Radiation Curing of Composites Tutorial

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CENTER FOR COMPOSITE MANUFACTURING TECHNOLOGY

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http://www.ornl.gov/etd/etdfctsh.htm

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Introduction - Radiation Curing Of Composites

- Radiation processing is a revolutionary technology for manufacturing high-performance composite parts ***efficiently*** and ***inexpensively***.
- Ionizing radiation - in the form of high energy electrons or x-rays - is used at controlled rates to cure polymers.
- Result is very fast, non-thermal, non-autoclave curing.

Outline

- Polymer Matrix Composites
  - A ***brief*** introduction to polymers and composites
  - Thermal curing processes - technology baseline
- Radiation Processing Technology
  - Ionizing radiation - what is it?
  - Production and control of radiation
  - Commercial uses of radiation processes
- Radiation Curing of Polymer Matrix Composites
  - Radiation chemistry for polymers
  - Processing composite materials
  - Tooling options
  - Materials and properties
  - Facilities and equipment
  - Health and safety
- Issues and Unknowns

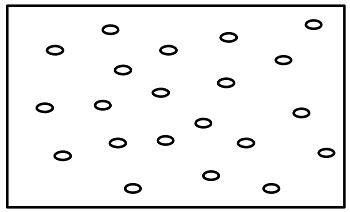
Composite

- A new material formed from two or more materials combined on a macroscopic scale.
- Composites can exhibit the best qualities of the constituents as well as new characteristics.
- Composites have the advantages of <u>flexibility</u> and <u>tailorability</u>.

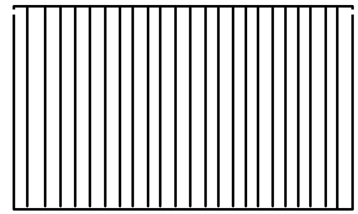
Types of Composites

- Particulate
  - concrete, aluminum flakes in paint, short fiber/whisker reinforced materials, SiC
- Fibrous
  - fiberglass, advanced composites
- Laminated
  - bimetals, safety glass, clad metals

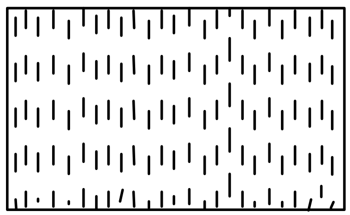
Types of Reinforcement



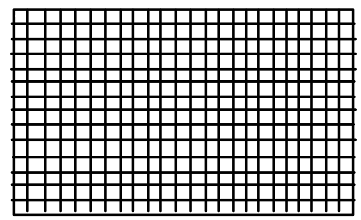
Particulate Composite



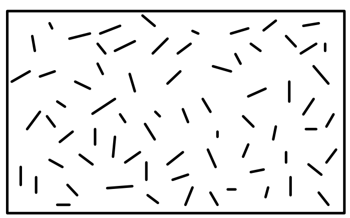
Unidirectional Continuous Fiber Composite



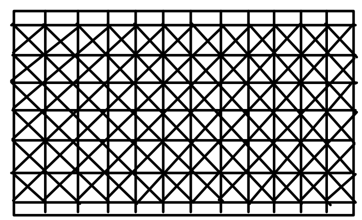
Short-Fiber Unidirectional Composite



Crossply Composite



Short-Fiber Random Orientation Composite



Multidirectional Composite

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Types of Matrices

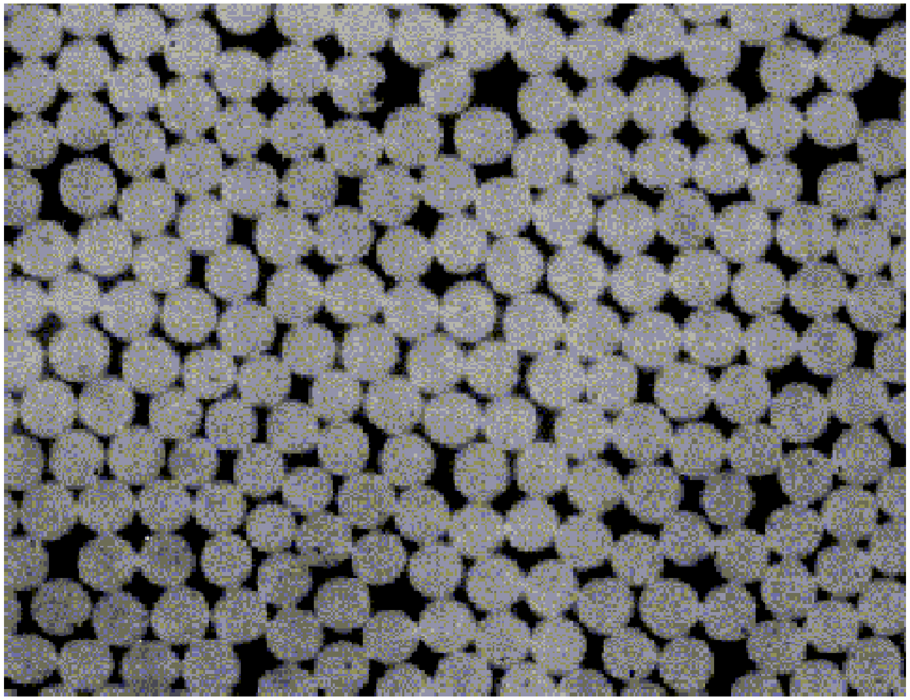
- Metallic
  - aluminum
  - titanium
  - copper
- Organic
  - thermosetting polymer
  - thermoplastic polymer
- Ceramic
  - glass
  - silicon carbide
- Carbon
  - high modulus - derived from pitch
  - high strength - derived from acrylonitrile

Two Basic Classes of Fiber Reinforced Composites

- Advanced (aerospace) Composites
  - Primarily used when performance is the driving issue.
  - Used primarily for weight advantage
  - Usually long (continuous) filaments
  - High specific strength and stiffness
  - Anisotropic bulk properties

- Commercial Composites
  - Low to medium performance
  - Usually short fiber or particle reinforcements.
  - Fiberglass is the most common composite used in manufacturing.

Advanced Composites

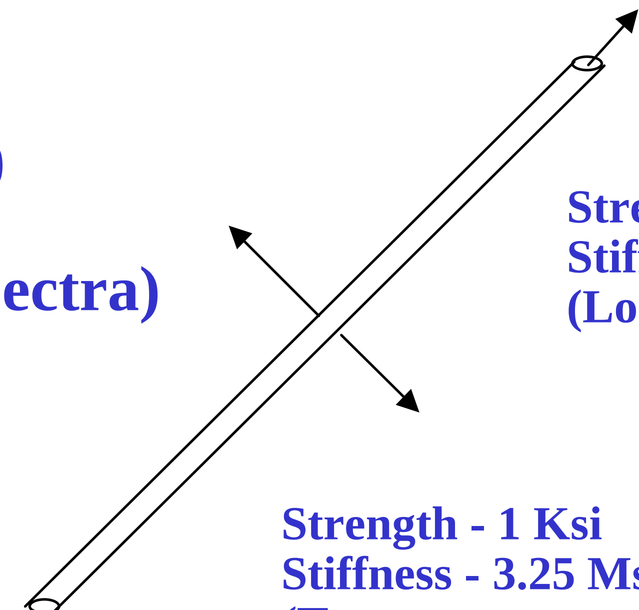


- Fibers
  - provide the mechanical properties (load bearing component).
- Matrix
  - maintains alignment, protects the fibers and transfers load between the fibers.

Fiber Reinforcements

- Glass
- Carbon
- Aramid (Kevlar)
- Polyethylene (Spectra)
- Silicon Carbide
- Boron

Example: T300 Carbon Fiber



Strength - 325 Ksi
Stiffness - 33.5 Msi
(Longitudinal direction)

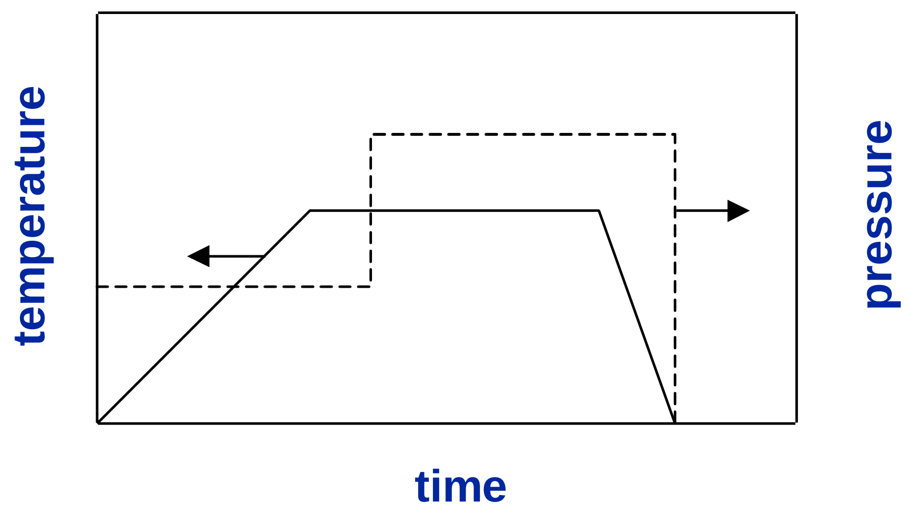
Strength - 1 Ksi
Stiffness - 3.25 Msi
(Transverse or radial direction)

Polymer Matrix Materials

- Thermoset Resins
  - Supplied in “liquid” form
  - Viscosity is a function of polymerization chemistry
  - Chemical triggers (hardeners) cause solidification
  - Heating used to accelerate solidification and crosslinking
  - Cannot be reprocessed by additional heating
- Thermoplastic Resins
  - Supplied in “solid” form
  - Viscosity is a function of temperature
  - Liquified by heating in fabrication processes
  - Solidified and hardened by cooling
  - May be softened and re-melted by additional heating

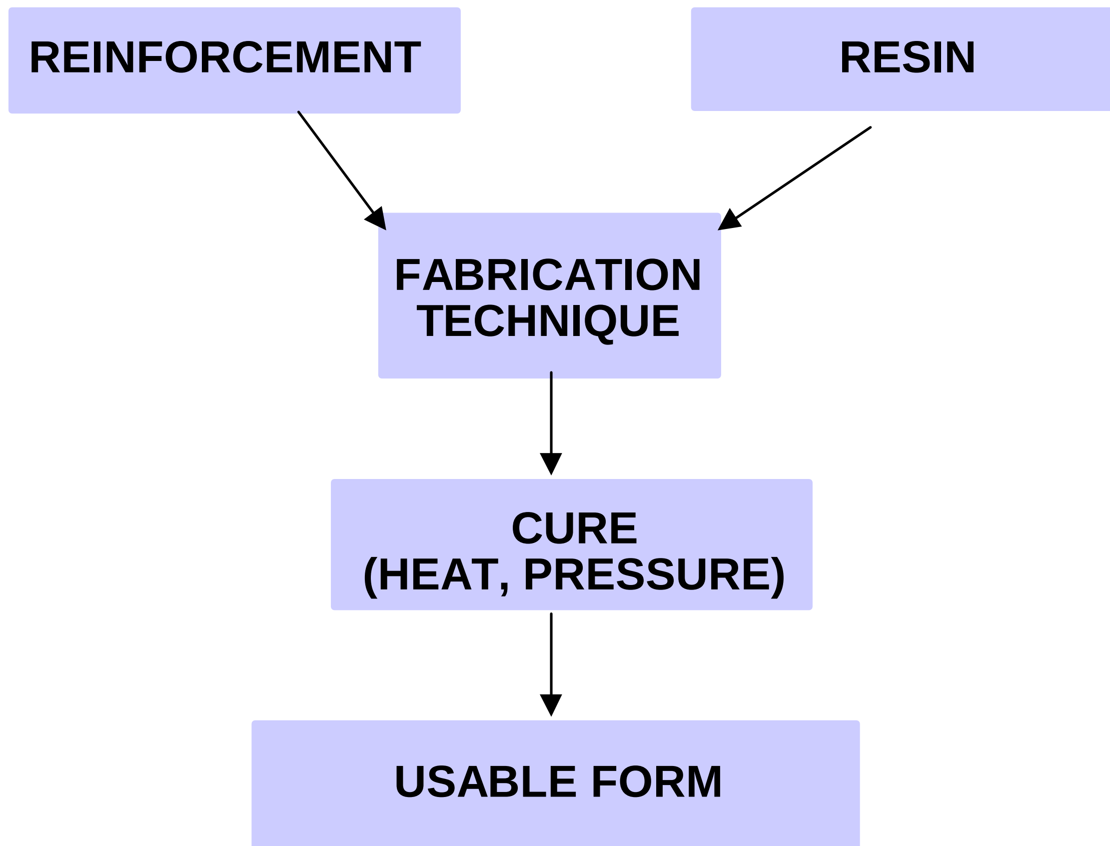
Typical Cure Cycle for Thermoset Resin

- Heating rate and cooling rate are important
- Vacuum may be needed to remove volatiles and trapped air



- Oven curing may use vacuum, but does not use pressure
- Most resins cure at 250EF to 450EF

Fabrication of Composites



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  - Tooling options
  - Materials and properties
  - Facilities and equipment
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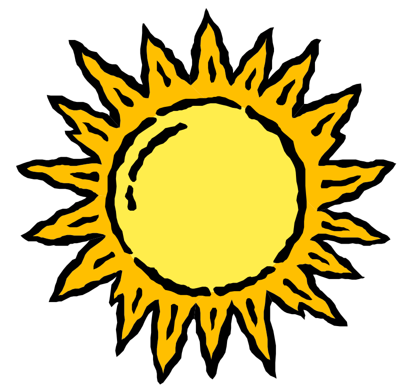
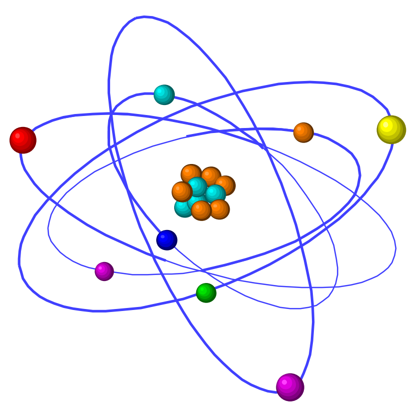
“Radiation” And “Radioactive” Should Not Be Confused

- Radiation is a term to describe energy transport
  - Sunshine
  - Radio waves
  - X-rays
- Radioactive is a term to describe a substance
  - Radon
  - Cobalt
  - Tritium





Definitions

- Radiation
  - electromagnetic energy transmitted by waves (light) or a stream of energetic particles (e.g., electrons)
  - emitted from natural sources (e.g., the sun)
  - emitted from a radioisotope (e.g., thorium, cobalt)
  - produced by a particle accelerator
- Ionizing Radiation
  - photons and/or particles with sufficient energy to remove an electron from a stable atom
- Activation
  - conversion of a stable material to a radioactive material
  - can be caused by high-energy ionizing radiation

Definitions

- Gray (Gy) = J/kg
  - the SI unit of measurement of *absorbed radiation*
  - one joule of energy is absorbed per kilogram of matter being irradiated
  - 1 kGy = 1000 Gy
- Electron volt (eV) = 1.602 x 10^{-19} joules
  - a unit of *energy* equal to the energy acquired by an electron accelerating through a potential difference of 1 volt.
- Rad
  - another common dose unit. 100 Rad = 1Gy
- Sievert and REM
  - special units for measuring radiation effects in people

Typical Energies

- 1.8-3.1 eV: visible light
- 3.1-250 eV: ultraviolet light
- 10-100 eV: outer shell electron binding energies
- 25 keV: television tube electron beam
- 200 keV: electron beam welder
- 100-200 keV: medical radiography
- 100-300 keV: electron curtain for curing inks, films,coatings
- 100 kev-10MeV: part radiography for nondestructive evaluation
- 1.17 MeV and 1.33 MeV: gamma rays from Cobalt-60

Typical Energies

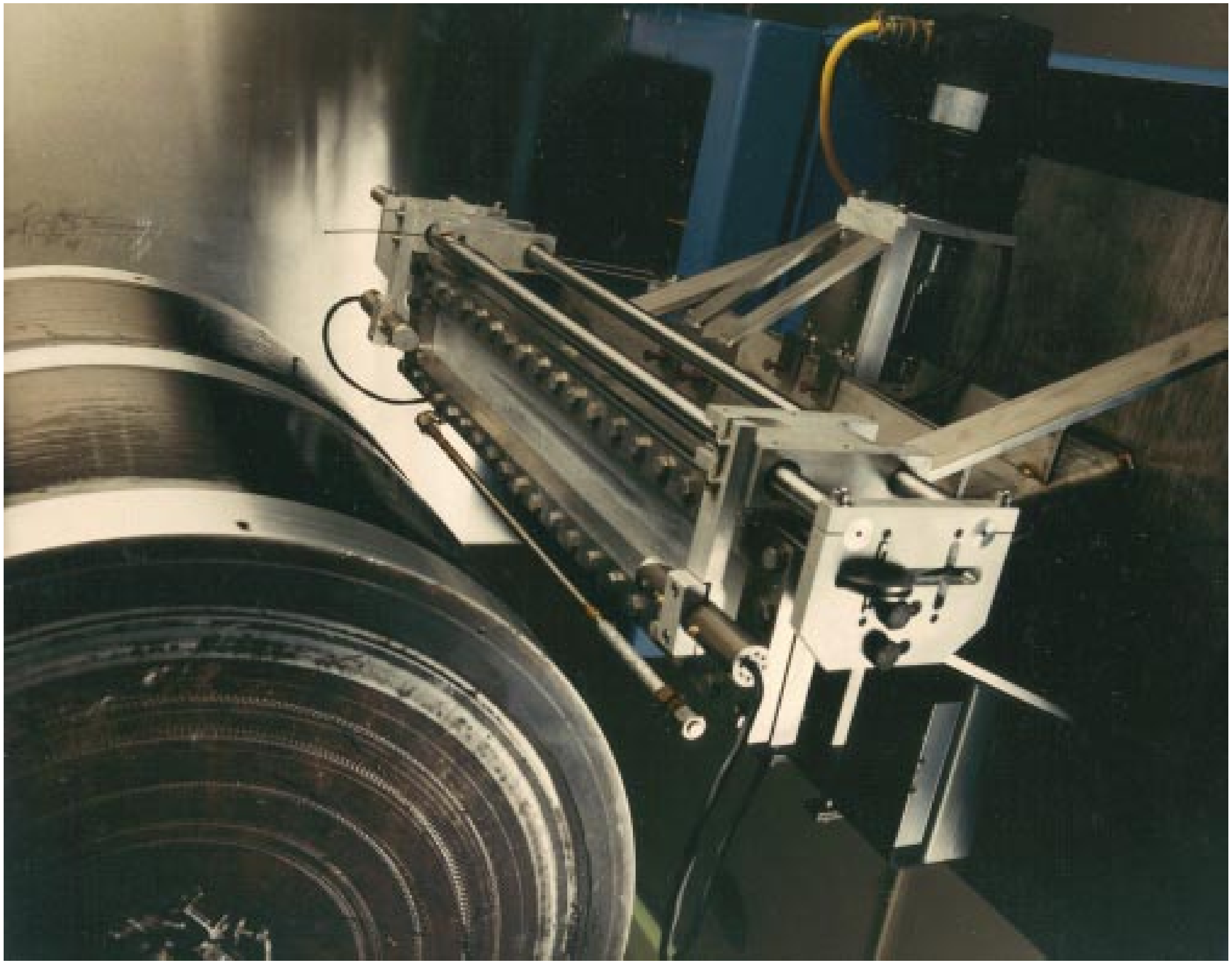
- <5MeV: electrostatic accelerators
- 10 MeV: industrial RF accelerators
- 150 MeV: ORELA (Oak Ridge, TN)
- 4GeV: CEBAF (Hampton, VA)
- 50 GeV: SLAC (Stanford, CA)
- 90 GeV: LEP (CERN, Switzerland)
- 7 TeV: LHC (CERN, Switzerland - planned)
- 20 TeV: SSC (cancelled)

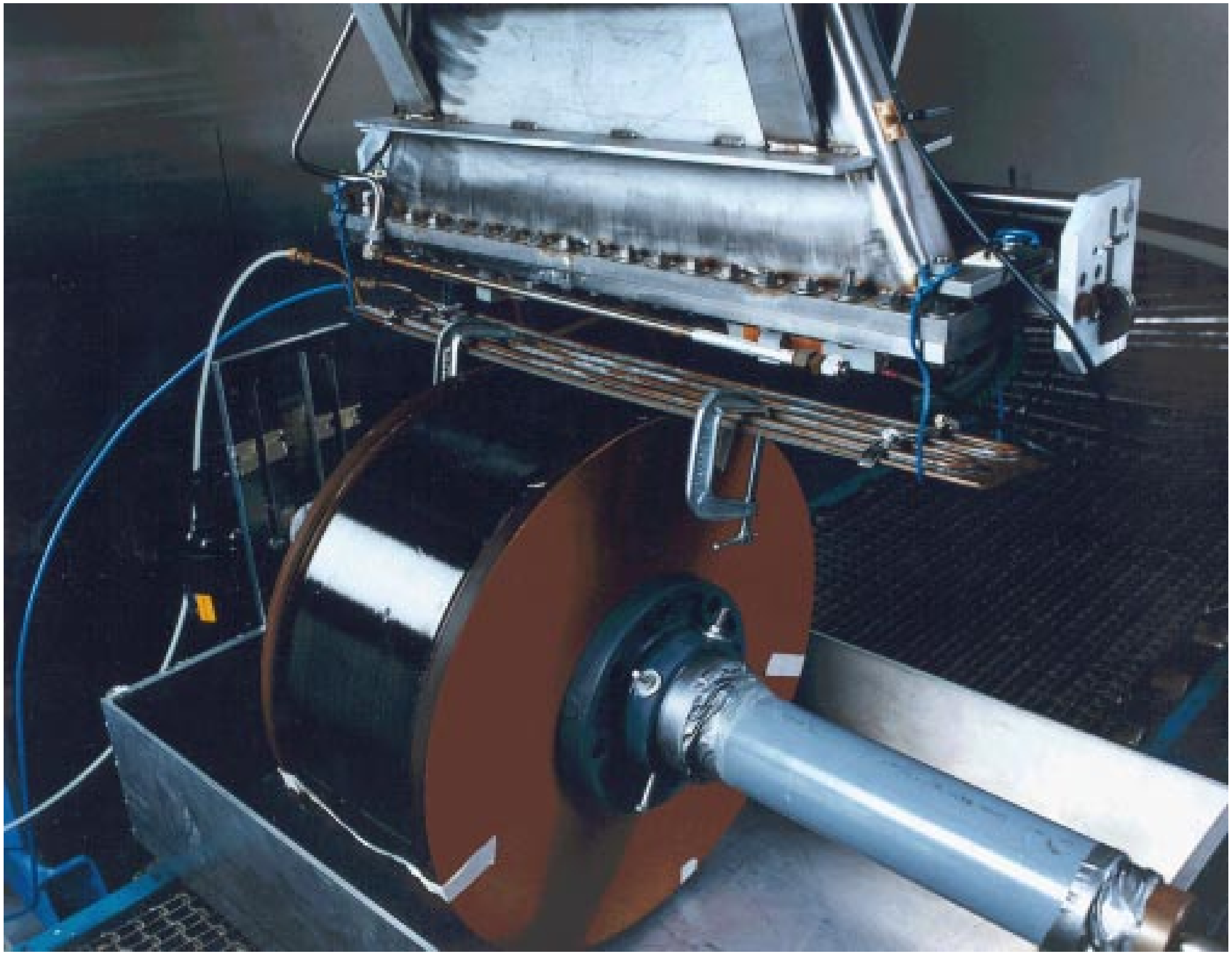
Effects of Typical Radiation Doses

- 50 mGy: allowable *annual* dose for radiation worker
- 10 Gy: lethal dose for humans
- <1 kGy: Teflon structurally unstable
- 15-35 kGy: sterilization
- 20 kGy: curing of polyester resins
- 100-200 kGy: curing of epoxy resins
- 200 kGy: natural rubber unsuable
- 1000 kGy: polyvinylchloride unusable
- 50-100 MGy: polyimide degraded significantly

Accelerator Systems For Radiation Processing

- Accelerator Schematics
- Typical Configuration
- Scan Horn
- Foil Window
- X-ray Conversion Plate
- Shielding Considerations





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Radiation Curing of Composites

- Visible and ultraviolet light curable resins can be cured by electron beams or X-rays.
- Usually, the thermal and mechanical properties of these resins are not suitable for high-performance applications (e.g., aerospace).
- The ionizing radiation initiates reactions in the resin that cause molecules to crosslink.
- Radiation-cured cationic photoinitiator epoxy resins have thermal and mechanical properties that meet most requirements for high-performance applications.

Radiation Induced Polymerization and Cross-linking of Resin Systems

- Schematic for epoxy acrylates
- Epoxy resin formulations
- Cationic resin chemistry with photoinitiators
- Photoinitiator chemistries
- Cationic epoxy material properties

Unique Capabilities

- Selectable cure temperatures
- Improved part performance and quality
- Ability to cure thick parts in one cycle
- Part thickness limited to 1-2" (electron) or 12" (X-ray)
- Material integration flexibility
    - different resin systems and fibers
    - metal fasteners
    - low temperature materials
- Tight tolerances from minimal thermal mismatch
- Removes need to "balance" fiber architectures
- Curing may be interrupted and restarted

How Radiation Curing Works

- Electrons are accelerated to near the speed of light.
- Magnets direct the stream of high energy electrons toward the part that is to be processed.
- The electrons may be converted to X-rays using a suitable target material placed near the part.
- The high energy electrons or X-rays deposit the energy needed to initiate polymerization and crosslinking reactions in suitable polymers.
- Energy is deposited volumetrically and near instantaneously (nano-microseconds)

Radiation Curing

- Epoxy resin + cationic initiator (1-3 parts per hundred) + tougheners/additives/fillers/diluents

Radiation → Cured polymer matrix

- No harmful chemical hardeners or catalysts
- Longer pot life and shelf life
- Less volatile emissions
- Composite material costs, fabrication time, and end-uses comparable to conventional thermally cured products

Radiation Curing

- *Throughput* ↔ ***Power*** level
  - high velocity electrons lose their energy through interaction with the target materials
- *Penetration Depth* ↔ ***Energy*** level
  - beam penetration also depends on part density

Radiation Curing

- Dose profiles at different beam energies
- Beam penetration through composite structure
- Temperature profile during processing
- Effect of varying temperature on part stability

Thermal Curing of Composites

- Thermal energy initiates crosslinking of the polymer
- Has a significant impact on the composite quality (overcure/exotherm)
- Requires long cure times (diffusion from surface of part to interior)
- High energy consumption
- Cure process cannot be interrupted once it is initiated
- A significant cost in the manufacture of polymer matrix composites

Radiation Curing Vs. Thermal Curing

RADIATION CURING
IS AFFORDABLE, FAST,
AND SAFE

- Reduced manufacturing costs and energy requirements
- Reduced tooling costs
- Generally at least ten times faster
- Simplified processing and material handling
- Reduced costs related to environmental, safety and health compliance

Dosage and Dose Rate

- Radiation curable carbon/epoxy laminates can typically be cured with a dose of 100-200 kGy
- Dose rate must also be considered for process tooling to control temperature rise

$$T_{max} = D/C_p$$

T_{max} = temperature rise (°C)

D = exposure dosage (kGy)

C_p = material specific heat (J/g•° C)

Energy Requirements
Thermal Curing Versus Radiation Curing

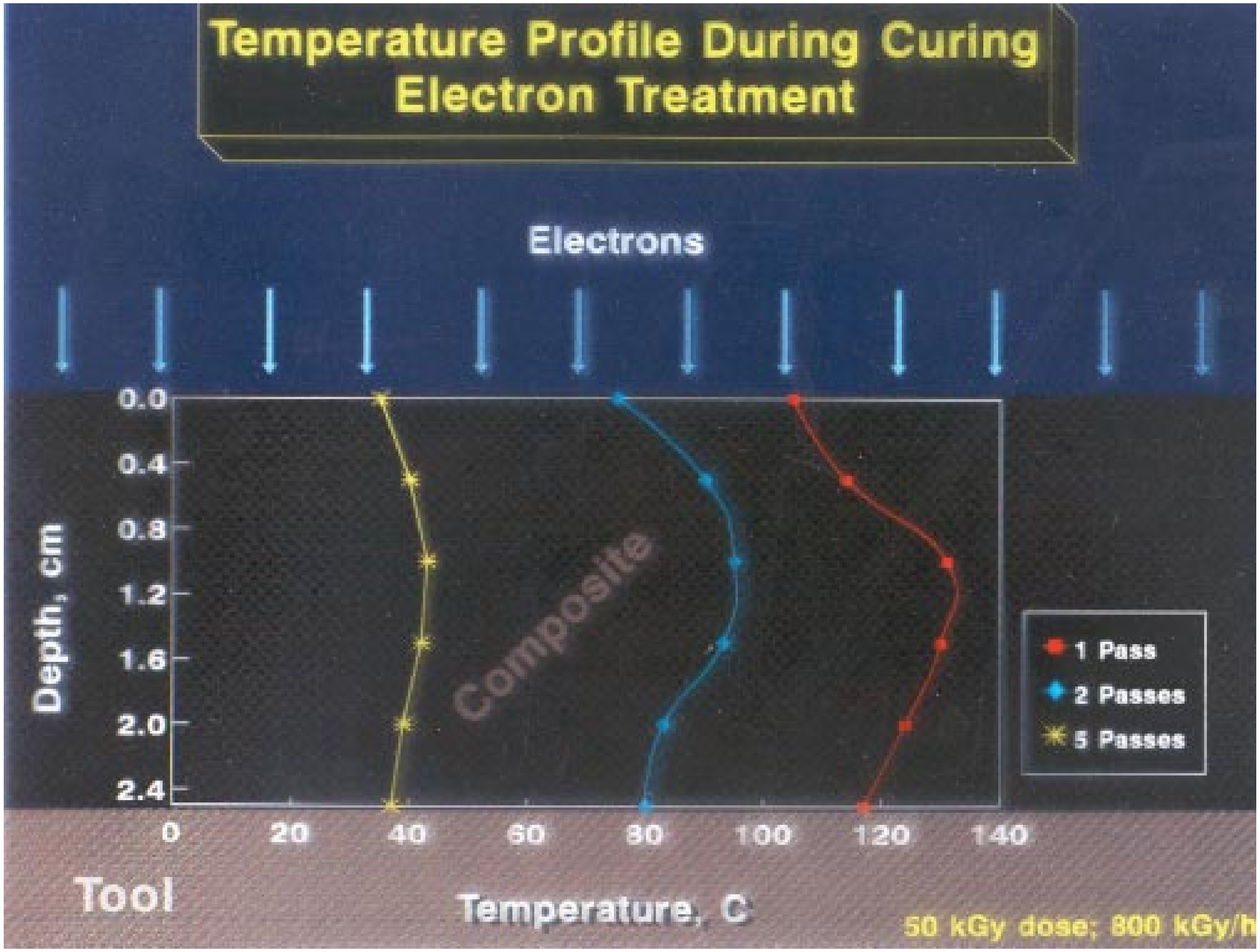
Product Description	Size (cm)	Mass (kg)	Thermal Cure Energy (kWh/part)	Radiation Cure Energy (kWh/part)
Hatch Cover (1)	122 cm x 244 cm x 3.3 mm	15.8	35	4.12
Sports Equipment (1)	Cylinder wall 1.5 mm thick	0.3	0.24 **(3)**	0.02
Filament Wound Tube (2)	Cylinder wall 5.1 mm thick	2.0	13.5	1.73

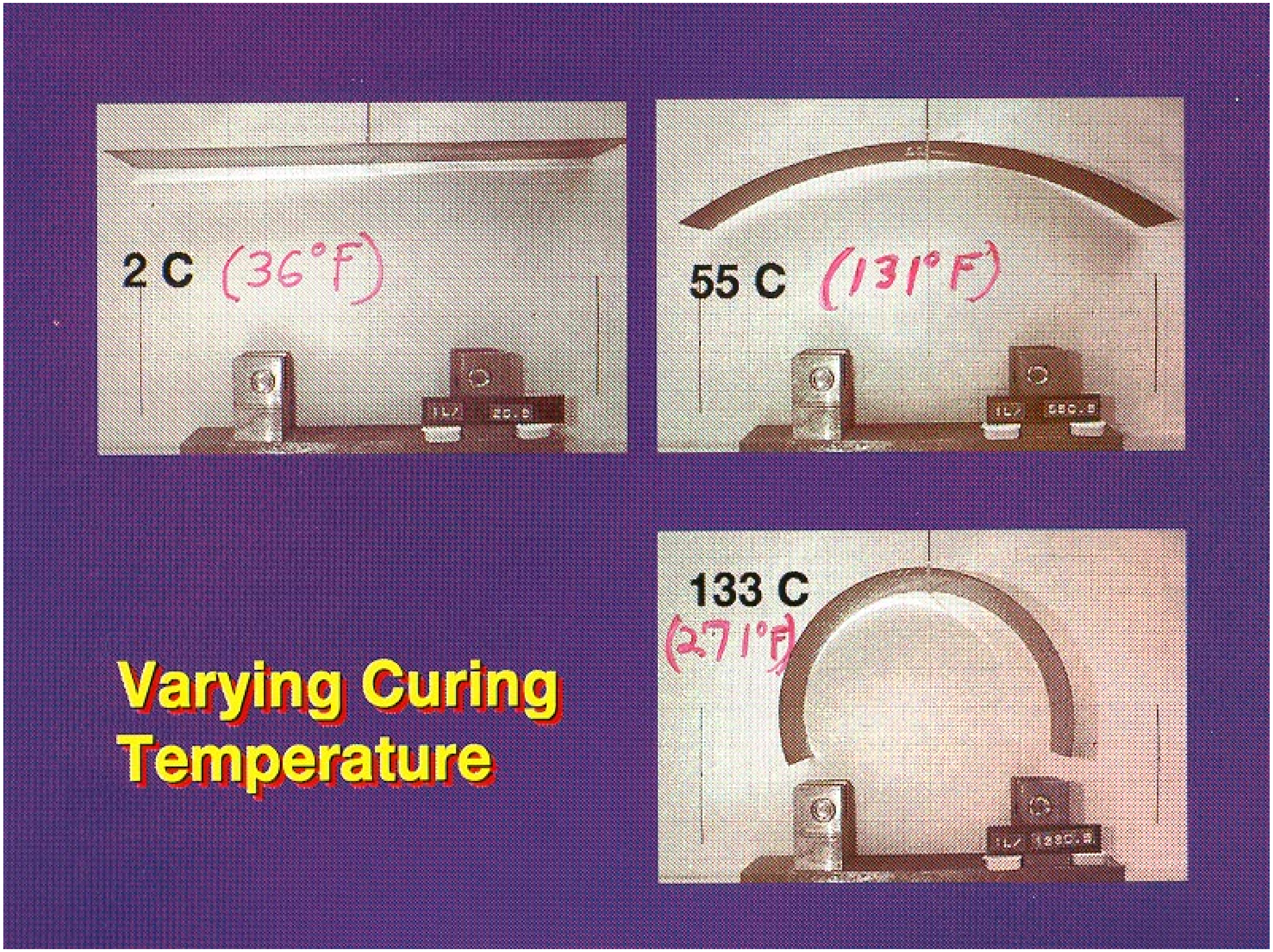
(1) Graphite/Epoxy (2) Glass/Epoxy (3) Post Cure Only

Data courtesy of AECL

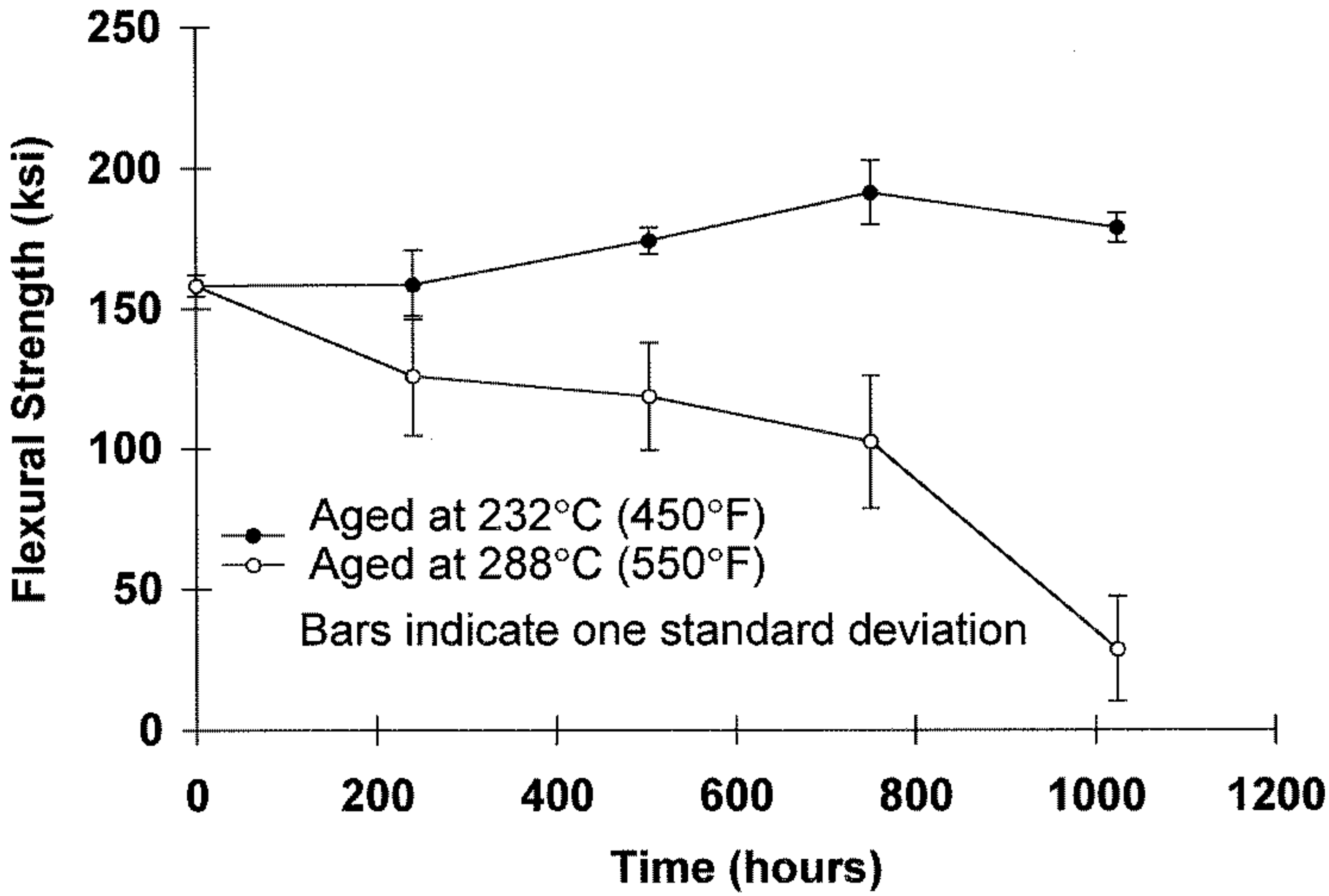
Conversion of High-Energy Electrons To X-Rays

- Greater Penetration
- Reduced Dose Rate
- Lower Temperature Rise

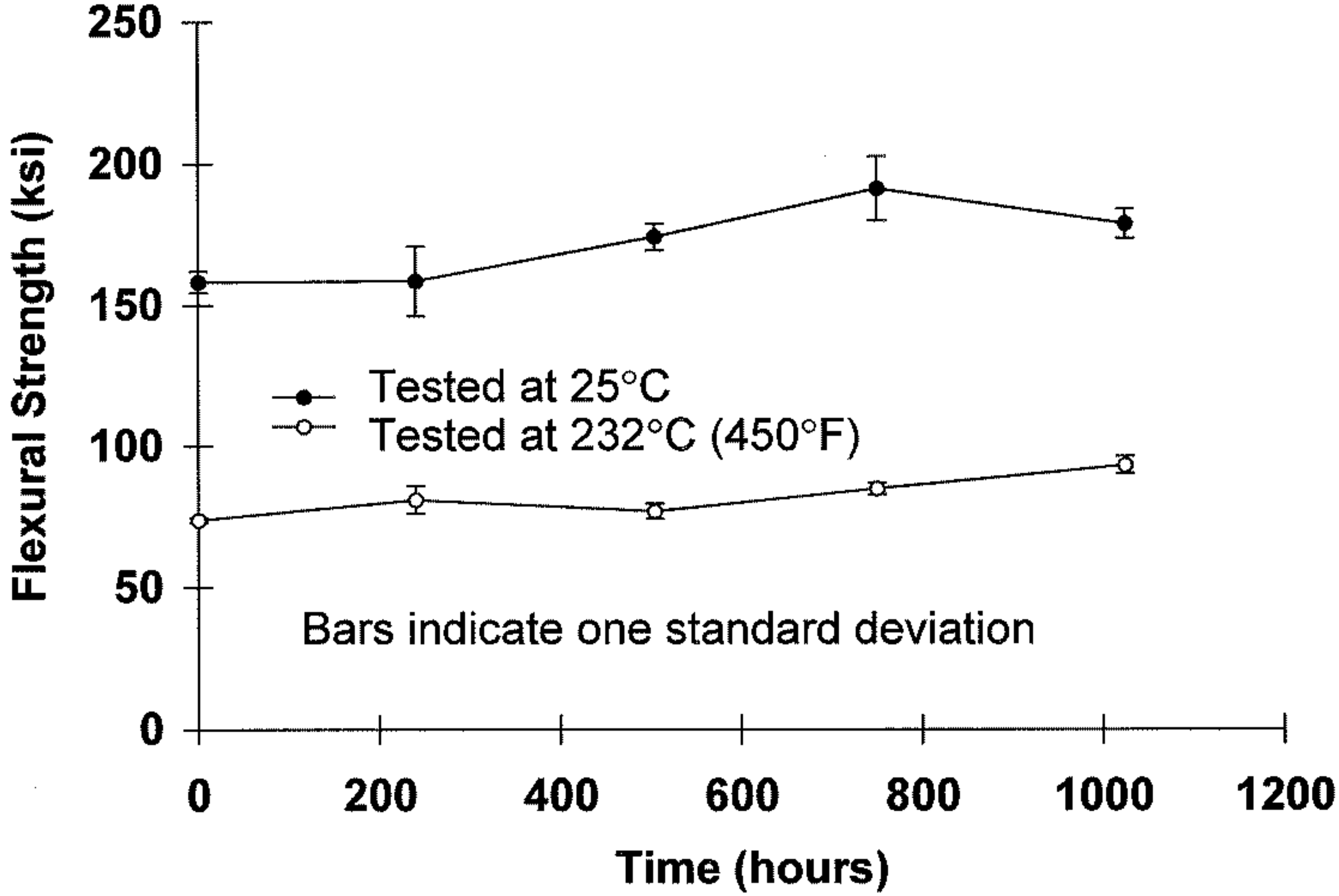

Temperature Profile During Curing
Electron Treatment
Electrons
0.0
0.4
0.8
1.2
1.6
2.0
2.4
Depth, cm
Composite
1 Pass
2 Passes
5 Passes
0
20
40
60
80
100
120
140
Tool
Temperature, C
50 kGy dose; 800 kGy/h


2 C (36°F)
55 C (131°F)
133 C (271°F)
Varying Curing Temperature

FLEXURAL STRENGTH OF ELECTRON BEAM RESIN 8H/IM7 UNIDIRECTIONAL LAMINATES VERSUS AGING TIME IN AIR-TESTED AT 25°C



FLEXURAL STRENGTH OF ELECTRON BEAM RESIN 8H/IM7 UNIDIRECTIONAL LAMINATES VERSUS AGING TIME IN AIR AT 232°C (450°F)



Tooling Flexibility

- Electron beam curing opens the door for alternative tooling materials and cost effective solutions
- Foams, plasters, woods, plastics, metals,
- Tooling should be optimized for:
    - weight
    - cost
    - temperature rise
    - ability to pass energy through for a closed mold
- Cure possibilities: total cure on tool, partial cure in mold, cure in-situ

Design Factors for Tooling

- fabrication process itself
- ***dimensional stability/ achievable tolerances***
- mold fabrication process
- maintenance, handling
- repair
- venting
- ***part curing pressure***
- temperature level
- ***need for resin flow***
- required thermal expansion
- ***part release***
- wear/durability
- mold fabrication process
- thermal mass/conductivity
- cooling
- undercuts/hardware/inserts
- surface finish
- ease of mold duplication
- radiation absorption

Tooling Test Results and Observations

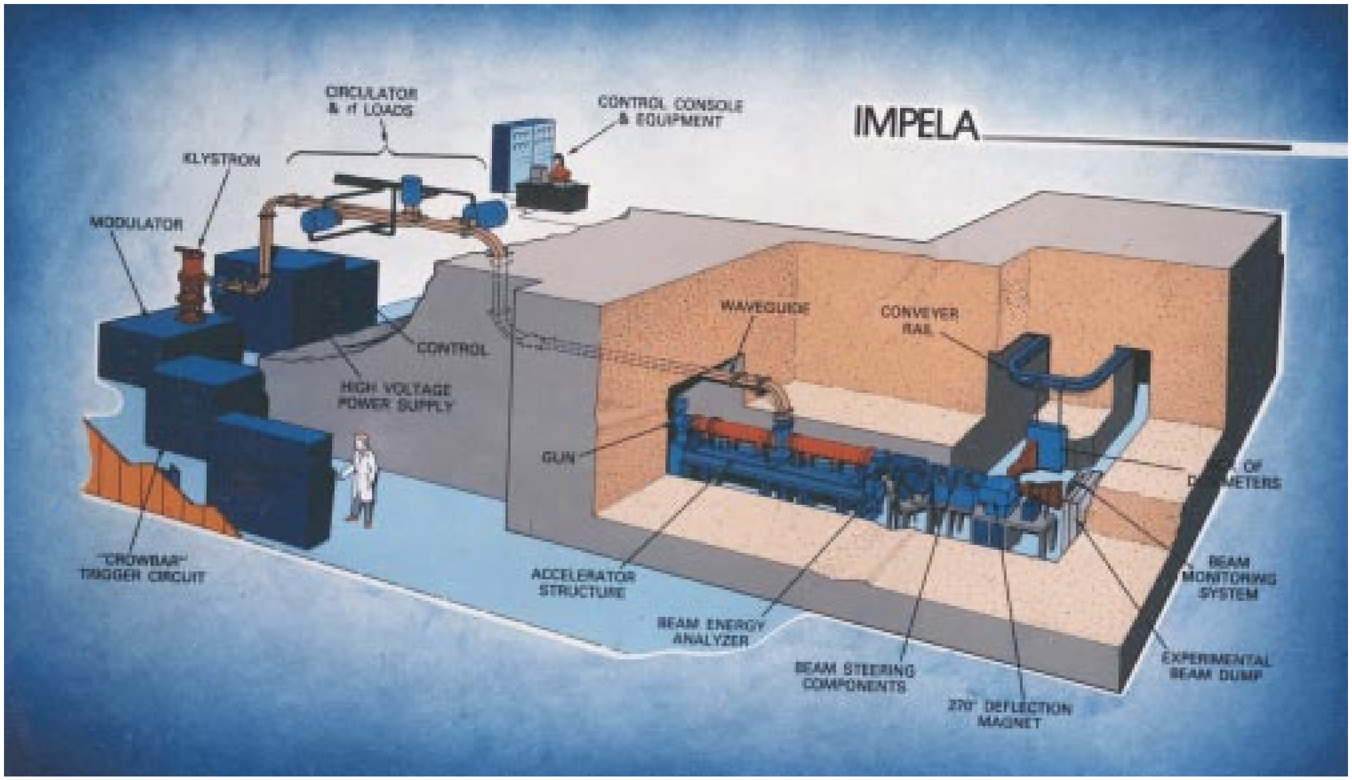
- Ceramics
  - Cures of 4500-7500 kGy
  - No failures to date
- Epoxies
  - Six of seven stable past 7000 kGy
  - One material lost dimensional stability at 4500kGy
- Plasters
  - Dimensional failures at 4125-7125 kGy
- Polycyanate
  - No failure to data at cures of 5625-6750 kGy
- Polyvinyl Chlorinate
  - Dimensional stability and hardness failed at 0-4125 kGy

Tooling Test Results and Observations

- Urethanes
  - Eight of 15 stable to 5000-7500 kGy
  - Seven lost dimensional stability at >750 kGy
- Woods
  - Mahogany lost hardness at 3750kGy
  - Jelutong lost harness at 750 kGy
- Others
  - Acrylate lost hardness at 6750 kGy
  - Phenolic lost hardness at 3750kGy

Accelerator Facility Schematics

- Unipolis Facility
- Impela Facility



IMPELA
CIRCULATOR & rf LOADS
CONTROL CONSOLE & EQUIPMENT
KLYSTRON
MODULATOR
CONTROL
HIGH VOLTAGE POWER SUPPLY
WAVEGUIDE
CONVEYER RAIL
GUN
"CROWBAR" TRIGGER CIRCUIT
ACCELERATOR STRUCTURE
BEAM ENERGY ANALYZER
BEAM STEERING COMPONENTS
270° DEFLECTION MAGNET
BEAM MONITORING SYSTEM
EXPERIMENTAL BEAM DUMP

Product Size Limits - Contract Facilities 1996

- E-BEAM Services (Cranbury, NJ)
  - 3.7 m x 0.8 m x 0.8 m (12 ft x 2.5 ft x 2.5 ft)
- Iotron (Vancouver, BC)
  - 2.5 m x 1.1 m x 1.0 m (8 ft x 3.5 ft x 3 ft)
- Aerospatiale (Bordeaux, FR)
  - 10.0 m x 4.0 m dia. (32.5 ft x 13 ft)
- Acsion (Pinawa, MB)
  - 2.7 m x 1.2 m x 0.6 m (8.5 ft x 3.5 ft x 2 ft)
- New facilities coming online will be discussed in workshop.

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Materials Issues

- Effect of curing temperature on the performance of composites over the expected use temperature range
- Mechanical property requirements
  - *material qualification*
- Curing under pressure is often impractical
  - vacuum bagging
  - debulking/consolidation under pressure
  - voids
- Fiber selection
  - use of organic fibers (polyethylene, nylon) must be done with caution

Materials Issues

- Fiber sizings for e-beam curing
  - G-sizing is most compatible so far
- Shear properties require improvement
  - New DOE CRADA research partnership is being formed to address issue
- Applicability of radiation curing process to wider range of resins
- X-ray cured materials need additional characterization

Facility Issues

- Existing facility infrastructure is limited
  - size
  - availability
  - accelerator power and energy
  - locations (concentrated on coasts)
- Dedicated facility costs
  - Accelerator facility costs are projected to be somewhat less than high volume autoclaves
  - Current estimates are on the order of10 million for multi-purpose, high-throughput facility, more if vault is to be extremely spacious

Facility Issues

- ES&H issues associated with ionizing radiation
  - Routine industrial hazards
    - falls and accidents
    - material handling
    - electrocution
  - Removal of Ozone
  - Radiation protection
    - shielding
    - time
    - distance

Potential Applications And Demonstrations

Ground Vehicles

- Compressed Natural Gas Tanks
- Tires and Tank Treads
- Molded Parts (rapid prototyping)
- Integrated Polymer/Metal Parts

Buildings and Infrastructure

- Foam-Filled Polymer Structures
- Polymer/Wood Composites

Industrial Systems

- Lightweight/Low Vibration Parts

Aircraft and Space Vehicles

- Cryogenic Fuel Tanks & Lines
- Integrated Polymer / Metal Composites
- High Temperature Composite Shafts
- Rocket Nozzle Structures
- Flywheel Components

Weapon Systems

- Ballistic Protection Structures
- Rocket and Missile Casings
- Antennas and Reflectors