Critical Irradiation Parameters

LTR CRADA Irradiation Team

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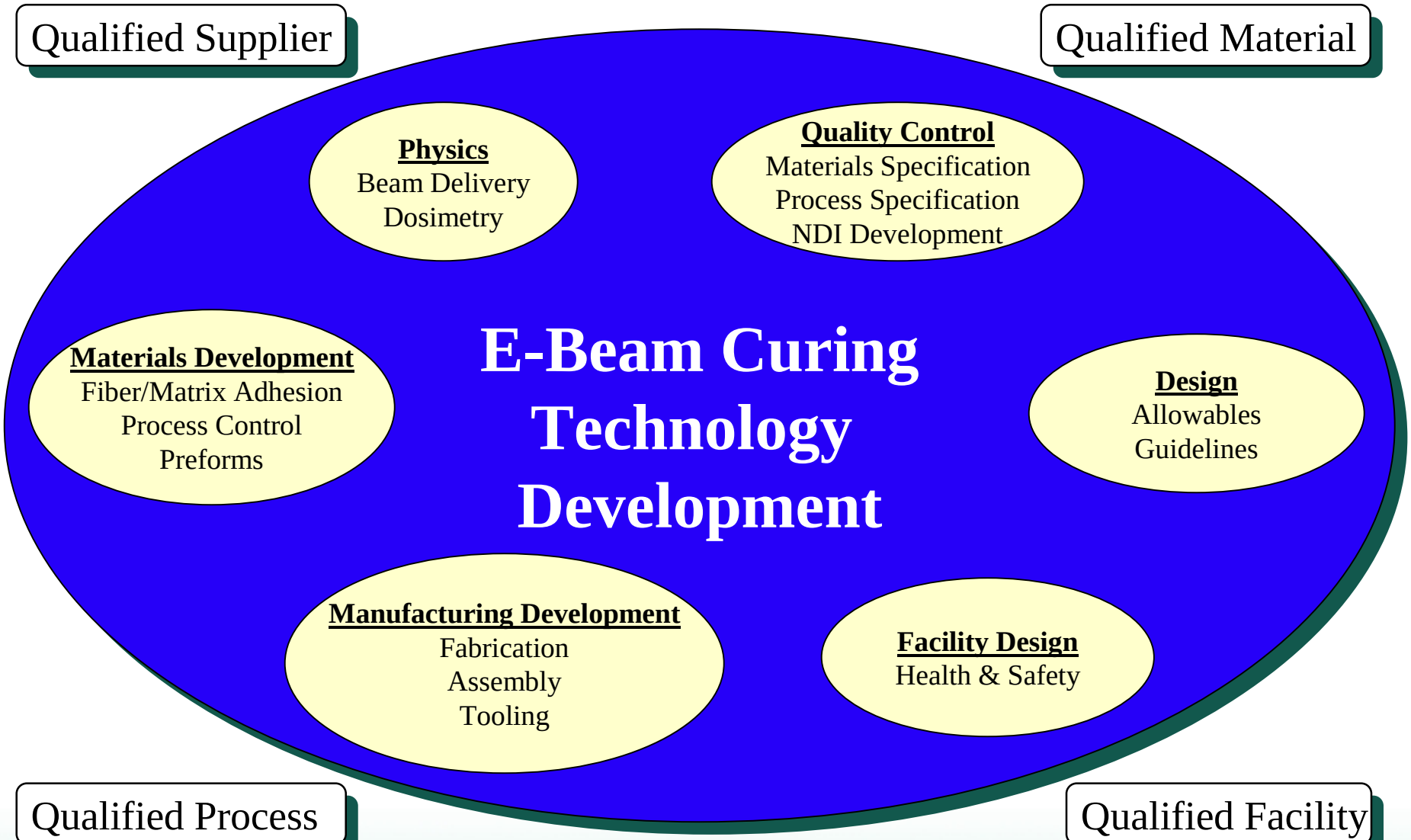
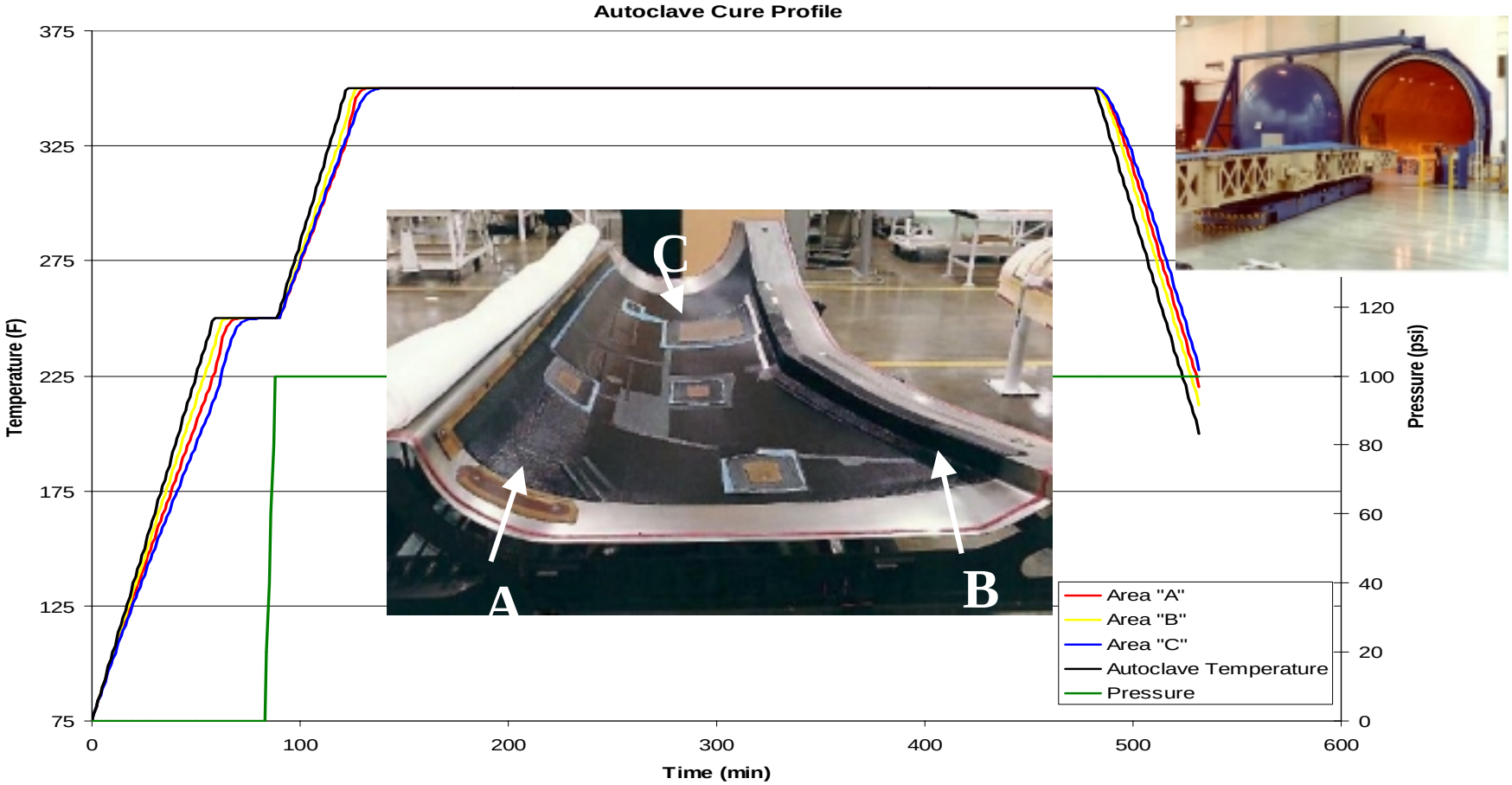
Presentation Outline

- **Irradiation Process Standardization Needs**
- **Parametric Sensitivities in E-Beam Curable Resins**
- **R&D Paths**
- **Summary**
- **Acknowledgements**

Production Implementation Needs

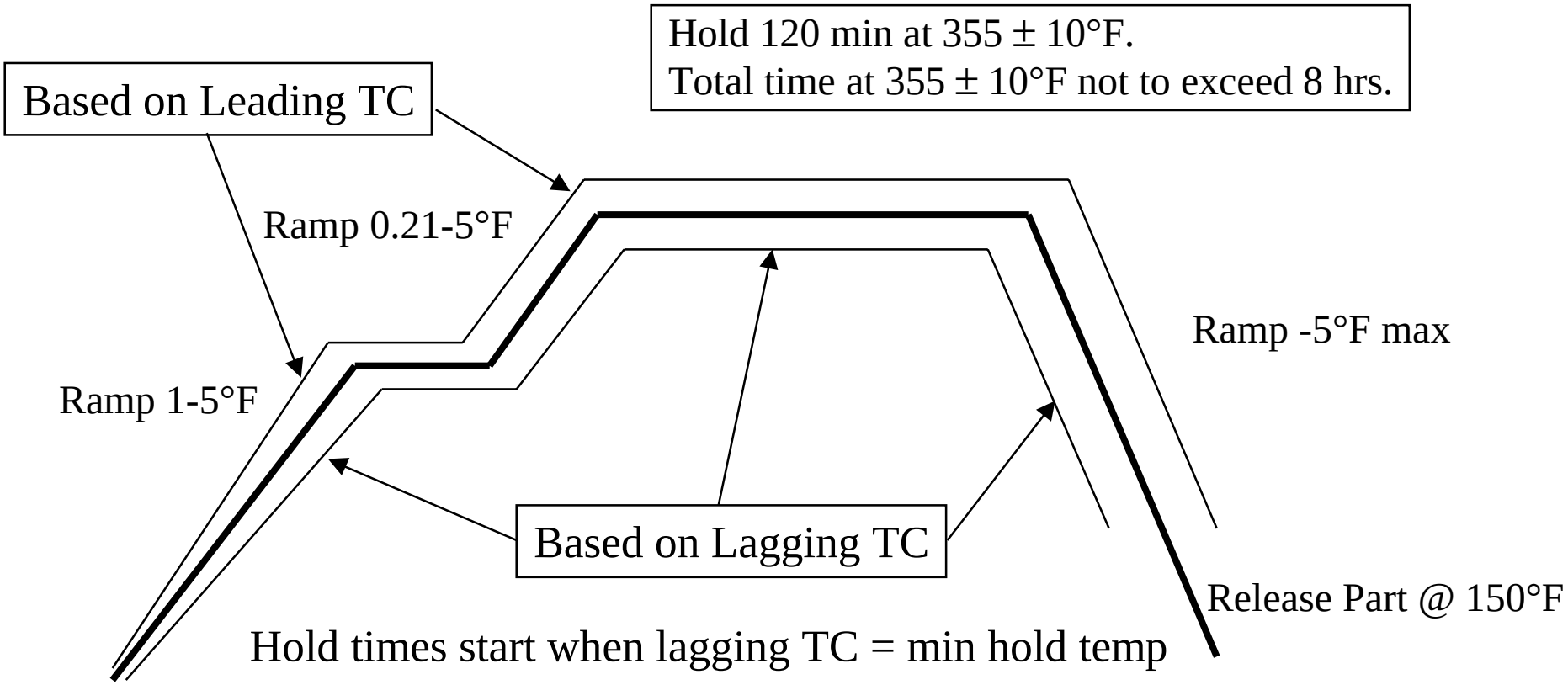


Cure Variation in Thermally Cured Parts



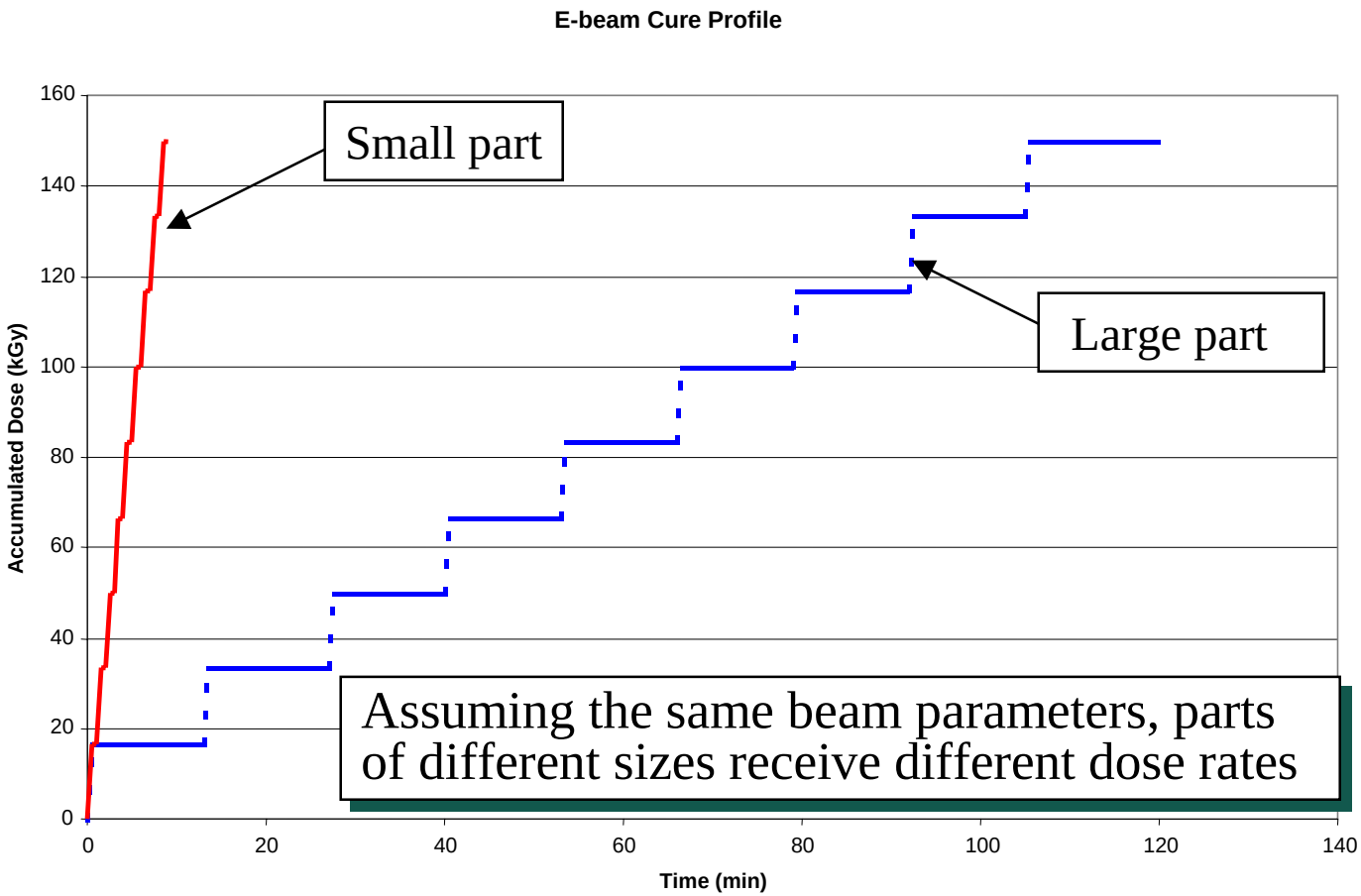
- **Small temperature variations exist in thermal cure cycles because the thermal contribution from the heat of reaction is small and slow ramp rates are used.**
- **The temperature variations generally arise from tooling mass and heat transfer variations**

Thermal Cure Profile



Thermal cure cycles are designed to minimize the temperature variation across the part, thus guaranteeing consistent material performance from all regions of the part. The use of Leading and Lagging control thermocouples helps insure this.

Cure Variation in Current EB Cured Parts



Radiation Cure Process Specification

Any method for specifying the radiation profile must have the following characteristics:

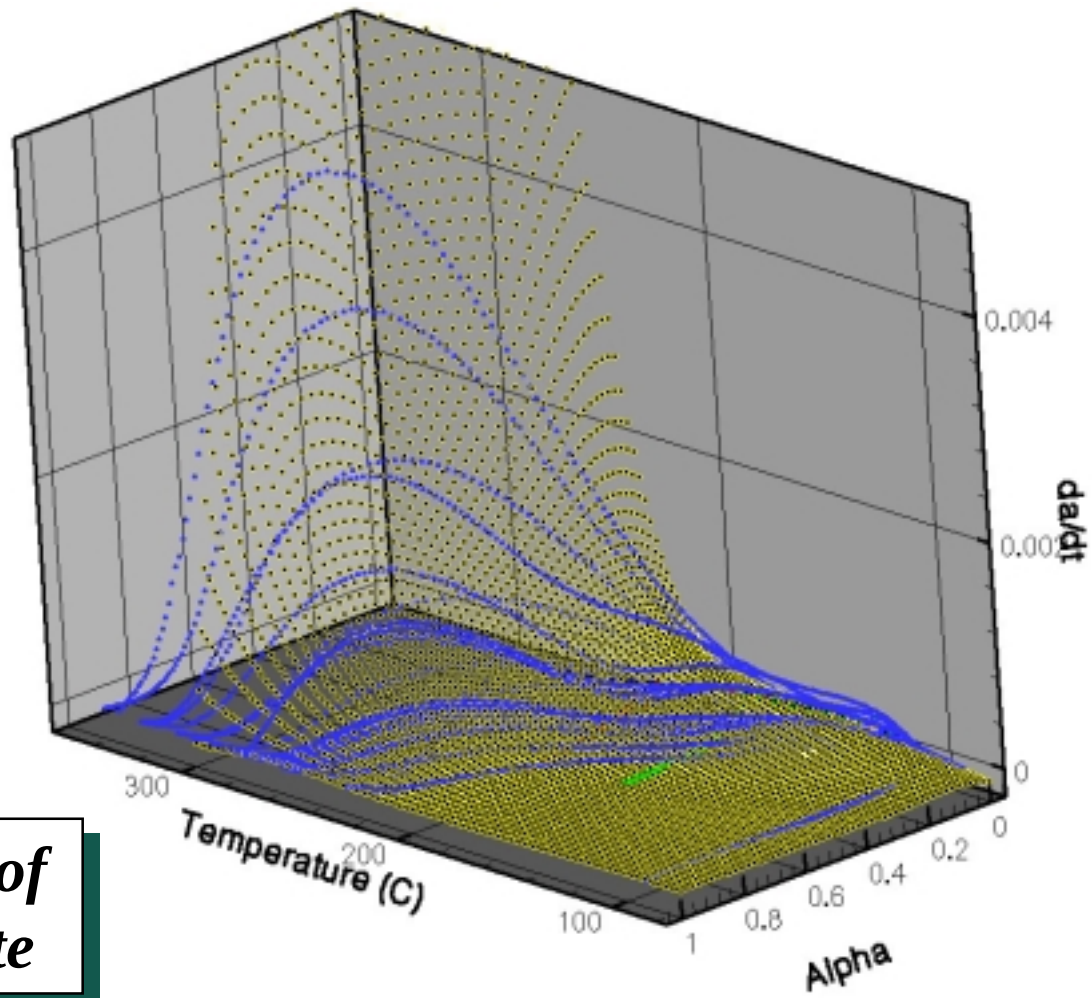
- Repeatable
- Robust
- Verifiable
- Machine independent
- Geometry independent
- Easy to understand & use

- The cure profile for any position on any point of any part created with a particular resin system must be within the parameters dictated by the specification.

Thermal Cure Variables

- **Thermal cure**

$$d\alpha/dt = f(T, \alpha)$$



Temperature and degree of cure control the resin state

Radiation Cure Variables

- **Radiation cure** $d\alpha/dt = f(T, \alpha, D, \varphi_a, \varphi_i, \omega, F, t)$?

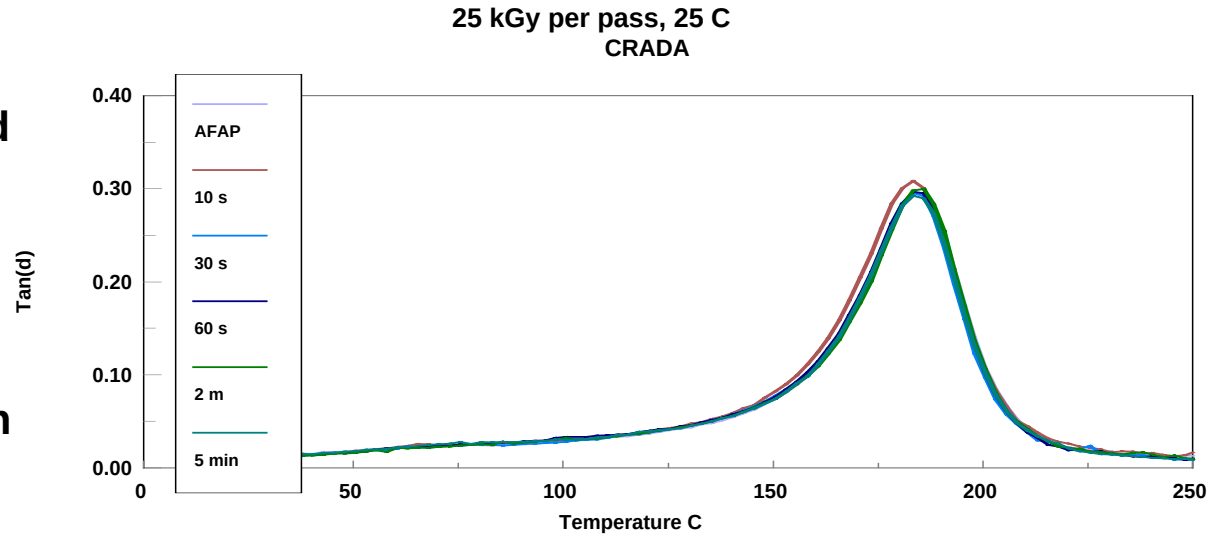
T - temperature
α - degree of cure (mer consumption)
D - total absorbed dose (includes light exposure)
φ_a - time-averaged dose rate
φ_i - instantaneous dose rate
ω - moisture content
F - radiation form (electron or γ /x-ray)
t - time

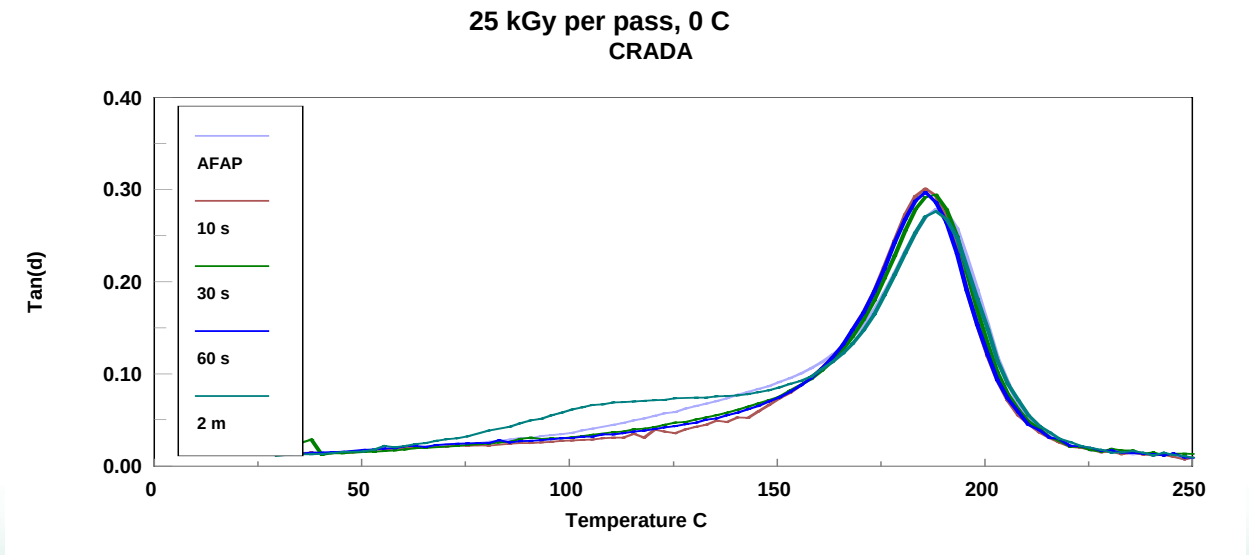
*Resin state **<u>may</u>** be a function of several variables*

Temperature Effects

- **Resin temperature effect on acrylated epoxy Tg and curing kinetics quantified by Defoort et. al. (Proc. SAMPE 2000, p. 2223)**

- **Resin temperature shown qualitatively to affect Tg in cationic epoxy systems**

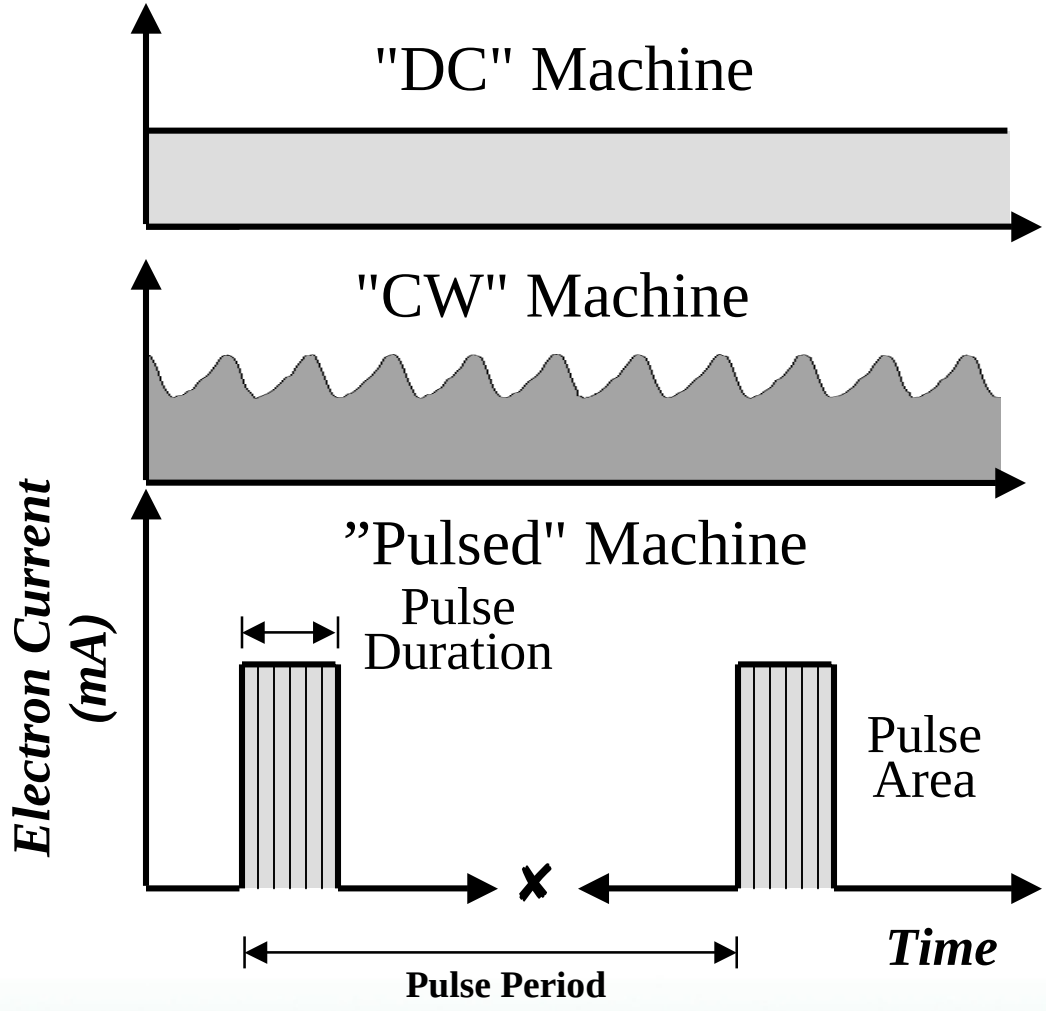




DMA Curves for Cationic Epoxy Neat Resin

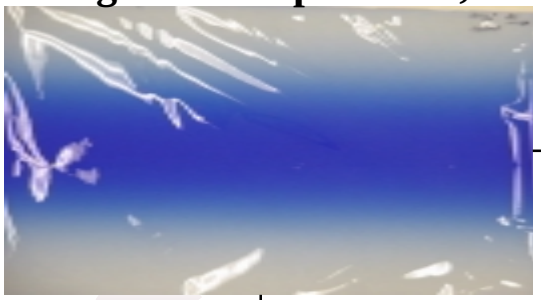
Dose Rate Effects

- **Dose rate does affect cure kinetics in free radical systems**
- **Dose rate effects are not known in cationic systems, and are a topic of much debate**
- **Instantaneous vs. average dose rates; does the beam's space-time structure matter?**



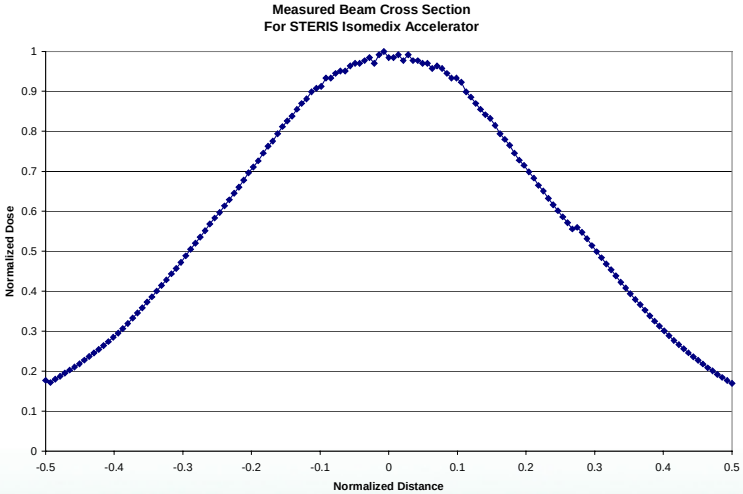
Beam Spot Dose Profile

Boeing Static Experiment, 18.25"

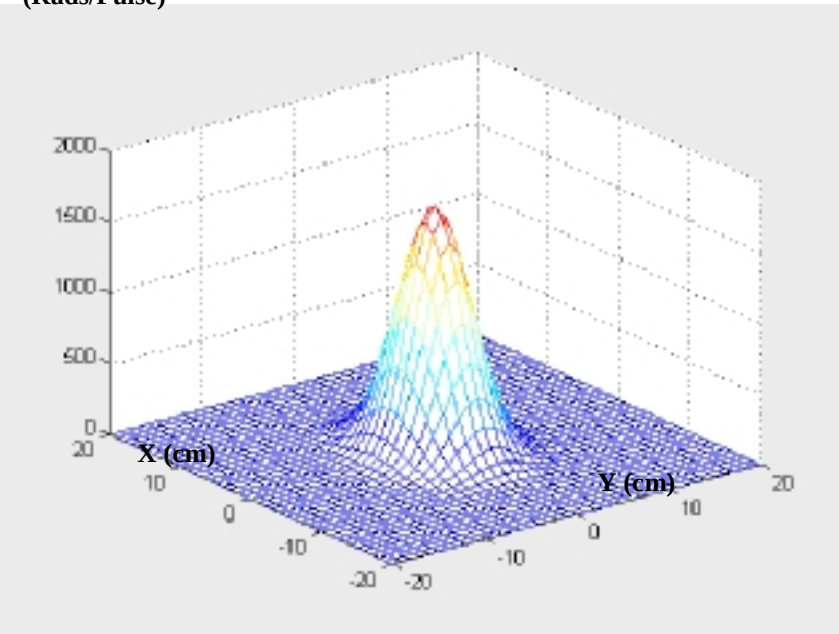


Scan Direction

Translation Direction



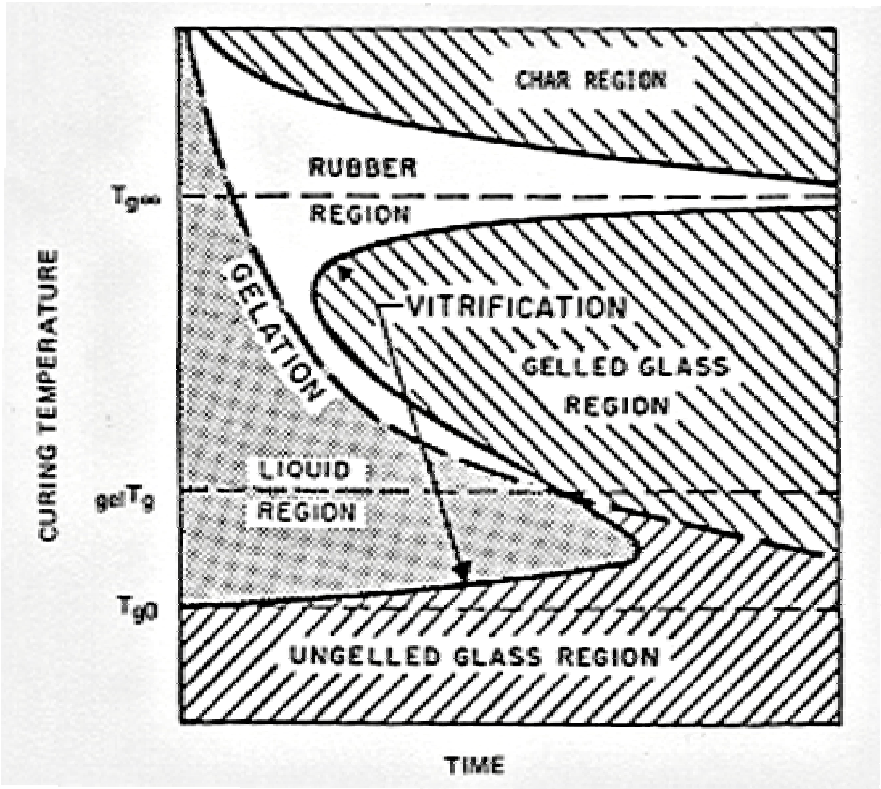
Surface Dose (Rads/Pulse)



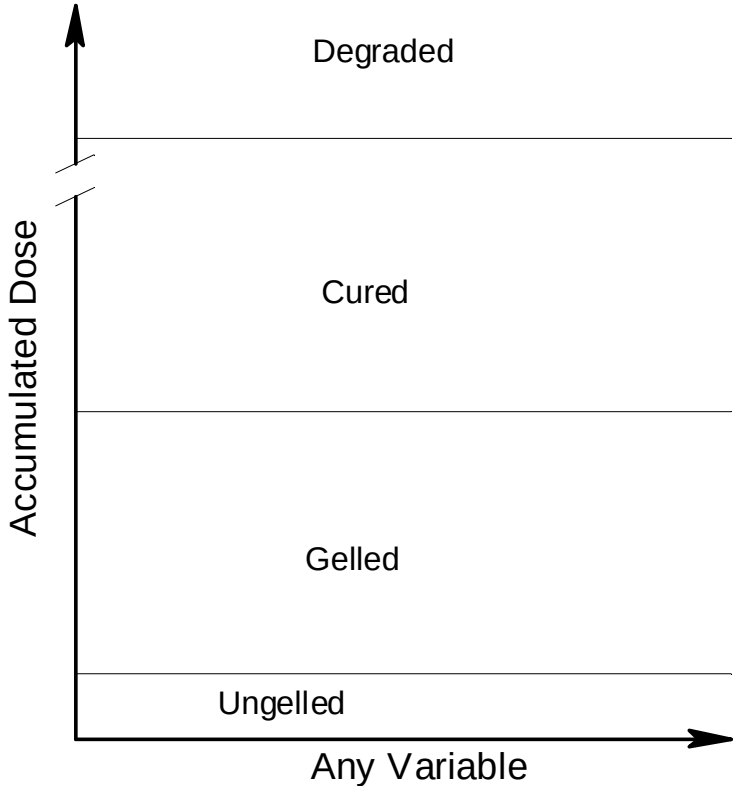
Effect of Other Variables

- **Total Dose**
  - **The cure state of all systems correlates to total absorbed dose**
  - **Total dose required for full cure *may* depend on other cure variables**
- **Moisture**
  - **Trace of moisture is beneficial**
  - **Palmese et. al. (Proc. SAMPE 2000, p. 1874) has shown that in cationic epoxies, the polymer molecular weight is reduced by moisture concentrations typical of resins exposed to normal ambient conditions**
- **Atmospheric composition**
  - **Free radical systems are normally oxygen inhibited**
  - **Cationic systems are normally insensitive to atmospheric composition**
- **Radiation type - electron vs. photon (γ/x-ray)**
  - **There is generally thought to be no effect; this is unproven**

Resin Transformation Diagrams



Thermally cured epoxy
(from *Epoxy Resins - Chemistry and Technology,* 2nd edition, ed. C. A. May)



Rad cured cationic epoxy - recent assumption

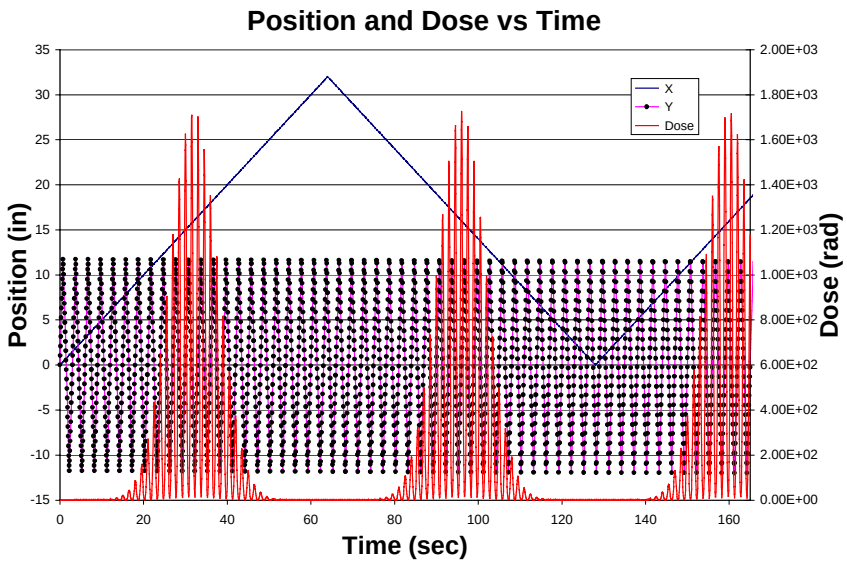
CRADA Accelerators

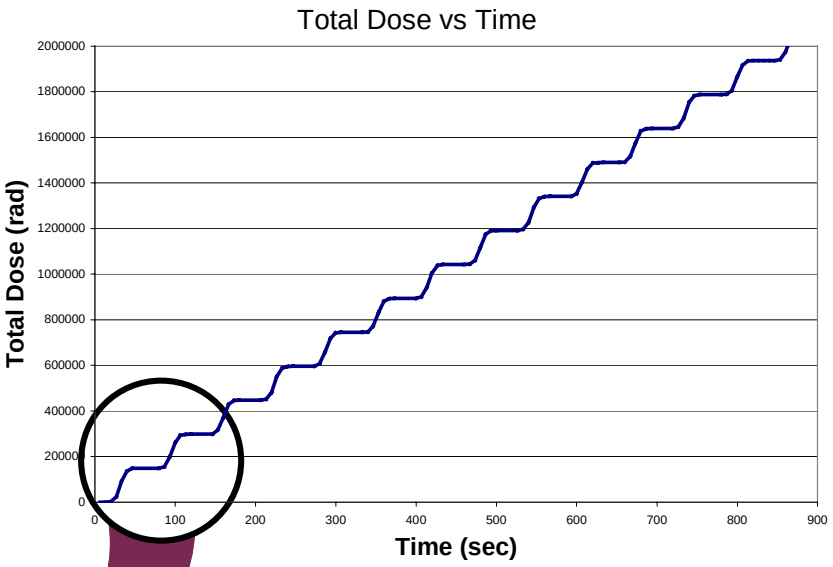
Energy/Power	Machine Type	Company
5 MeV/80 kW	Continuous Wave	STERIS Isomedix
10 MeV/50 kW	Pulsed	E-BEAM Services
4.5 MeV/150 kW	DC	E-BEAM Services
10 MeV/1 kW	Pulsed	Boeing
10 MeV/0.75 kW	Pulsed	Acsion Industries
8 MeV/<0.01 kW	Pulsed	Dept of Energy (at Notre Dame)

The CRADA is in the process of generating and comparing results from different accelerators

Calculating Dose Parameters

A beta version predictive Visual Basic code was created that calculates radiation delivery based on empirical input data. The code calculates total dose, as well as the instantaneous dose rate and average dose rate histories at any point on a surface.





Microscopic Result

Macroscopic Result

Summary

- Production implementation requires a well-understood and qualified irradiation process
- We must determine what conditions must be controlled (e.g., moisture, cure temperature, …) and quantify their effects
- We must develop process control and validation protocols to assure end users that their products are cured according to process specifications
- Efforts are underway by the CRADA and other researchers to resolve these issues

Acknowledgements

- CRADA team, especially:
  - Irradiators
  - Vince Lopata
  - Mark Wilenski
  - Chris Janke
- Jeanne Phillips
- Leesa Laymance