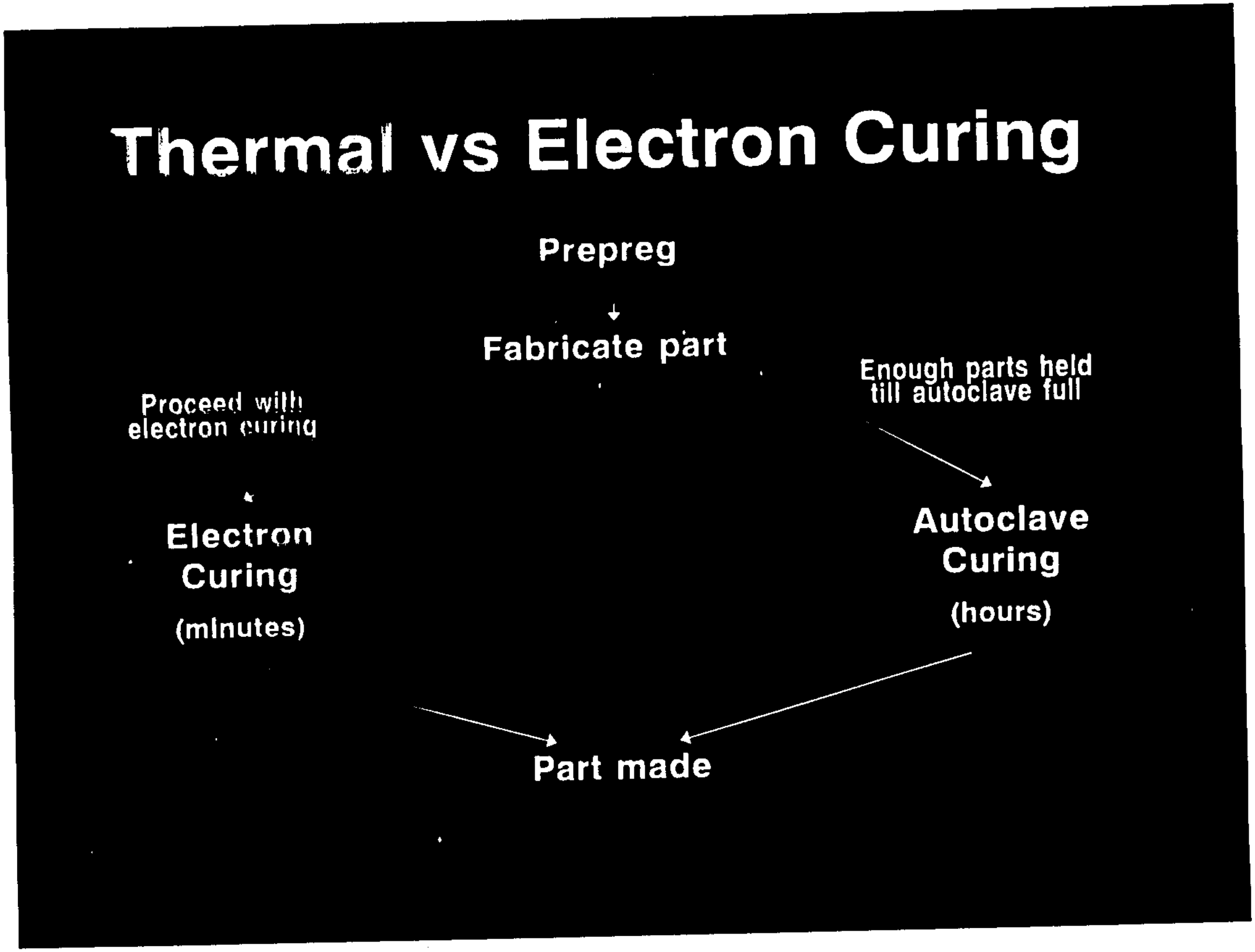
Radiation Processing
of
Advanced Composites

Industrial Applications for Fibre-Reinforced Advanced Composites

- Aerospace
- Aircraft
- Sports Equipment
- Automobile
- Marine
- Miscellaneous Consumer Items
- Importance
  - High strength to weight and stiffness to weight ratios

Annual Consumption: 1.5 x 10^6 kg/a

Growth: ~15%/a


Thermal vs Electron Curing
Prepreg
Fabricate part
Proceed with electron curing
Enough parts held till autoclave full
Electron Curing
(minutes)
Autoclave Curing
(hours)
Part made

Advantages
Electron Processing

- Ambient temperature cure reduces internal stresses
  Thermal curing: stresses at fibre matrix interface
  - precision of part dimensions affected
- Reduced curing times:
  Thermal: ~ 200 kg.h^{-1}
  Electron (50kW IMPELA): ~600 kg h^{-1}
- Reduced costs
  - improved resin stability at room temperature
  - parts cured immediately upon fabrication
  - energy costs for electron processing much lower

  Overall, cost reductions can be 30% or more.

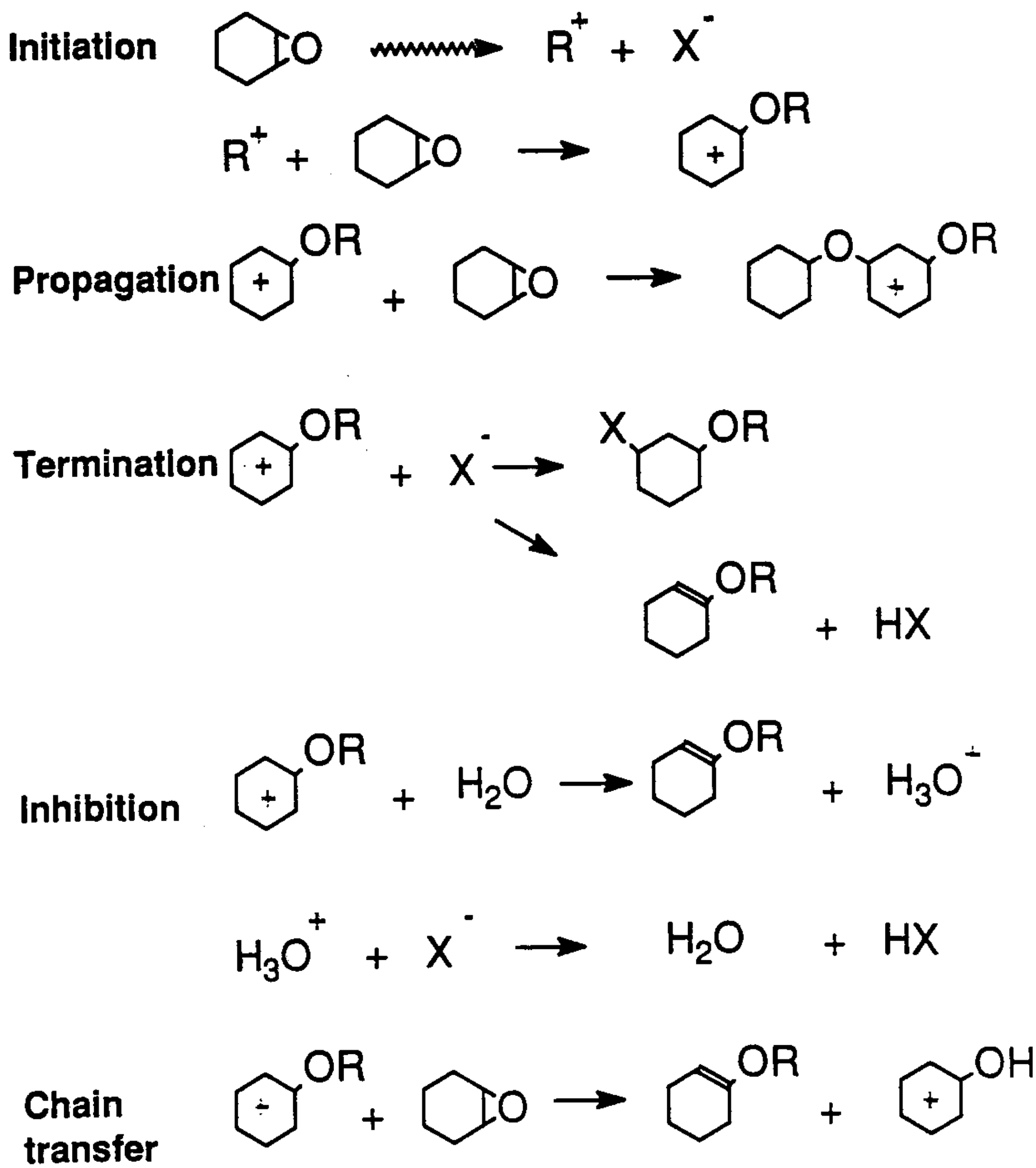
EB Curing - Constraints

- EB curable materials required
- Qualification procedures
- More complex, if pressure required during curing

Primary Components of Radiation Curable Formulations

- Multifunctional acrylates
- Acrylated oligomers
- Monofunctional diluent monomers
- Epoxies with radiation-initiators

Cyclohexene oxide
Radiation Polymerization

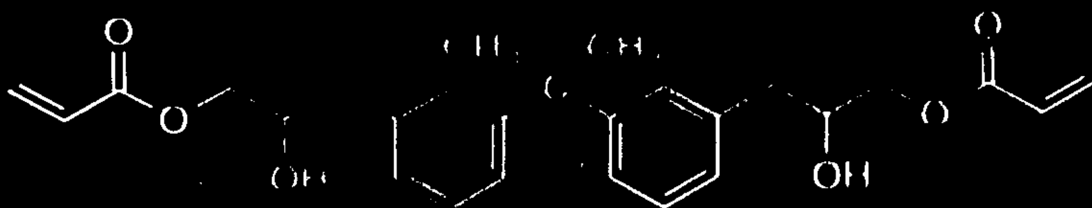


Typical Properties
Resins For Filament/Tape Winding

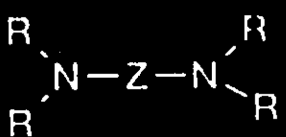
Property	Epoxies*			Acrylated Epoxies**			
				Difunc		Tetrafunc	
	#1	#2	#3	A	B	C	D
Ultimate Tensile Strength (MPa)	85	60	90	65	75	50	60
Tensile Modulus (GPa)	3	2.5	3	3	3	3	3
Elongation (%)	4-6	10	5	5	3	13	2
Glass Transition Temperature (°C)	145	100	175	120	120	85	180

* Thermally Cured; ** EB-Cured

Chemical Forms of EB-Curable Resins

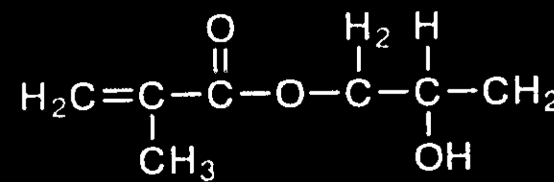


Difunctional Acrylated Epoxy

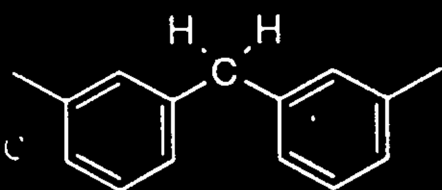


Tetrafunctional acrylated epoxy

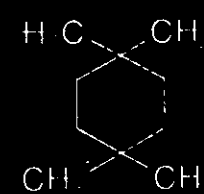
where R may be

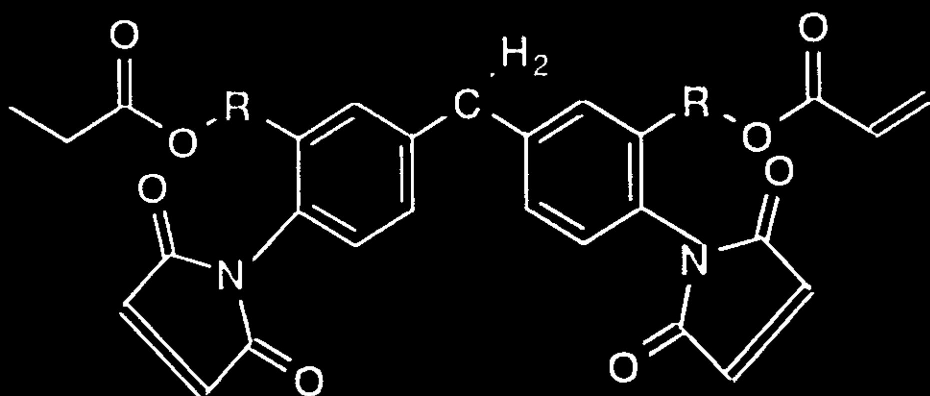


and Z may be aromatic



or cyclo aliphatic



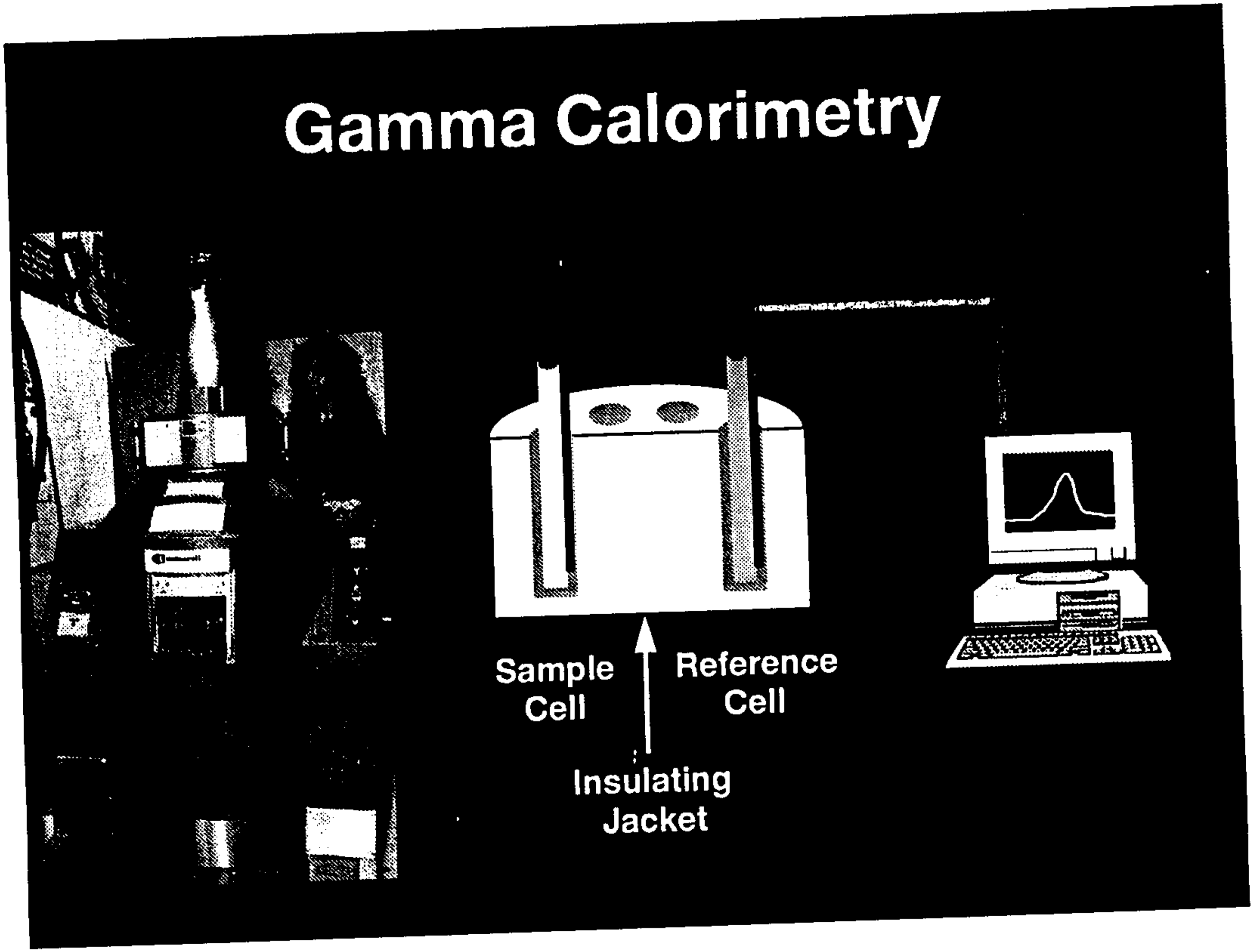


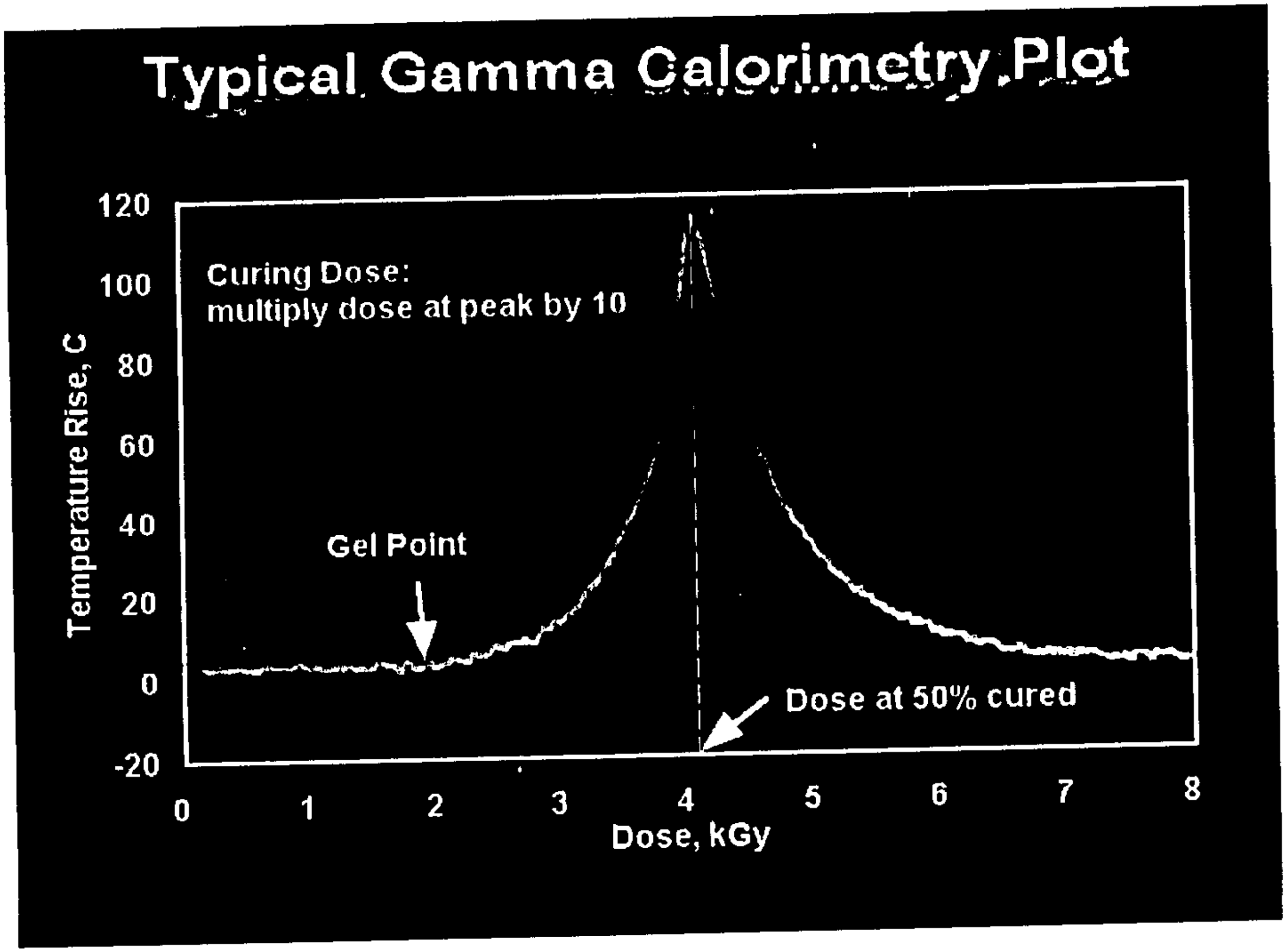
Acrylated bismaleimide

Relative Product Characteristics for Selected Resins

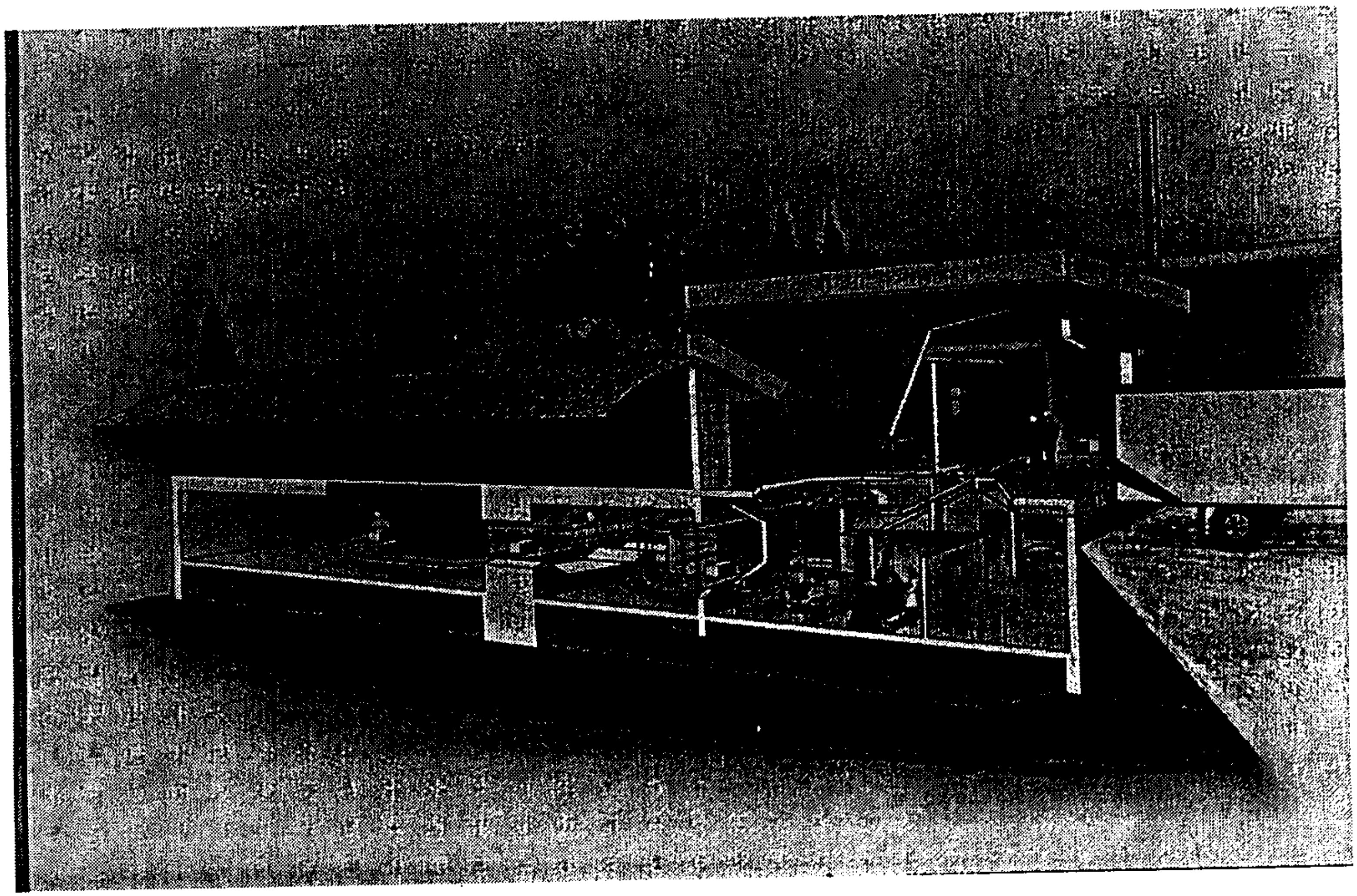
Property	Selected Resins				
	SR-399	SR-2000	SR-5000	SR-9503	SR-3000
Abrasion Resistance	X			X	X
Adhesion	X	X	X		X
Chemical Resistance	X				X
Flexibility	X	X	X	X	
Hardness	X				X
Impact Resistance		X	X		
Low Shrinkage		X	X	X	X
Water Resistance		X	X		X
Weatherability	X			X	

X-imparts specified property to the cured polymer

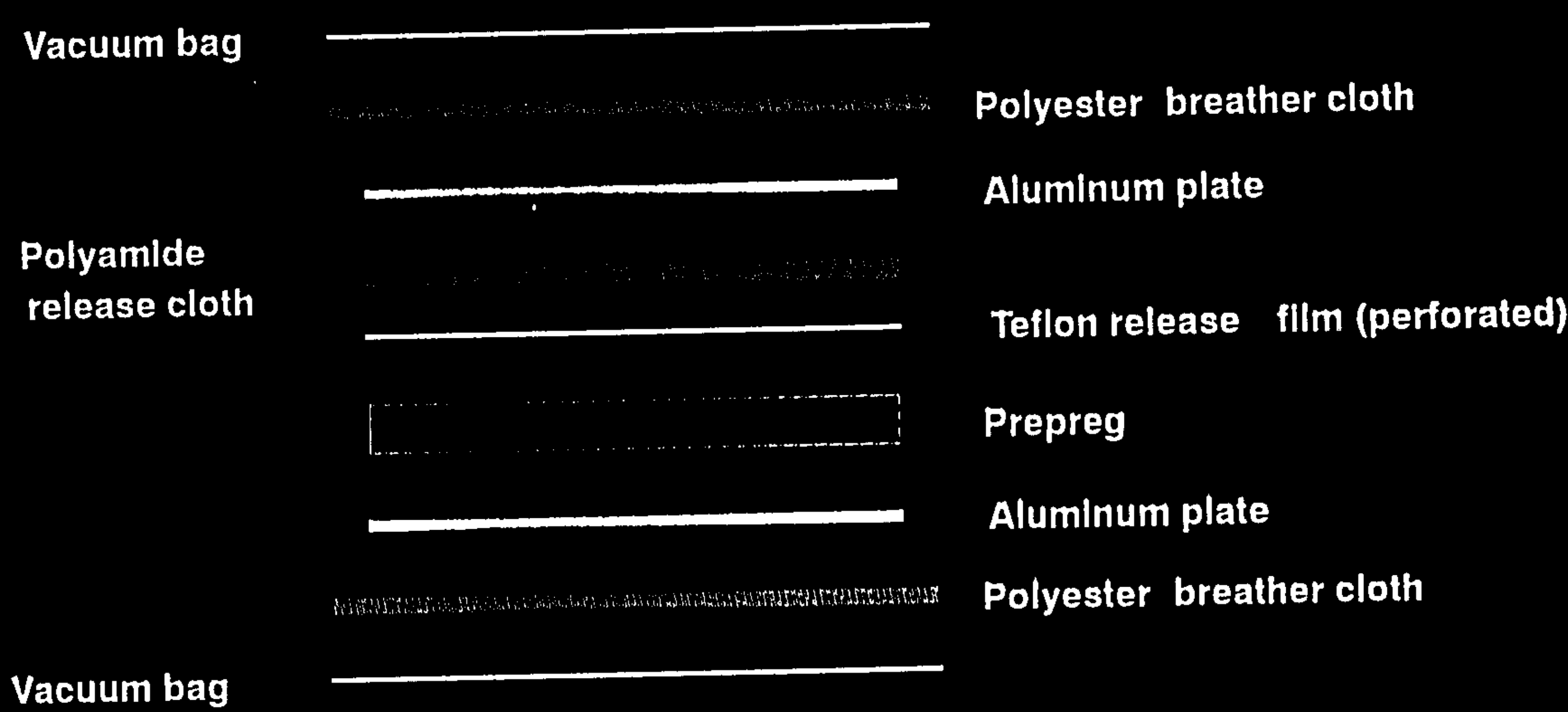

Gamma Calorimetry
Sample Cell
Reference Cell
Insulating Jacket


Typical Gamma Calorimetry Plot
Curing Dose:
multiply dose at peak by 10
Gel Point
Dose at 50% cured
Temperature Rise, C
120
100
80
60
40
20
0
-20
0
1
2
3
4
5
6
7
8
Dose, kGy

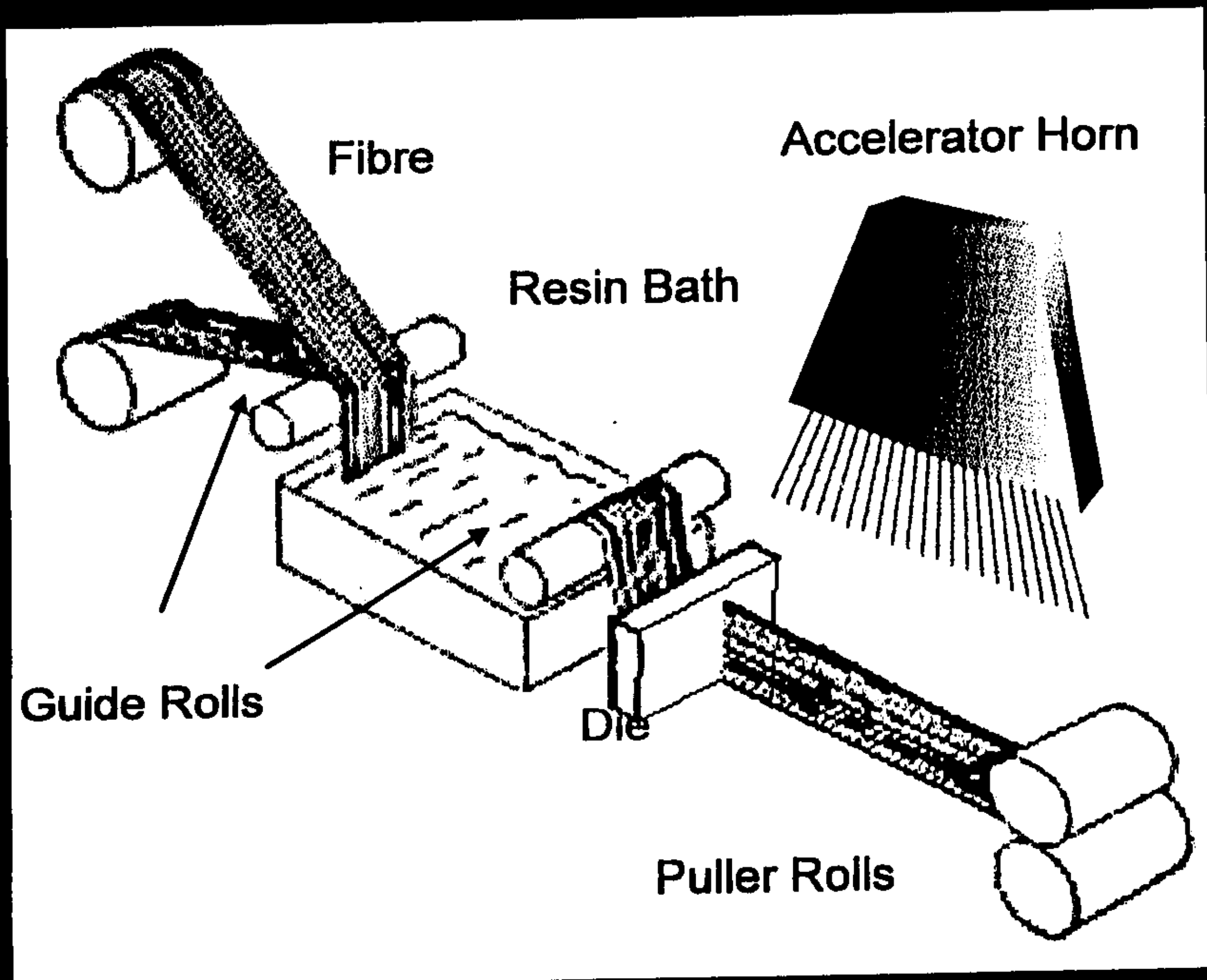
Whiteshell Irradiator I-10/1

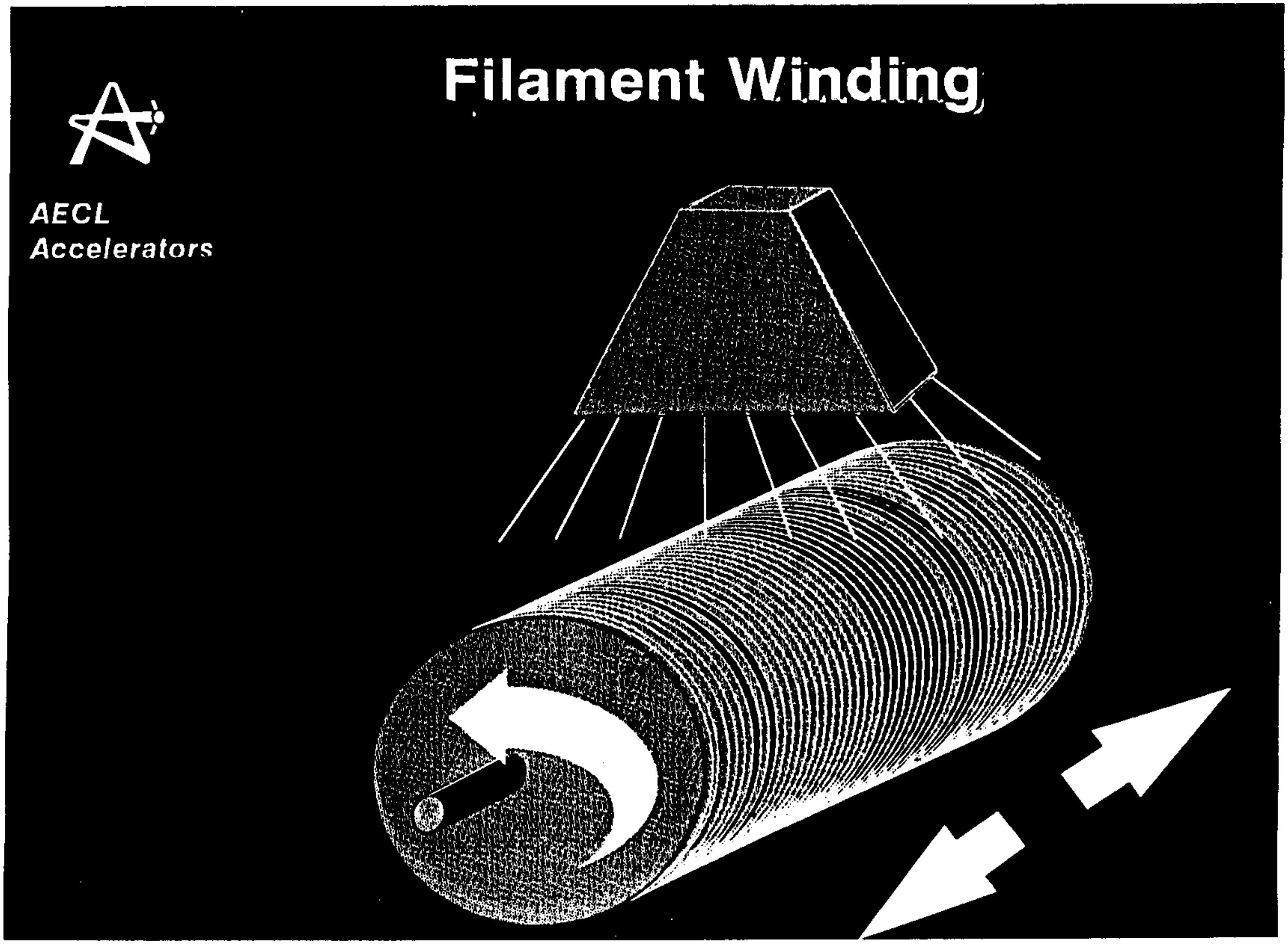


Carbon-fibre Epoxy Lay-up

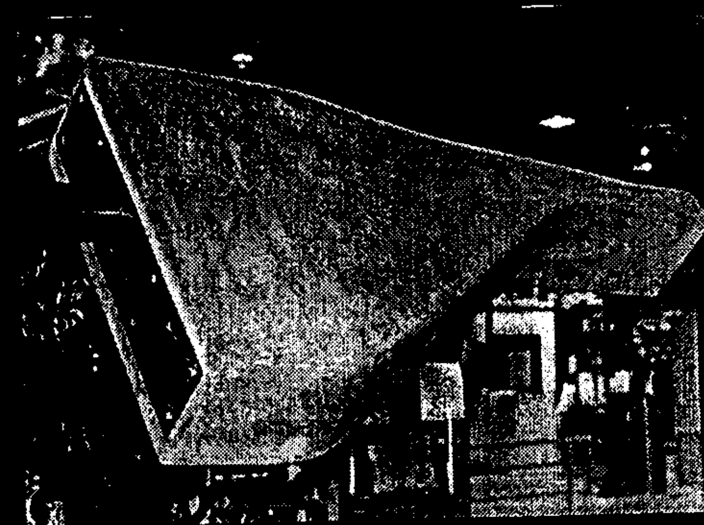


Pultrusion


Fibre
Accelerator Horn
Resin Bath
Guide Rolls
Die
Puller Rolls


Filament Winding
AECL
Accelerators

Typical EB Process



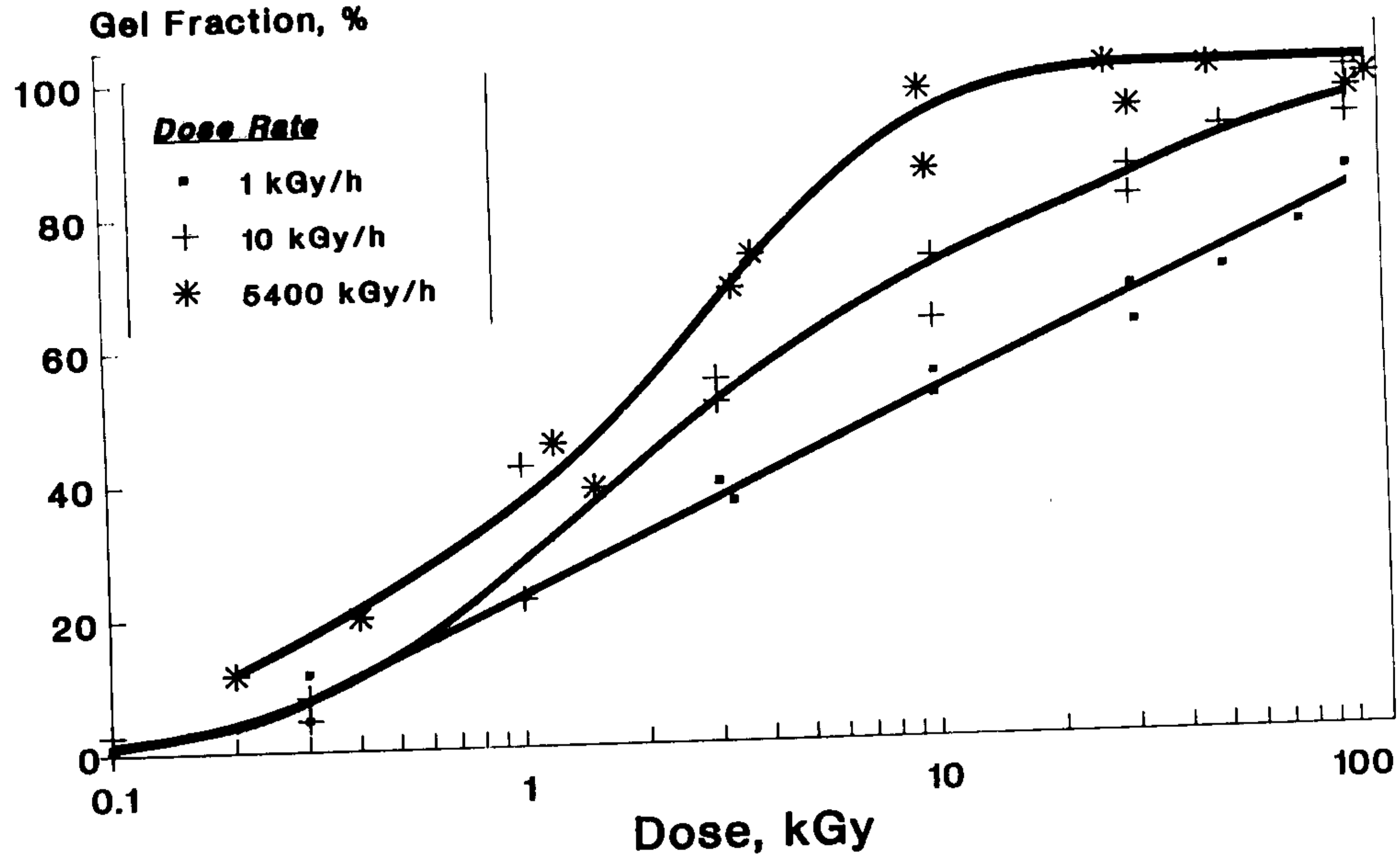
- Material selection
  - * Resins * Fibers
  - * Interface chemistry
  - *Adhesives
- Consolidation
- Fabrication
  - Layup * Tape placement
  - VARTM * Filament winding
- EB Cure/QA

Typical Mechanical Properties
EB-Cured Carbon Fabric Laminates

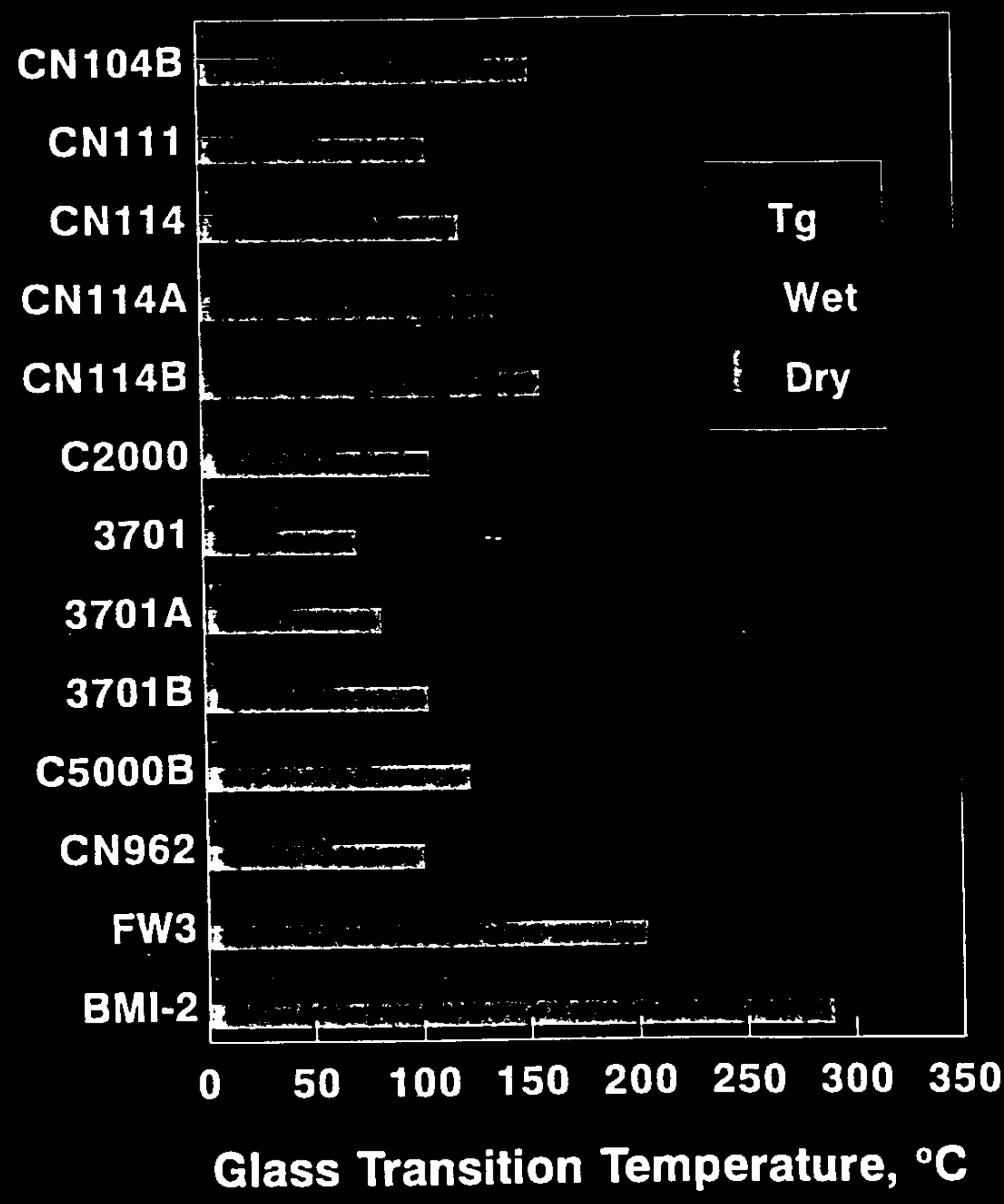
Property	Minimum Specifications Average	Minimum Specifications Value	Sample Properties Average	Sample Properties Minimum Value
Tensile:				
Strength, MPa	465	400	600	565
Modulus, GPa	57	53	60	50
Compression:				
Strength, MPa	460	300	460	390
Modulus, GPa	50	40	70	55

14-ply; same orientation; tested at 20°C

Gel Fraction
C3000 (Epoxy diacrylate)

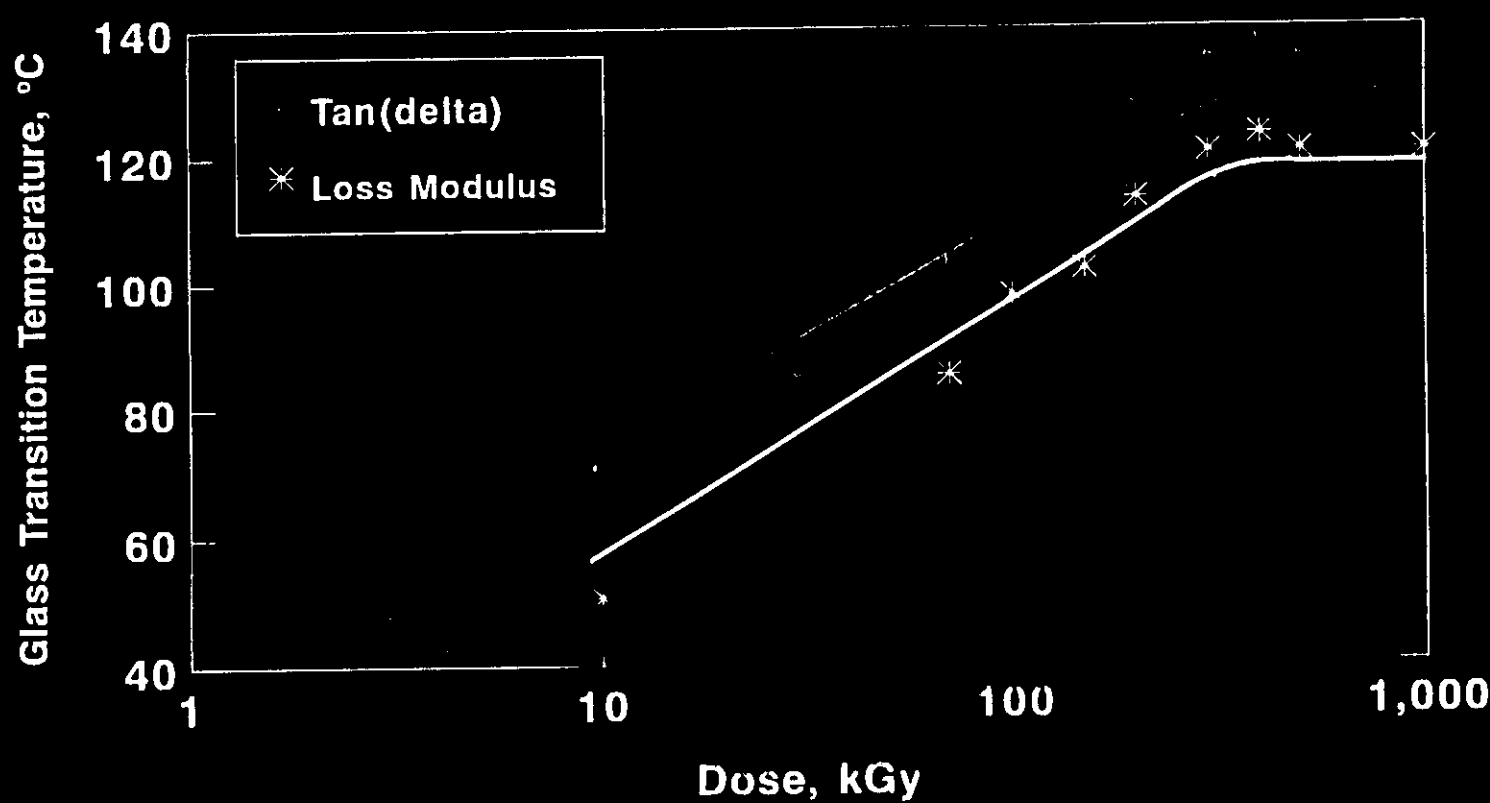


Glass Transition Temperature
Electron-cured Resins and Blends

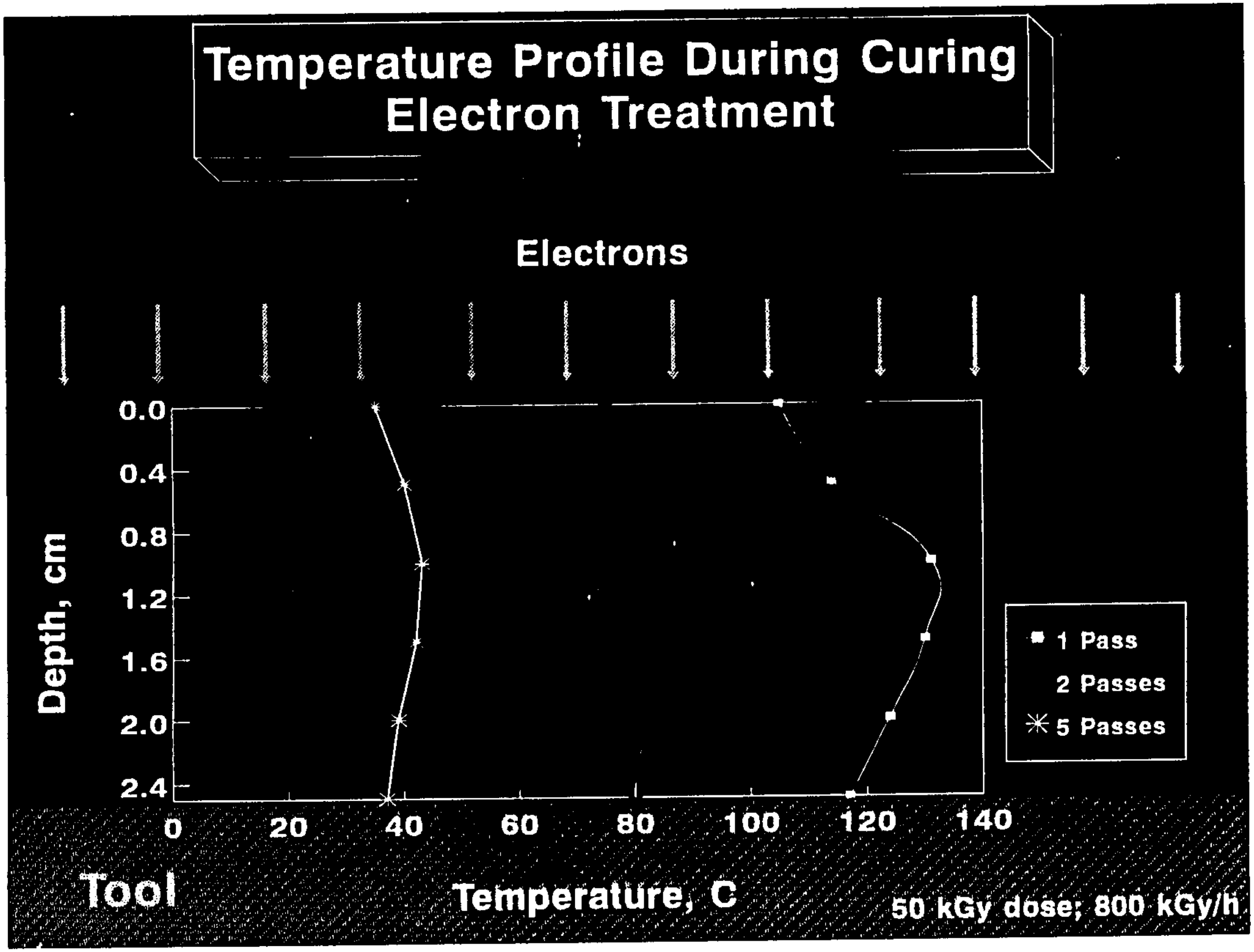


A: 10% pentaacrylate; B: 25% pentaacrylate

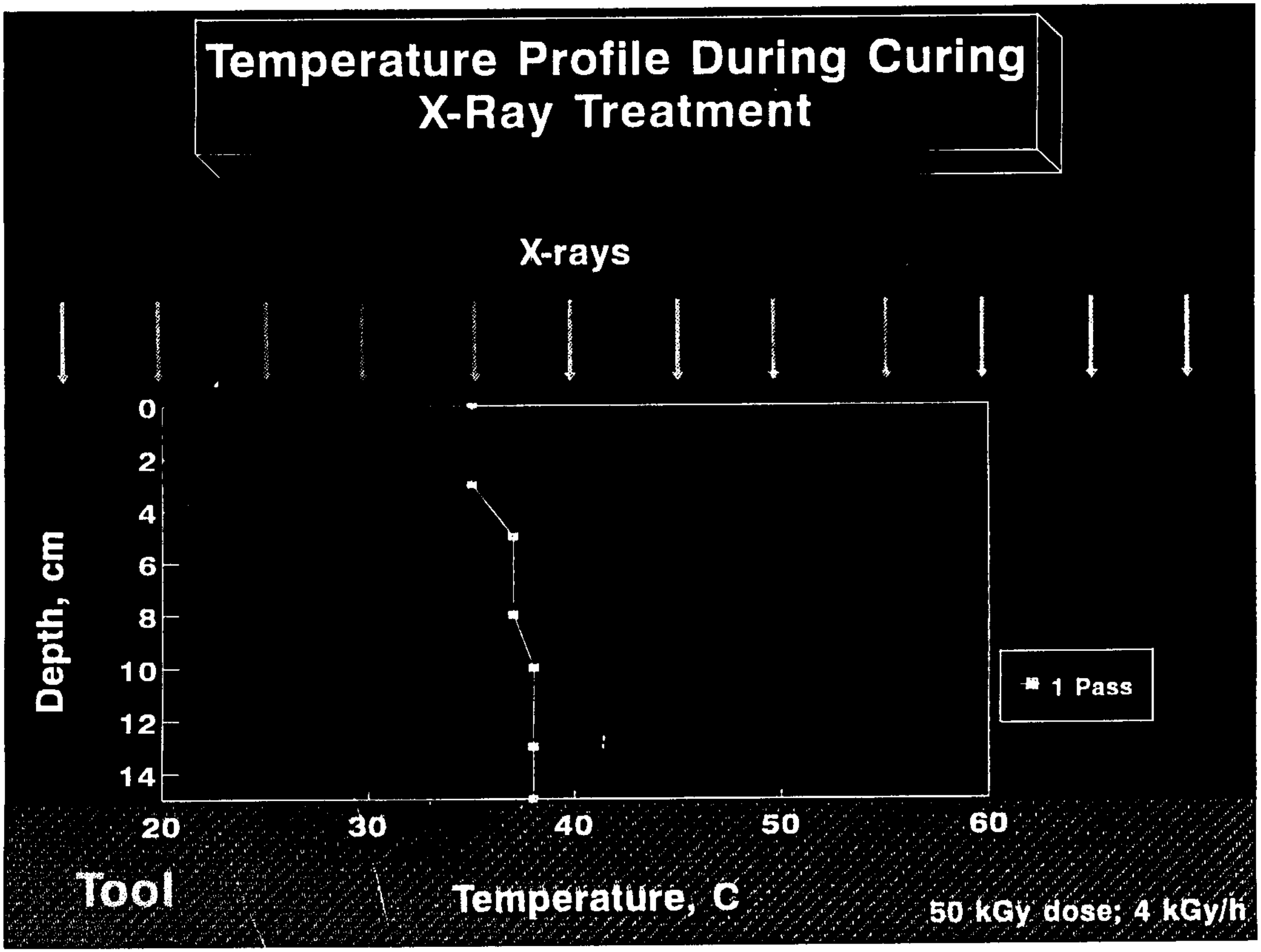
Effect of Electron Dose
Glass Transition Temperature



CN104, Epoxy Diacrylate



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


Temperature Profile During Curing
X-Ray Treatment
X-rays
Depth, cm
0
2
4
6
8
10
12
14
20
30
40
50
60
Temperature, C
1 Pass
Tool
50 kGy dose; 4 kGy/h

Amount of Volatiles Released from Selected Matrix Polymers During Curing

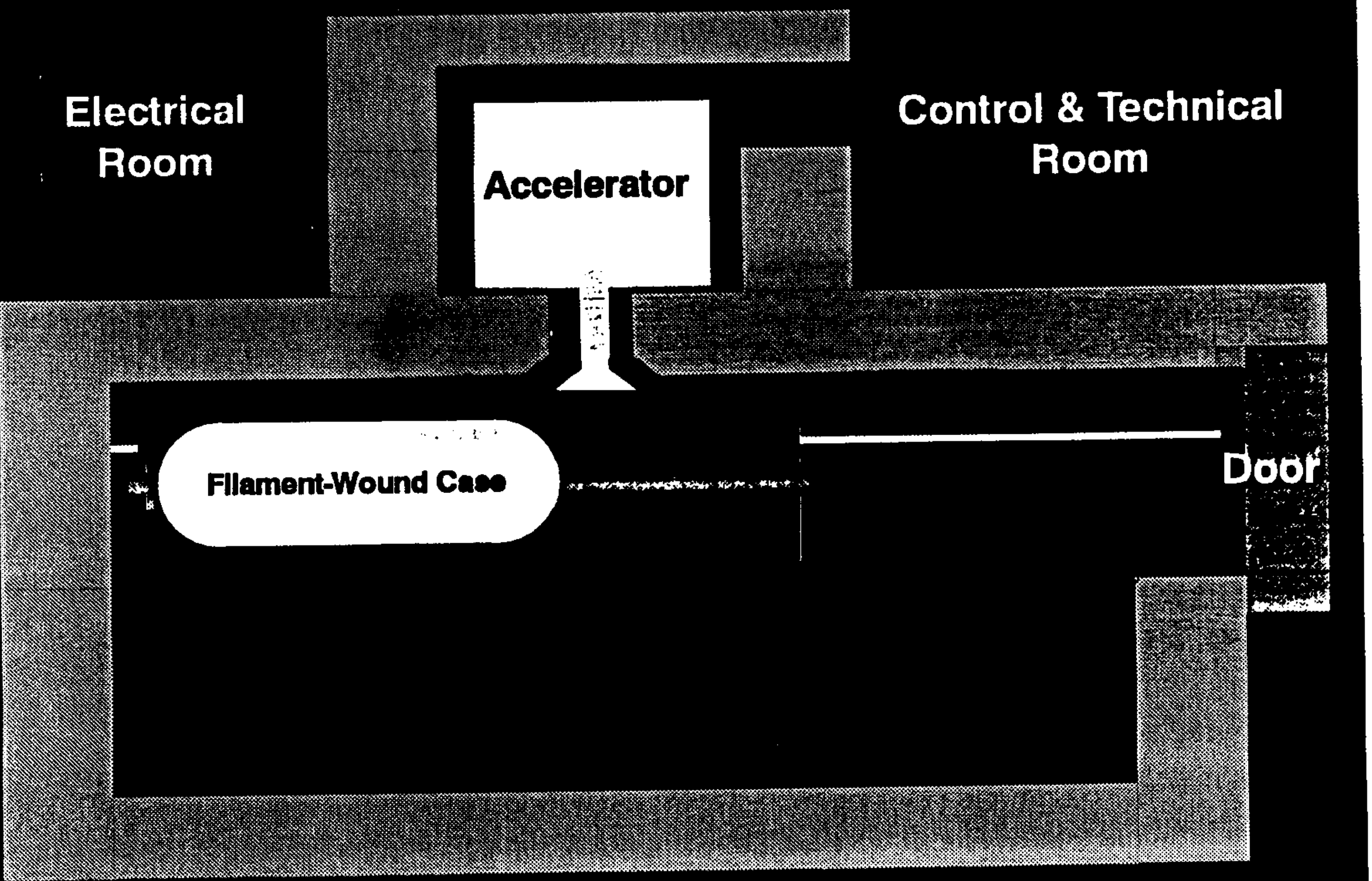
Curing Method	Material	Curing Cycle @25°C	Volatiles (mg/g)
Electron	CN-104	50-100 kGy	< 0.005
Electron	CN-114	50-100 kGy	< 0.005
Electron	Derakane 470-36	50 kGy	0.75*
Catalyst	Derakane 470-36	20 min	3.0
Thermal	Hysol epoxy RE-2039	2 hr @ 150°C	3.45
Thermal	PMR-15	300°C	1.38

* blank = 0.78

Aerospatiale's Composites Program

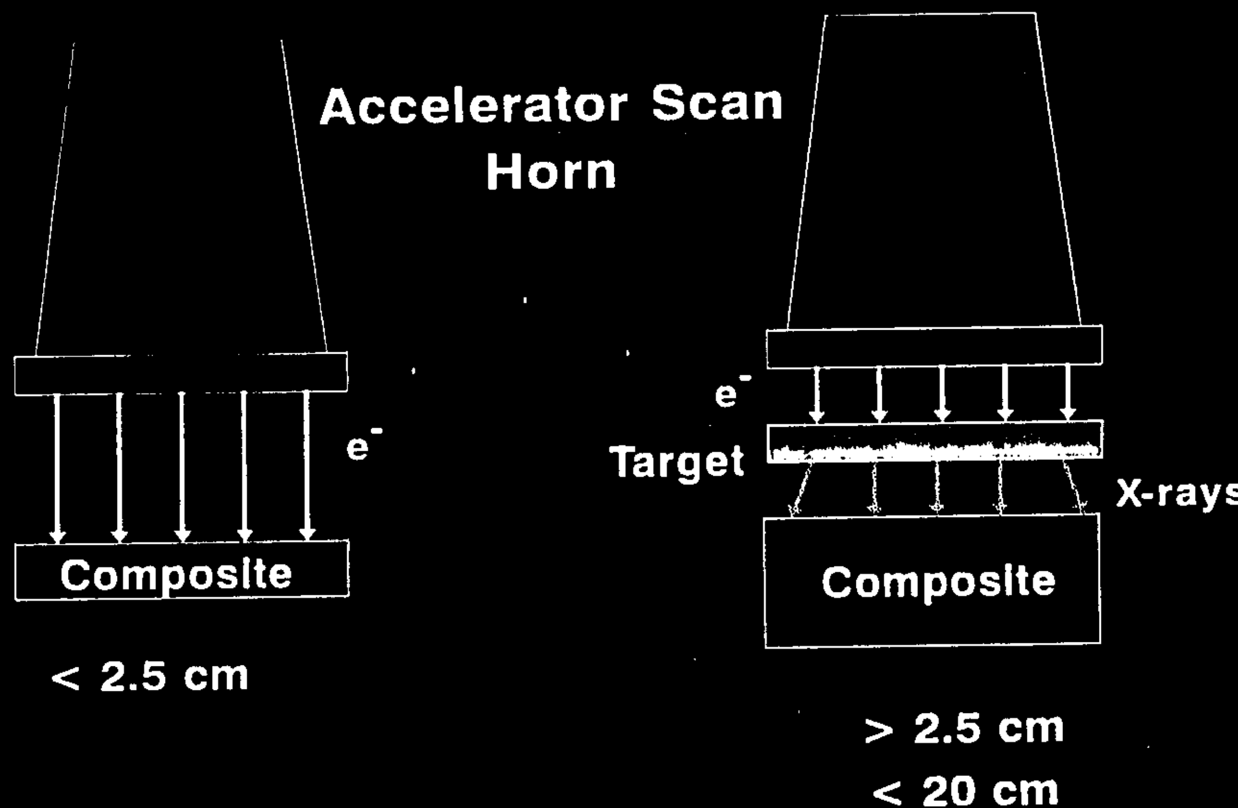
- R&D started, early eighties
- Endorsed technology (1987)
- Commercial facility approved (1988); operational in 1991
- Designed to cure tape-wound products
  - Diameter, 0.1 to 4.0 m
  - Length, 1.5 to 10.5 m
  - Thickness, 1 to 10 cm
- 10 MeV, 20 kW accelerator
- Cure time reduced, 100 to 8 hours

Aerospatiale Facility



AECL
Accelerators

Typical X-Ray Conversion



CRADA

Cooperative Research & Development Agreement

- Objective
  to conduct R&D to better understand and utilize electron beam polymer matrix composite curing technology

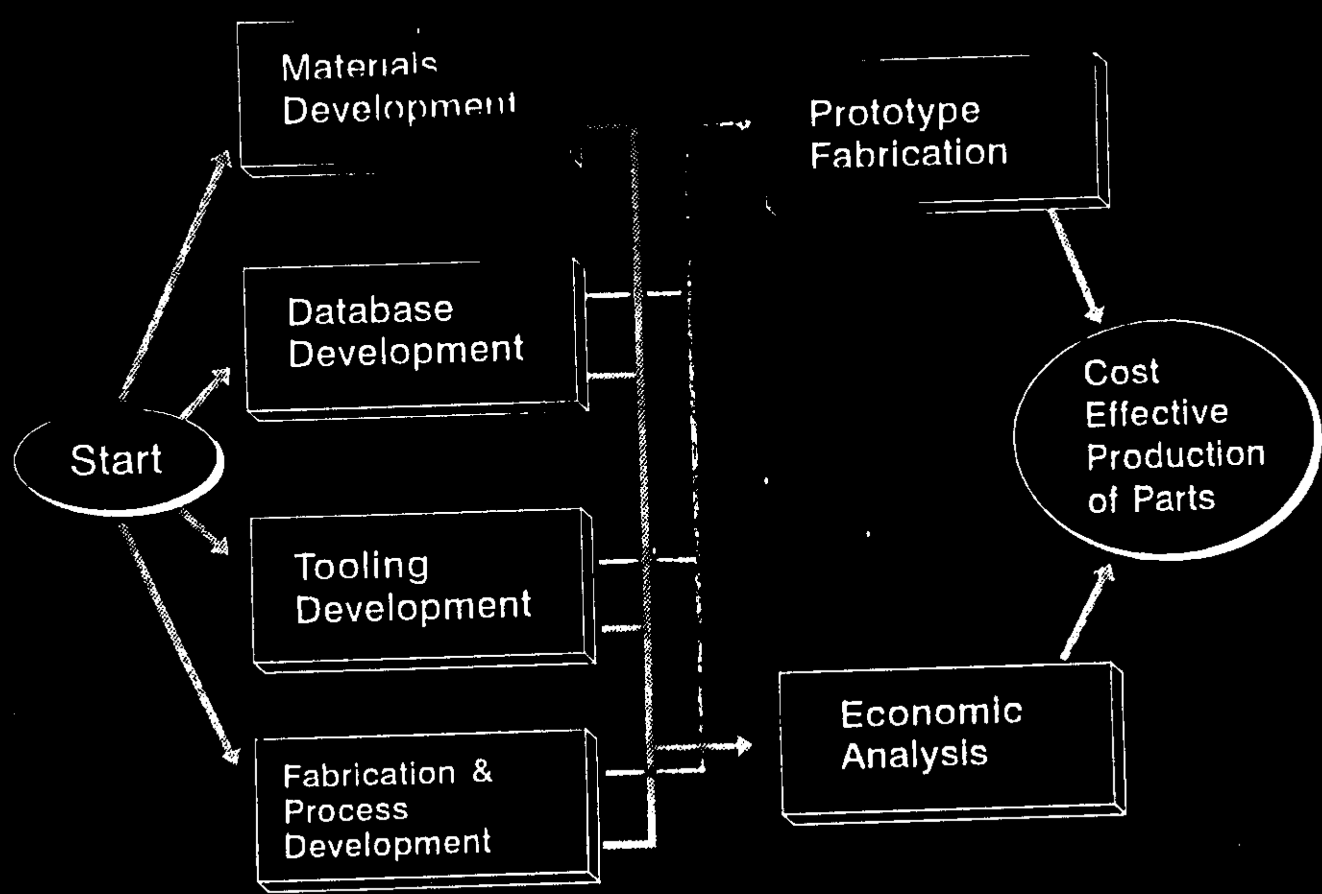
- Project length: 3 years

- Value: $Cdn 9 million
  $ 4.5 million contributed by industrial partners
  $ 4.5 million contributed by US DOE

- Partnership
  10 industrial partners
  2 national laboratories

- Areas of study
  - Electron beam resin development
  - Electron beam database development
  - Economic analysis
  - Low-cost electron beam tooling development
  - Electron beam curing systems integration
  - Demonstrate protype structures

EB Curing Technology Development Program



Radiation Curing of Epoxies in Mixtures

- *Epoxy - Catalyst Mixtures*

  - The addition of primary amines, ferrocene, triphenylsulfonium borofluoride, phenyldiazonium borofluoride, diphenyldiazonium borofluoride and maleic anhydride have been used to reduce the dose required for radiation polymerization of certain epoxies

  - No universal promoter discovered to date

Epoxy Resin Families

- Bisphenol A based
- Bisphenol F based
- Cycloaliphatic based
- Multifunctional
- Blends of the above

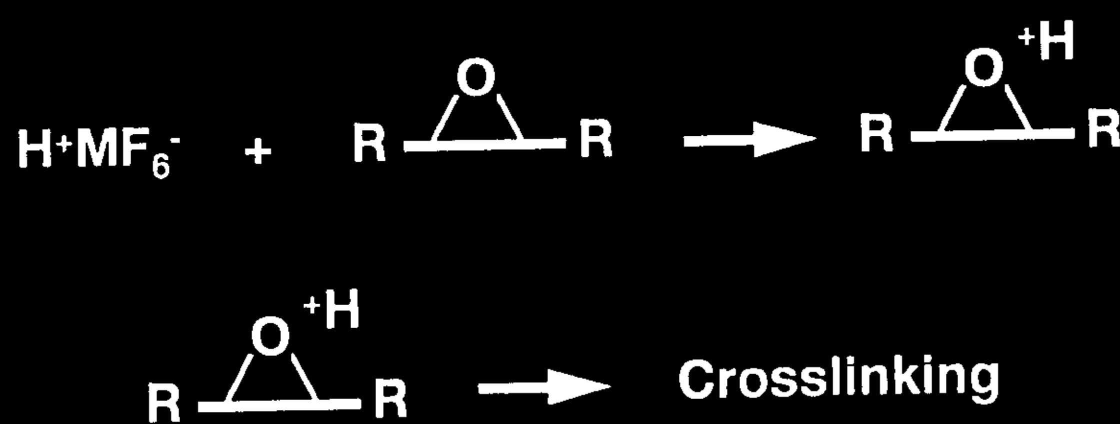
Optimizing Properties of EB-Curable Fiber Reinforced Composites

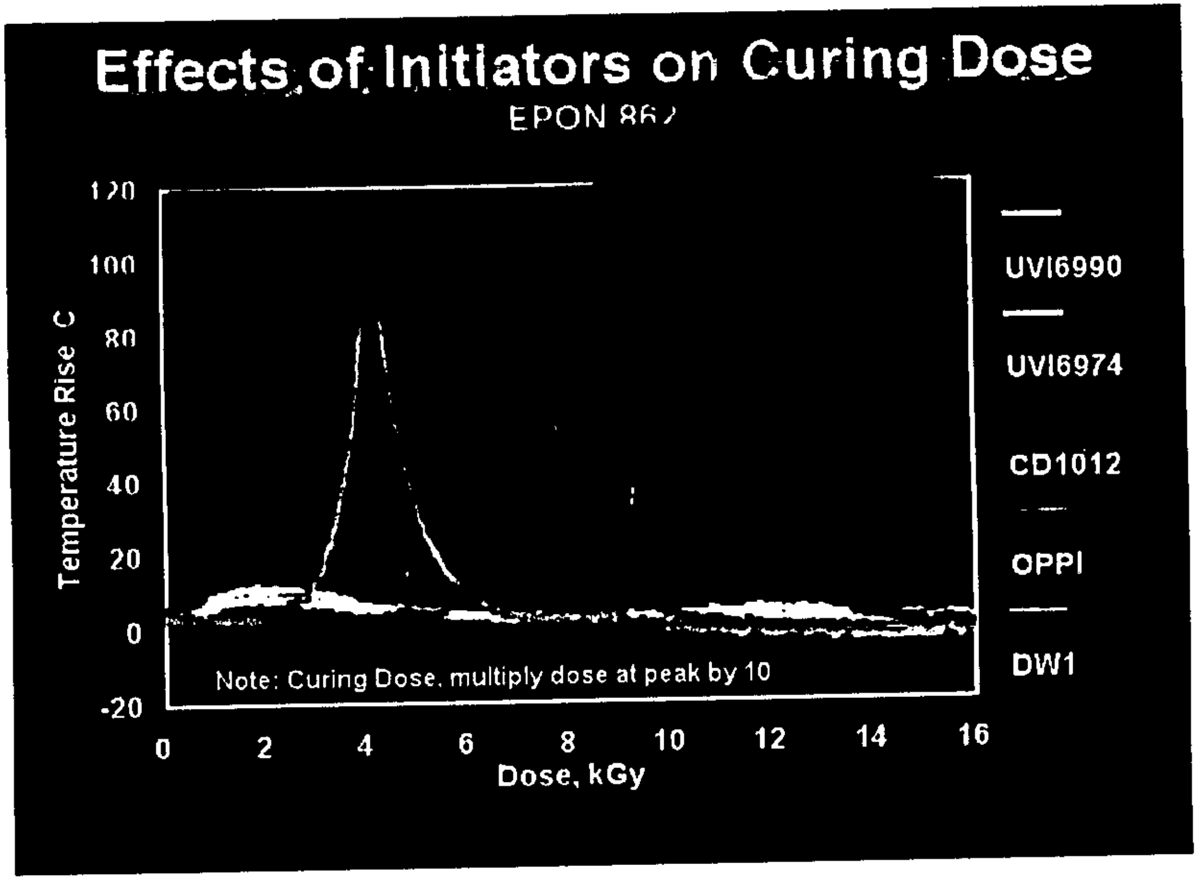
- Most Efficient Cationic Initiator
- Initiator Concentration
- Curing Dose
- Dose Rate and Radiation Type
- Epoxy Mixture for end-use
- Fiber Sizing
- Processing Conditions

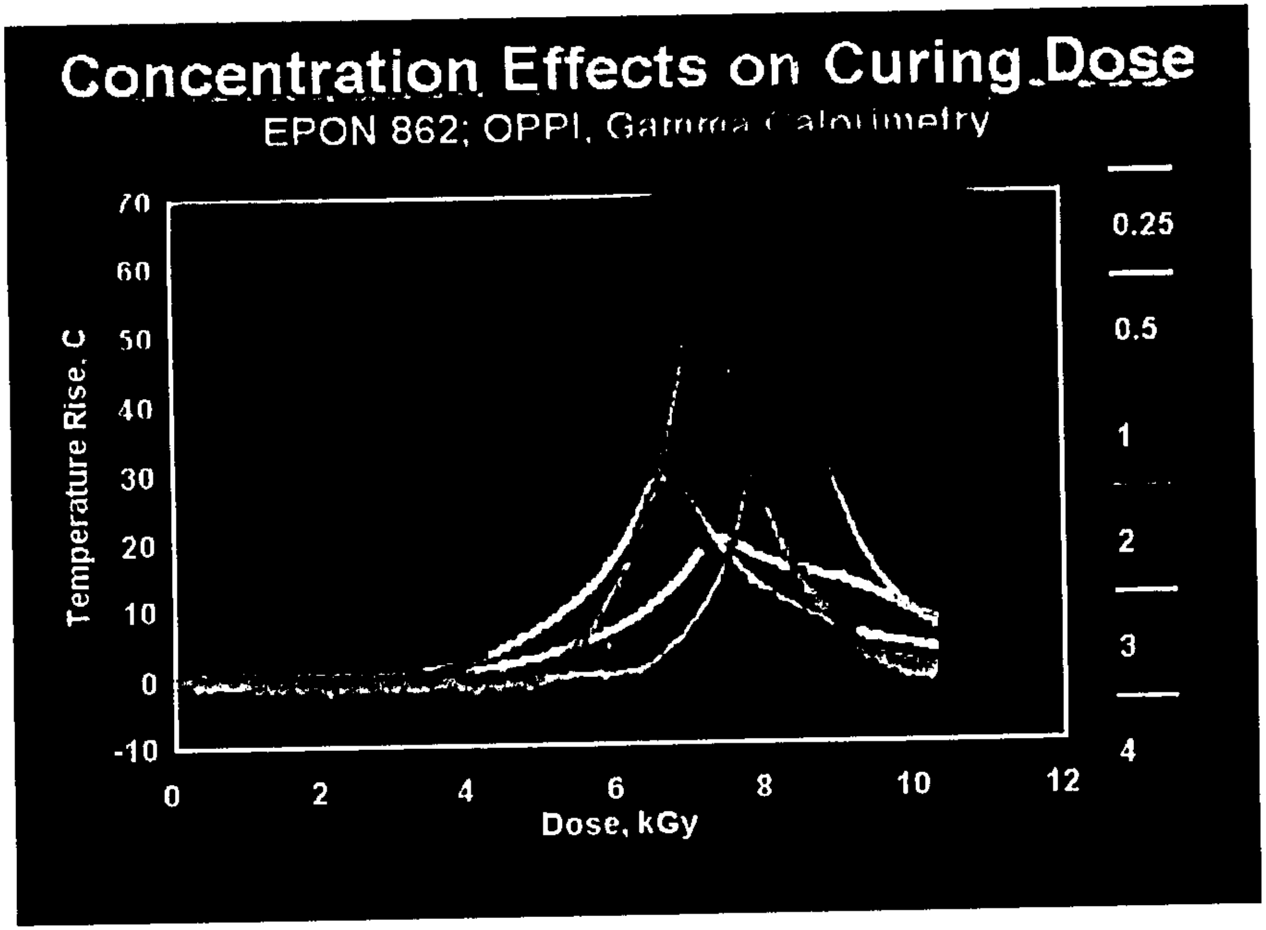
Cationic Intiators

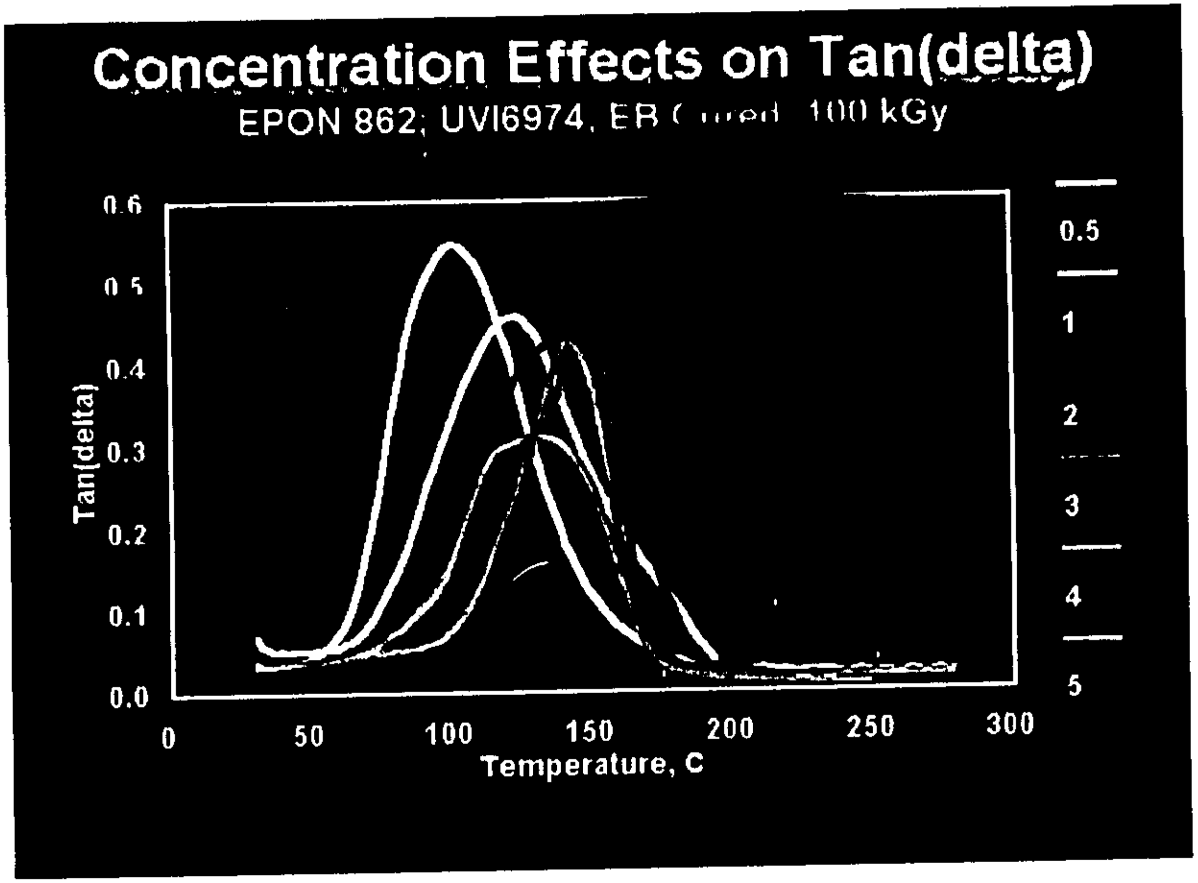
SbF_6^- > AsF_6^- > PF_6^- > BF_4^-

$Ar^+MF_6^-$ $\xrightarrow{e^-,\ e^-(x),\ \gamma,\ UV}$ $H^+MF_6^-$




Effects of Initiators on Curing Dose
EPON 86
Temperature Rise C
120
100
80
60
40
20
0
-20
0
2
4
6
8
10
12
14
16
Dose, kGy
UVI6990
UVI6974
CD1012
OPPI
DW1
Note: Curing Dose, multiply dose at peak by 10


Concentration Effects on Curing Dose
EPON 862; OPPI, Gamma Calorimetry
Temperature Rise, C
70
60
50
40
30
20
10
0
-10
0
2
4
6
8
10
12
Dose, kGy
0.25
0.5
1
2
3
4


Concentration Effects on Tan(delta)
EPON 862; UVI6974, EB Cured 100 kGy
Tan(delta)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
50
100
150
200
250
300
Temperature, C
0.5
1
2
3
4
5

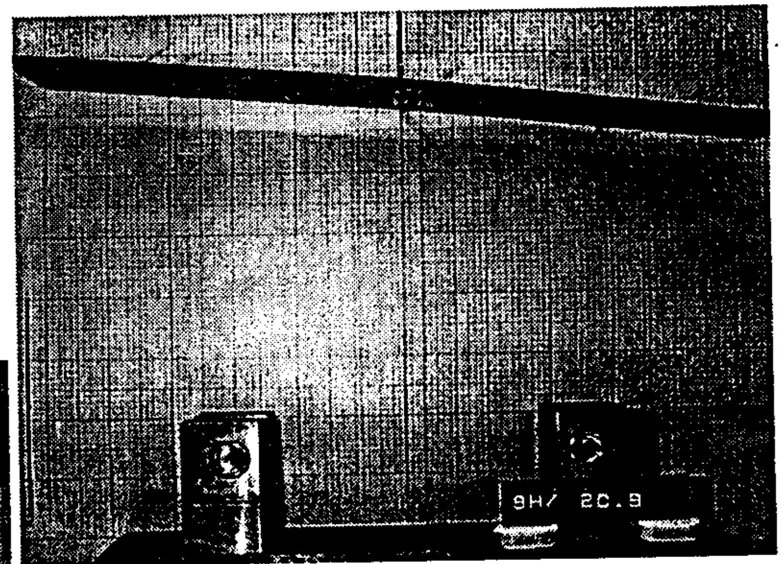
Curing and Rheological Properties

Resin	Initiator	Conc. phr	Curing Dose kGy	Service Temperature °C	Tg(E") °C
Epon 862	UVI6974	3	20	104	102
	CD1012	3	120	143	156
	OPPI	2	60	147	154
	DW1	2	38	145	155
Tactix 123	UVI6974	3	22	94	92
	CD1012	3	74	165	180
	OPPI	2	48	164	164
	DW1	2	29	161	163

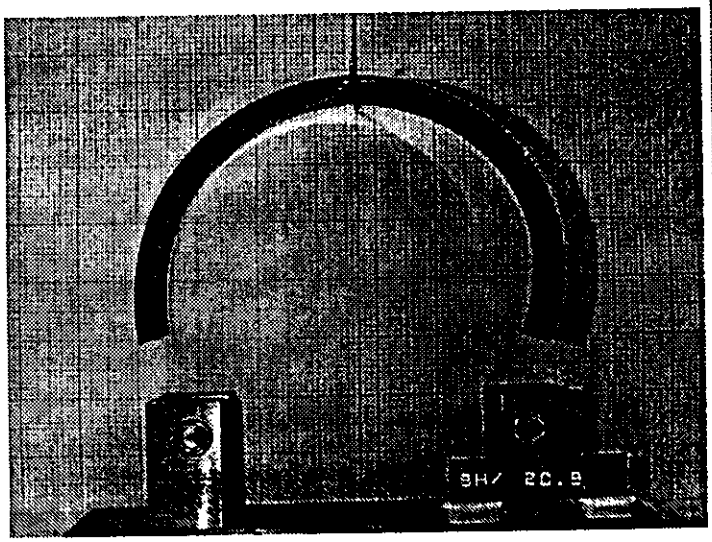
Curing and Rheological Properties

- Optimum initiator concentration 2-3 phr
- Curing dose changes with the initiator used
- Rheological properties change with the initiator used

Effect of Cure Temperature on Internal Stress



25^{0}C;EB-5; IM-7; 2-ply; 50% RH



133^{0}C;EB-5; IM-7; 2-ply; 50% RH

Features of EB-Curable Resins

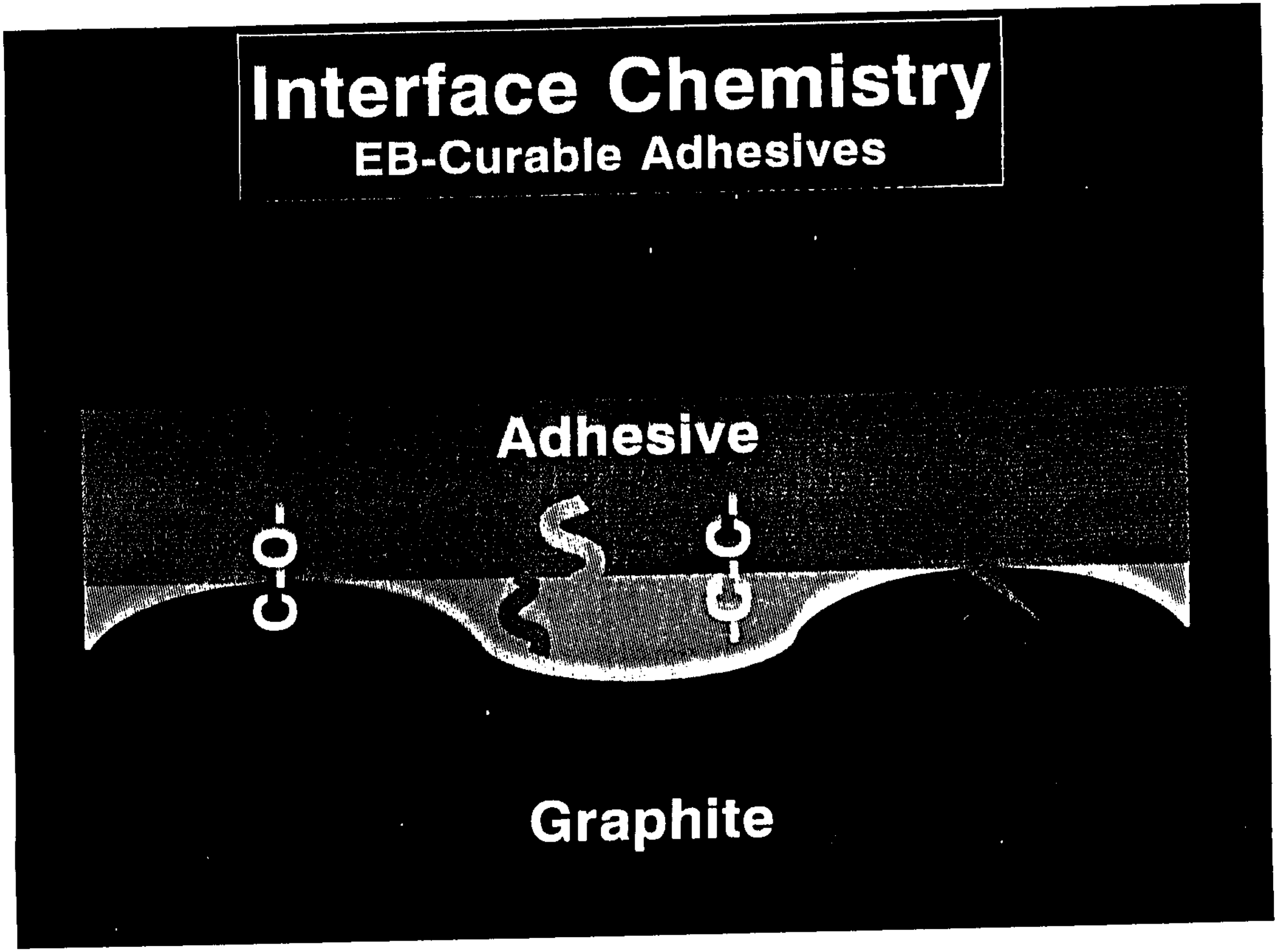
Features	EB-Curable Epoxy	Thermosetting Epoxy
Mechanical Properties	high-performance	high-performance
Manufacturing Costs	moderate	high
Prepreg Storage/Handling	extended life @ 20°C	limited life @ 0°C
Environmental Concerns	low	moderate to high
Shrinkage on Curing (%)	2-3	4-6
Volatile Emissions (%)	<0.1	<1.0
Transition Temp. (°C)	up to 400	up to 300
Residual Stresses	low	moderate to high
Water Absorption (%)	<2	<6
Production Throughput	Fast	Slow

Features of EB-Curable Resins

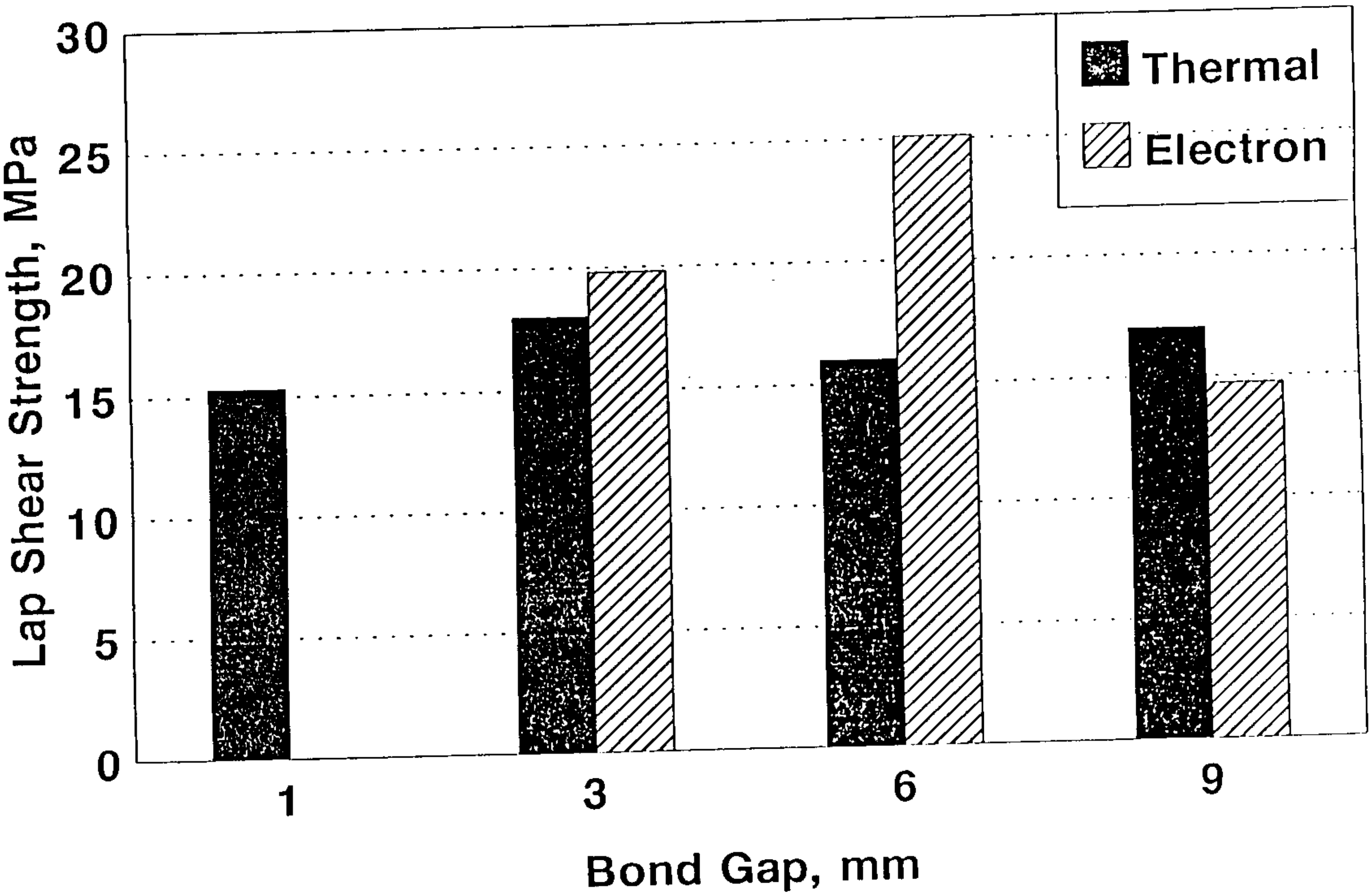
Features	EB-Curable Epoxy	Thermosetting Epoxy
Thickness Limit	50 mm (EB) 200 mm (X-ray)	20 mm
Tooling Materials	metals, wood, ceramics, plastics, waxes, foams	metals, ceramics, graphite
Tooling Costs	low-moderate	moderate-high
Cure Time (10-mm-thick)	seconds-minutes	hours
Energy Requirements	low to moderate	moderate to high
Capital Cost (facility)	high	high to very high
Materials Availability	Resins/Initiators Available	Resins/Hardeners Available
Material Cost - complete system ($/lb)	2-5 (commercial), 8-20 (high-perf.)	2-4 (commercial), 8-20 (high-perf.)

EB Curable Adhesives
Advantages

- Room temperature curing
- Internal stress much lower
- Energy efficient
- Faster curing cycle
- Lower volatile emmissions


Interface Chemistry
EB-Curable Adhesives
Adhesive
Graphite

Effect of Bond Gap

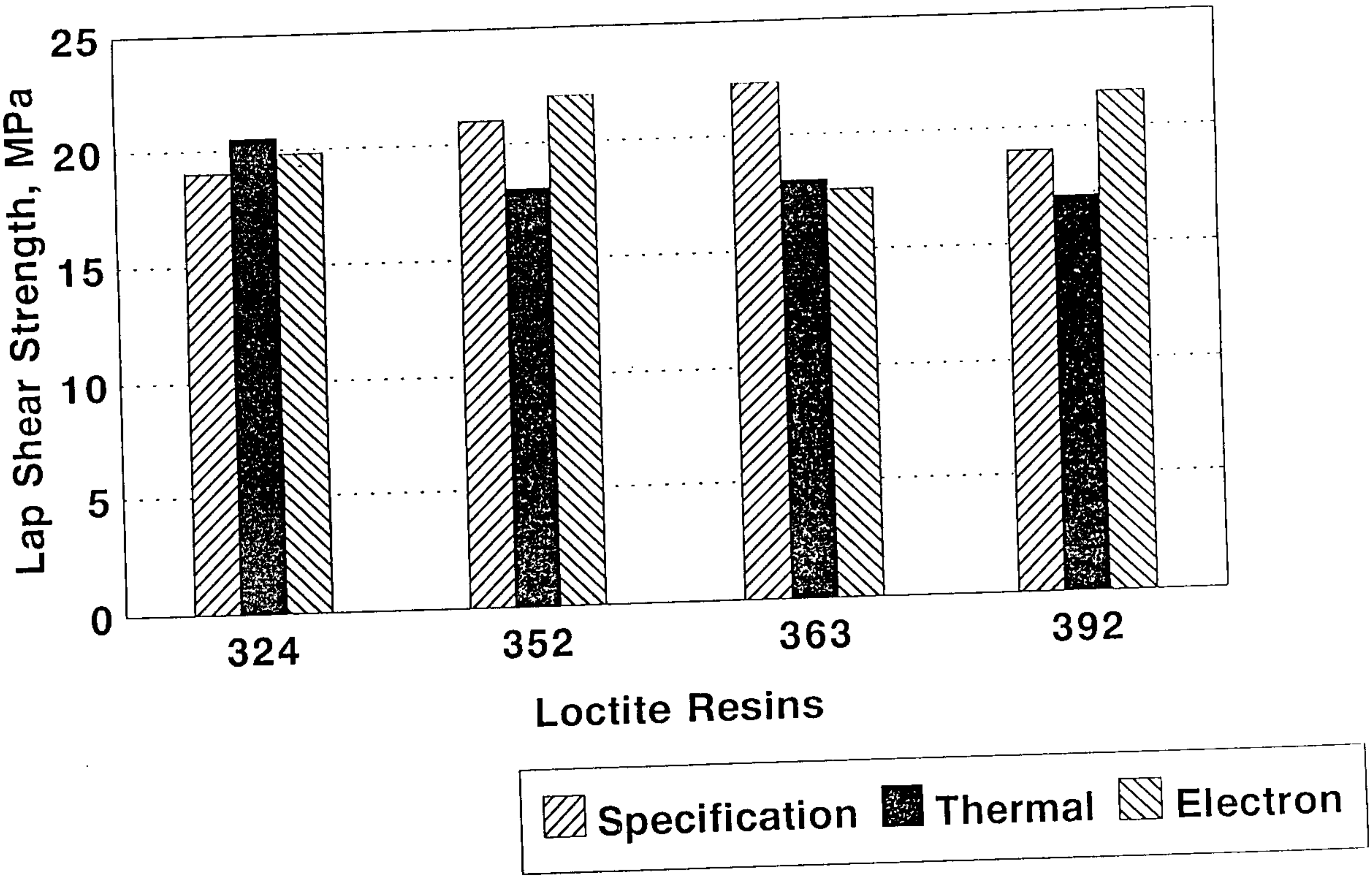


ctite 363; sanded; 50 kGy dose

Status

- Work started by Aerospatiale (~ 1983) and by us (~1986)
- Led to Aerospatiale dedicating (1988-1991) a 10 MeV, 20 kW electron accelerator to production of rocket motor casings (carbon fibre reinforced acrylated epoxy)
- We demonstrated production of thin and thick laminates of advanced composites using acrylated epoxies
- Led to extensive collaboration with North American aerospace industry
- Developed radiation curing of epoxies used by aerospace industry
- Feasibility studies on use of technology by the aerospace industry very positive

Adhesive Shear Strengths



nm bond gap; sanded; 50 kGy dose

Concluding Remarks

- Electron processing of advanced composites, at the threshold of commercialization
- Several types of fibre-reinforced composites can be electron processed
- Availability of 10-MeV industrial electron accelerators, important for this application
- Very large components can be radiation cured, with large enough target room
- Ability to join composite parts with radiation-curable adhesives, an added advantage