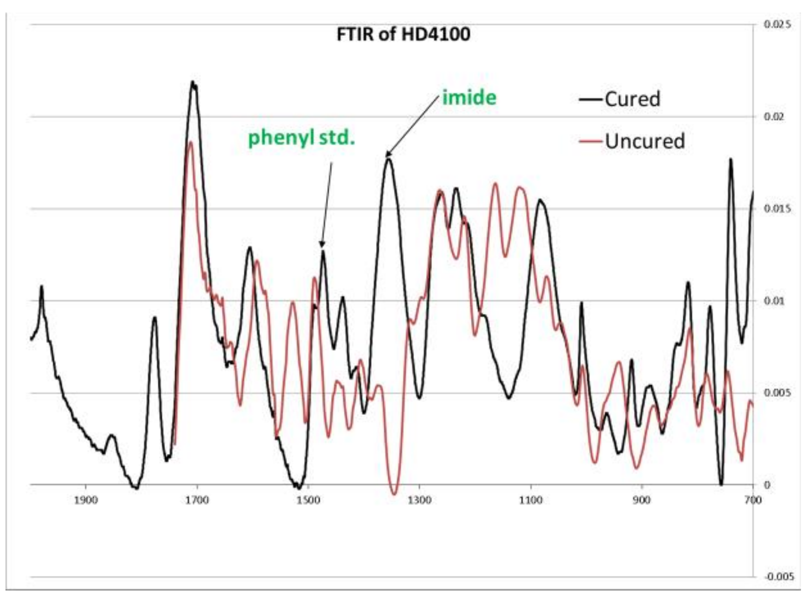


Standard oven cycle vs. example VFM cycles for HD4100

Chemical Stability from VFM Cure

- <u>Full imidization</u> at all conditions (230-270°C)
- FTIR data compares the emergence of the imide carbonyl to the reference of the un-changed phenyl ring

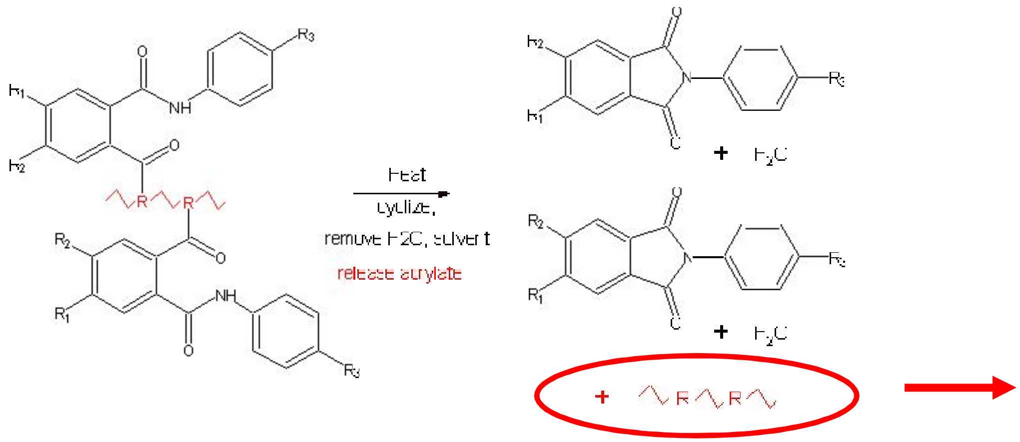




Note: resolution of imidization is not quantitative above 95%

Thermal Properties Reflect Residue Removal

- Imidization already complete; acrylate decomposition next



CO_2, other gasses

- Thermal decomposition removes the acrylates (low oxygen atmosphere)
  – Standard oven cure requires 375°C to thermally decompose acrylates*
  – VFM cure requires 350°C to thermally decompose acrylates*
  – VFM cure does not thermally decompose acrylate residues at 250°C
- Oxidation of the PI film requires > 300°C in air
  – VFM cure of PI in air at 250°C does <u>not</u> oxidize the film

.* Zussman et.al., Symposium on Polymers, 2008

Can VFM Oxidatively Decompose Residues?

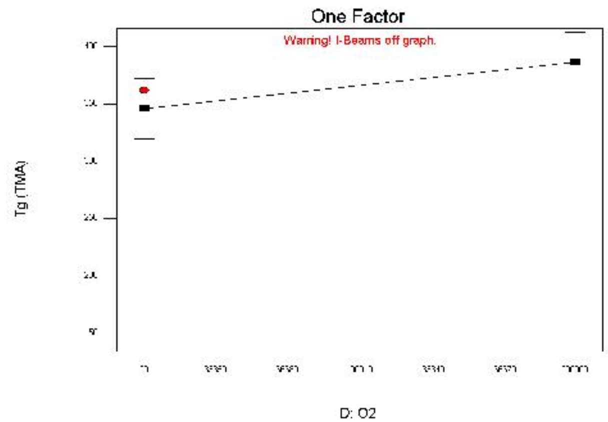
- VFM cannot decompose polymers at most temperatures
  - Microwave energy level too low to break bonds directly
  - Oxidative decomposition is a chemical reaction *
    - Crosslinks and chain scission produce oxyradicals
    - CO_2, alcohols, and other gasses are produced
- If VFM can oxidatively decompose the acrylate residues
  - Tg should increase, indicating greater thermal stability
  - Td1% and Td5% should increase, indicating lower residue levels
  - Weight loss temperature indicates first substantial outgassing
- No evidence of oxidation of polyimide film surface at 230-270°C

* Cameron and Davies, *Chem zvestia,* 26, 1972.

Thermal Stability

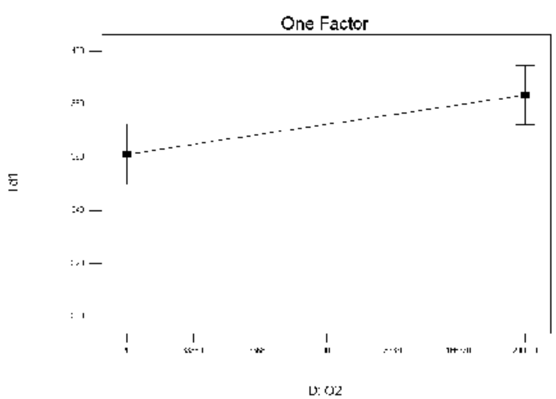
- Tg variables: temperature, time, ramp, oxygen

Tg (TMA) =
+280.54
+37.42 * A
+28.08 * B
-20.26 * C
+20.26 * D

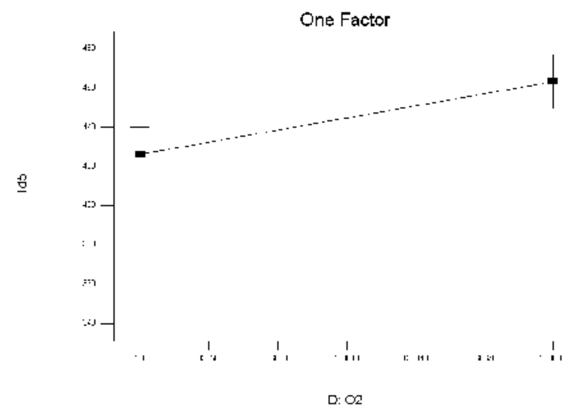


- Td1% and Td5% variables: temperature, time, oxygen

Td1 =
+345.47
+20.12 * A
+6.87 * B
+11.17 * D



Td5 =
+405.73
+29.37 * A
+9.62 * B
+18.50 * D



- Increased oxygen levels have increased acrylate residue removal

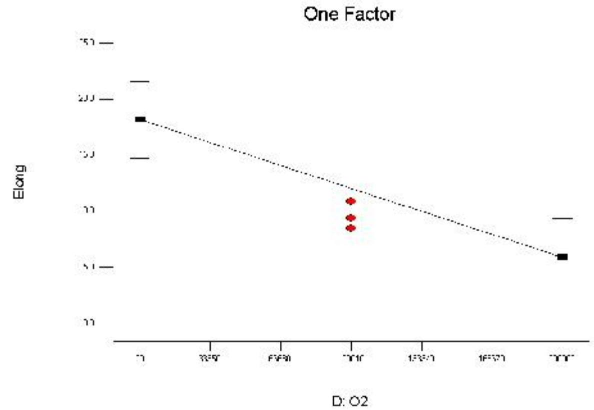
Other Tensile Properties

- Elongation variable: Oxygen only

Elong =

+12.06

-6.14 * D



- CTE variables: Temp/time interaction, ramp and oxygen

CTE-1 =

+54.32

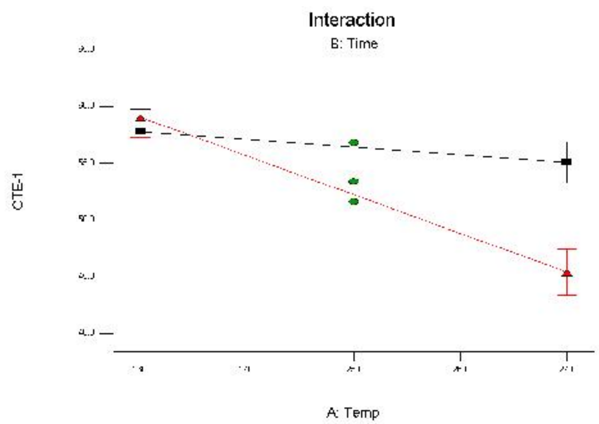
-4.08 * A

-2.09 * B

+1.73 * C

-6.11 * D

-2.74 * A * B

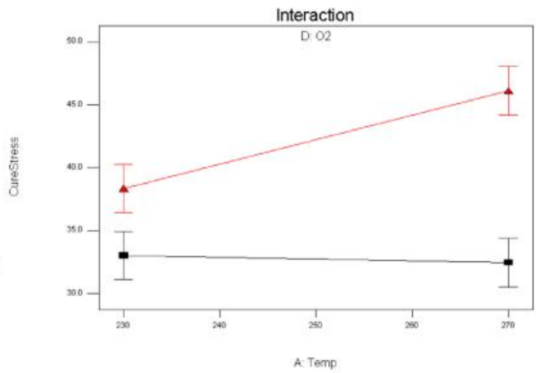


- Modulus and Strength: no significant variables

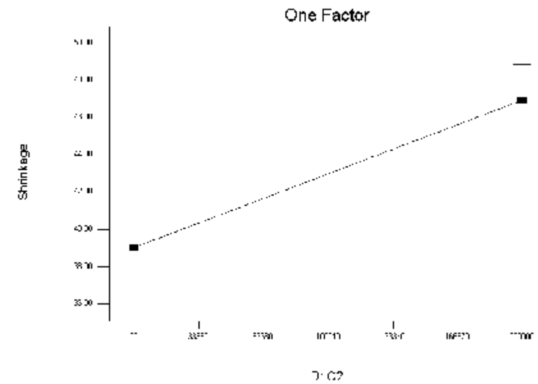
Stress and Bow

- <u>Stress and shrinkage</u>: oxygen is the biggest factor

CureStress =
+37.48
+1.80 * A
+4.74 * D
+2.08 * A * D

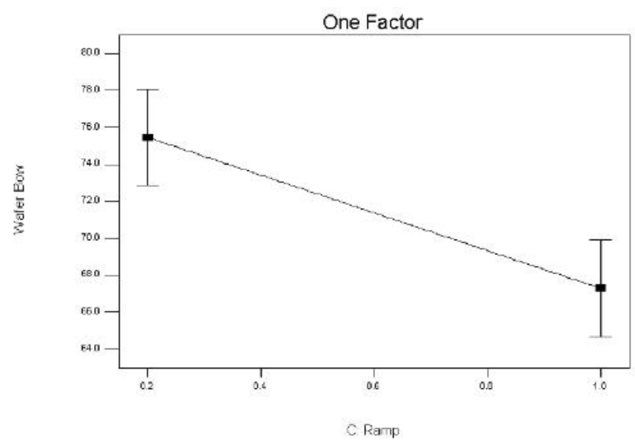


Shrinkage =
+42.98
+3.95 * D



- <u>Wafer bow variable</u>: only ramp rate!

Wafer Bow =
+71.36
-4.08 * C



- Cooling rate (ramp down): no effect on stress, shrinkage, or bow

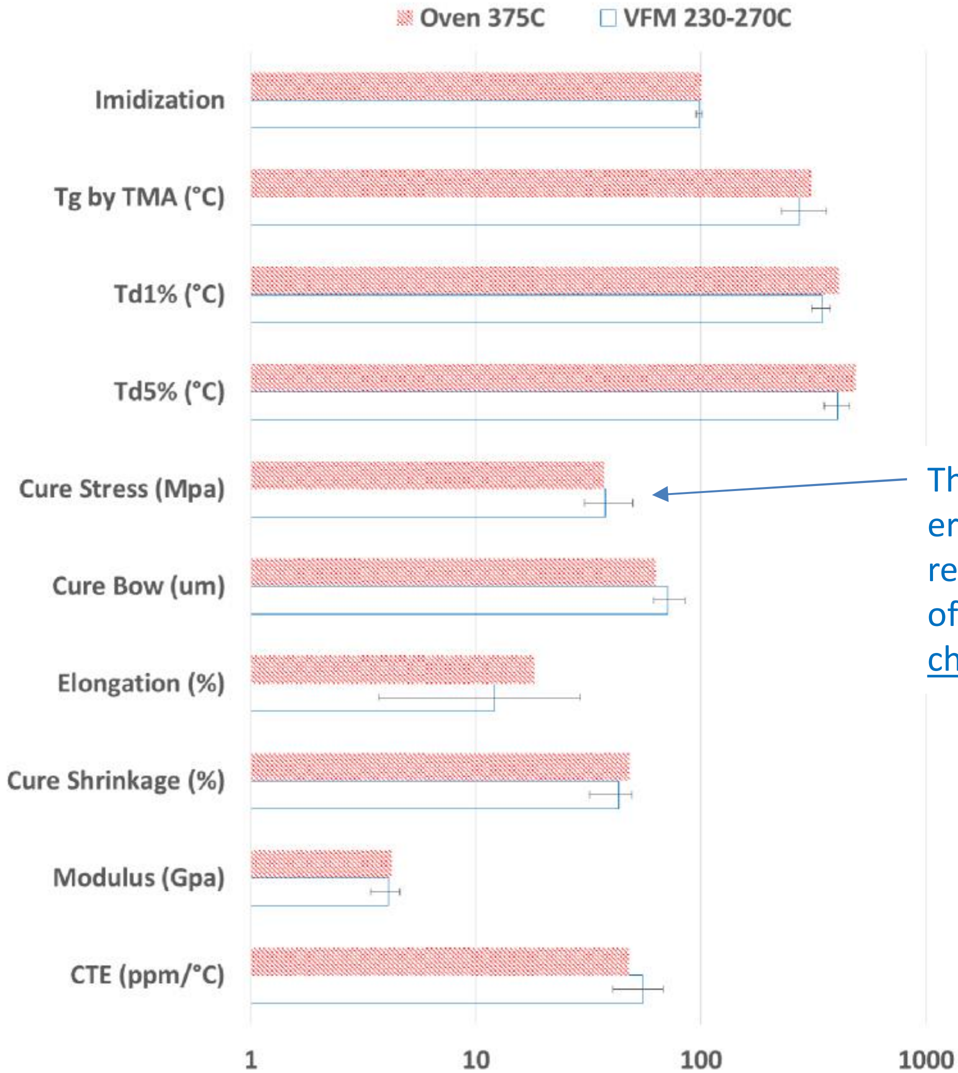
Stress and Bow Variables are Different!

- Measured film stress and bow is primarily caused by:
  - shrinkage in the out-of-plane (z) axis due to elimination of water, solvent, and acrylate residue
  - CTE mis-match between the PI film (45-70 ppm/°C) and silicon (3 ppm/°C)
  - Oxygen (and temperature) increased shrinkage and stress as expected but had no effect on wafer bow

- Uniform heating from VFM, at temperatures much lower than Tg_{∞} (313°C), would predict lower wafer bow and stress.
- Wafer bow and stress were not lowered in these experiments
- Additional experiments are planned with additional profile modifications.

Properties: 375°C oven vs. 230-270°C VFM

- DOE results:



These are NOT error bars. They represent the range of real results from changes of variables.

Property Trade-offs

- Examples of actual data:

	Temp C	Time Hrs	Oxygen ppm	Tg C	Td1% C	Td5% C	Stress MPa	Bow mm	Elong. %
Standard	375C	5	<100	310	410	487	37.3	63	18.2
Standard *	350C	5	<100	256	382	432	28.3		
VFM *	350C	0.2	<20	330	463	497	31.6		
VFM	230	3	air	282	336	394	31.8	67	10.5
VFM	250	2	air	306	365	429			9.4
VFM	270	1	air	337	374	454	44.5	77	5.5
VFM	270	1	<20	236	336	392	30.6	62	25.9
VFM	270	3	<20	362	370	441	35.2	73.2	5.7

* Zussman et.al., Symposium on Polymers, 2008

Optional Cure Profiles for HD4100

- Standard oven cure (375°C)
  - Full cure properties
  - Long cycle time (5 hours)
- Very fast VFM cure (340°C)
  - Full cure properties
  - Short cycle time (20 minutes)
  - Brief thermal exposure may have device advantages
- Low temperature VFM cure (230-270°C)
  - Full imidization – chemically stable
  - Most of the acrylate residues are removed with oxygen (and temperature)
  - If wafers do not see subsequent temperatures above 300°C there is no out-gassing in film (Td1% always > 300°C)
  - Oxidative decomposition lowers elongation
  - Wafer bow and stress are not reduced at 230-270°C