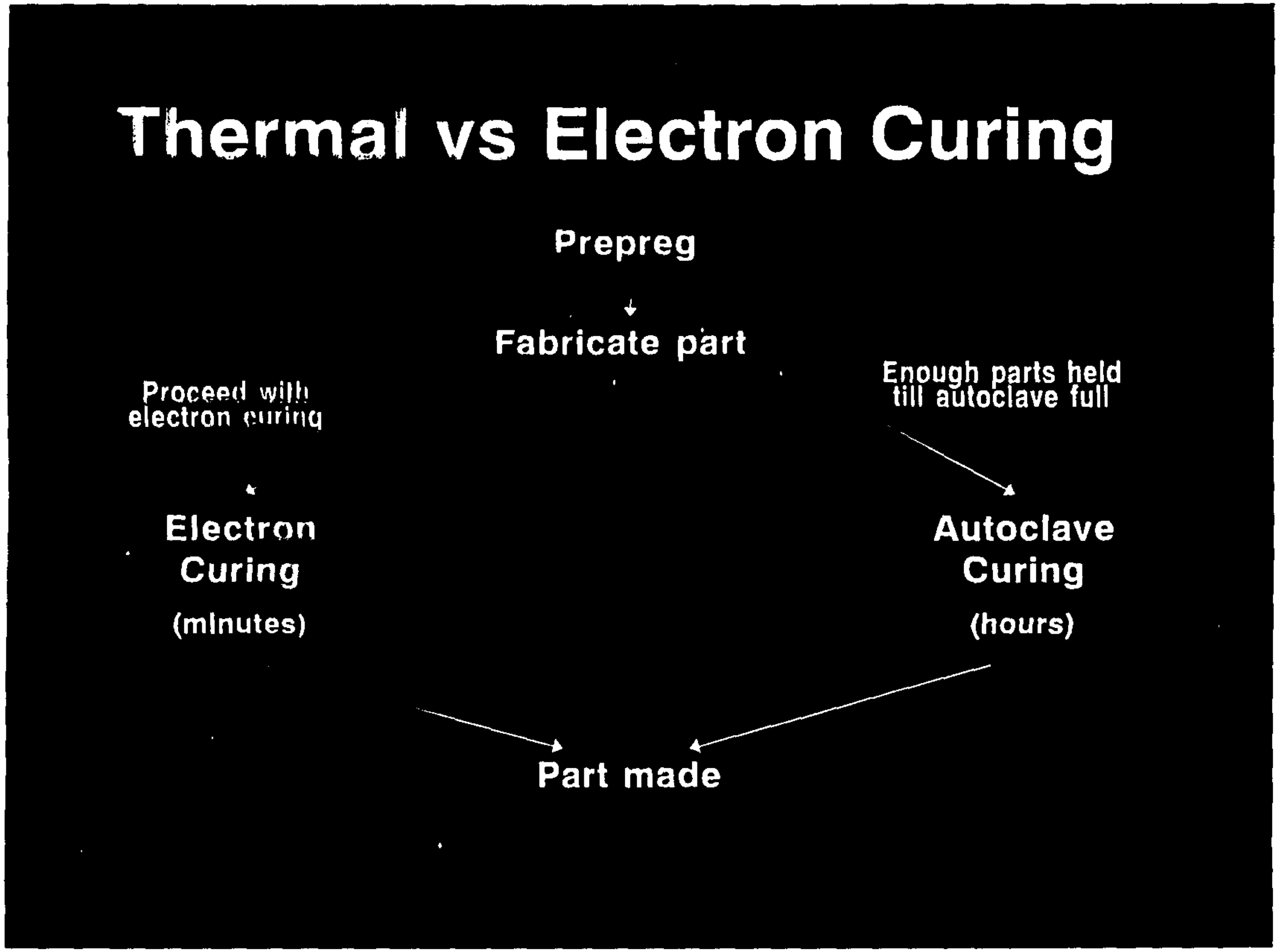
Radiation Processing of Advanced Composites

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.

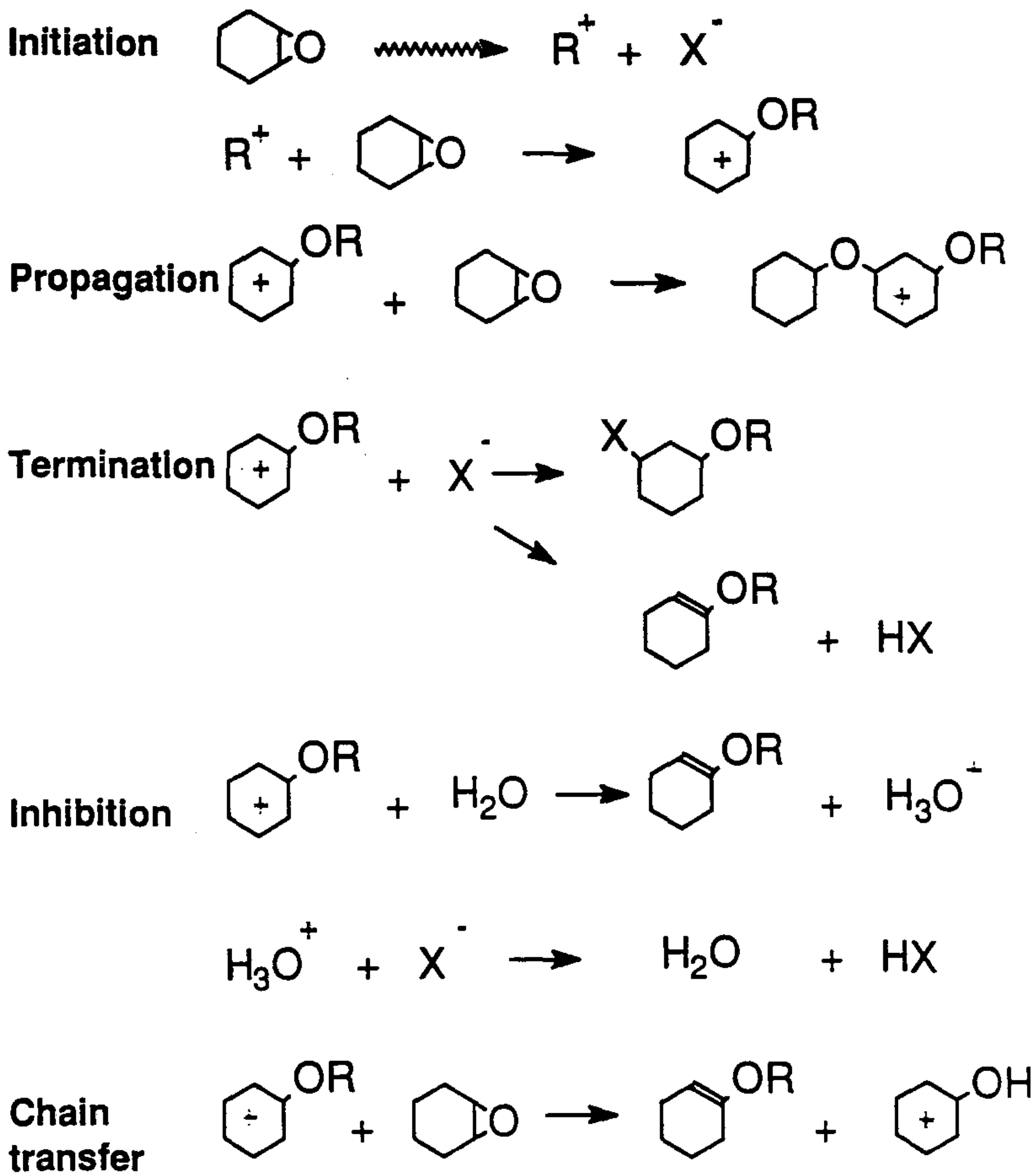
EB Curing - Constraints

- 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

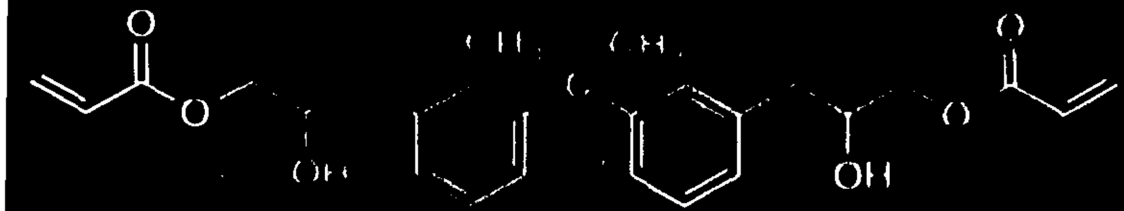


Typical Properties
Resins For Filament/Tape Winding

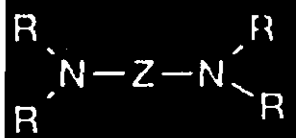
Property	Epoxies*			Acrylated Epoxies**			
				Difunc		Tetrafunc	
	#1	#2	#3	A	B	C	D
Ultimate Tensile Strength (MPa)	85	60	90	65	75	50	60
Tensile Modulus (GPa)	3	2.5	3	3	3	3	3
Elongation (%)	4-6	10	5	5	3	13	2
Glass Transition Temperature (°C)	145	100	175	120	120	85	180

* Thermally Cured; ** EB-Cured

Chemical Forms of EB-Curable Resins

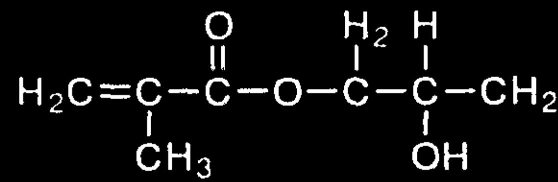


Difunctional Acrylated Epoxy

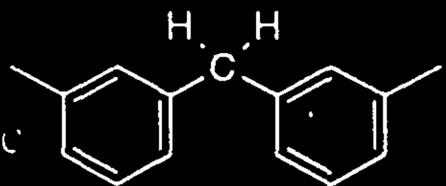


Tetrafunctional acrylated epoxy

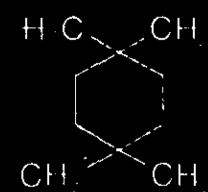
where R may be

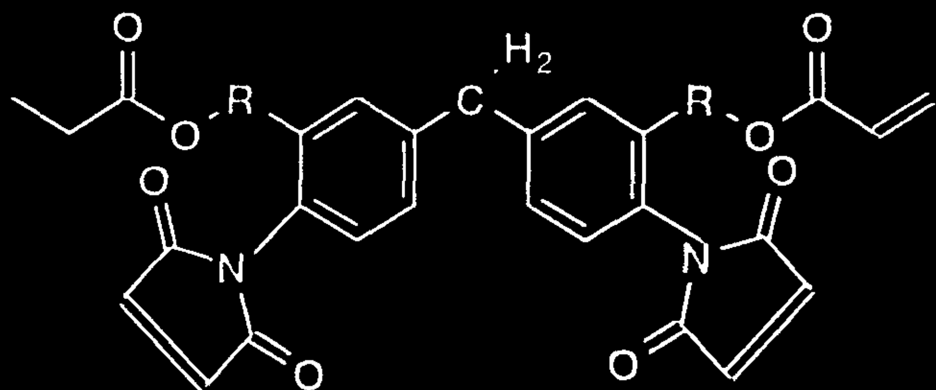


and Z may be aromatic



or cyclo aliphatic





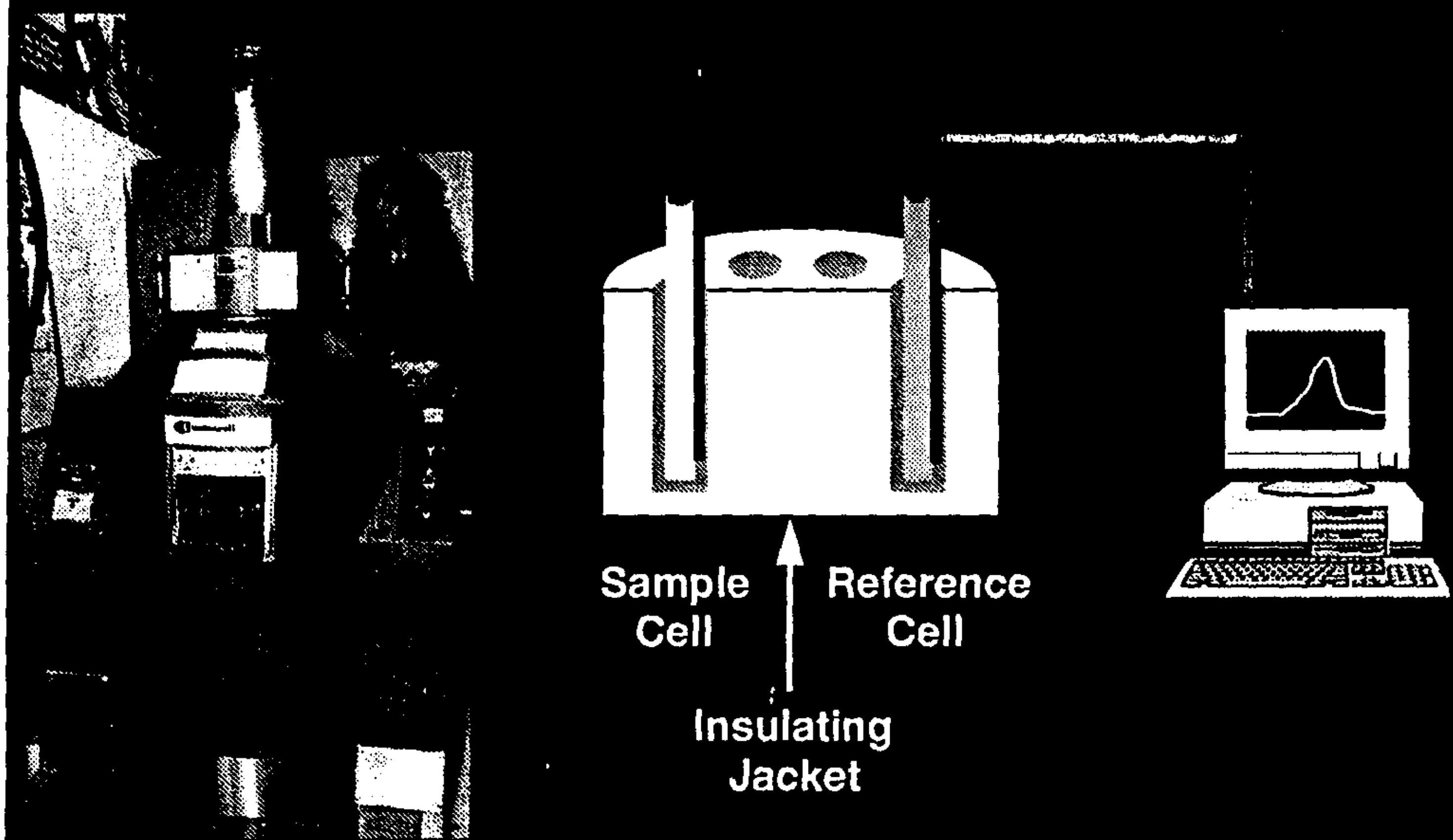
Acrylated bismaleimide

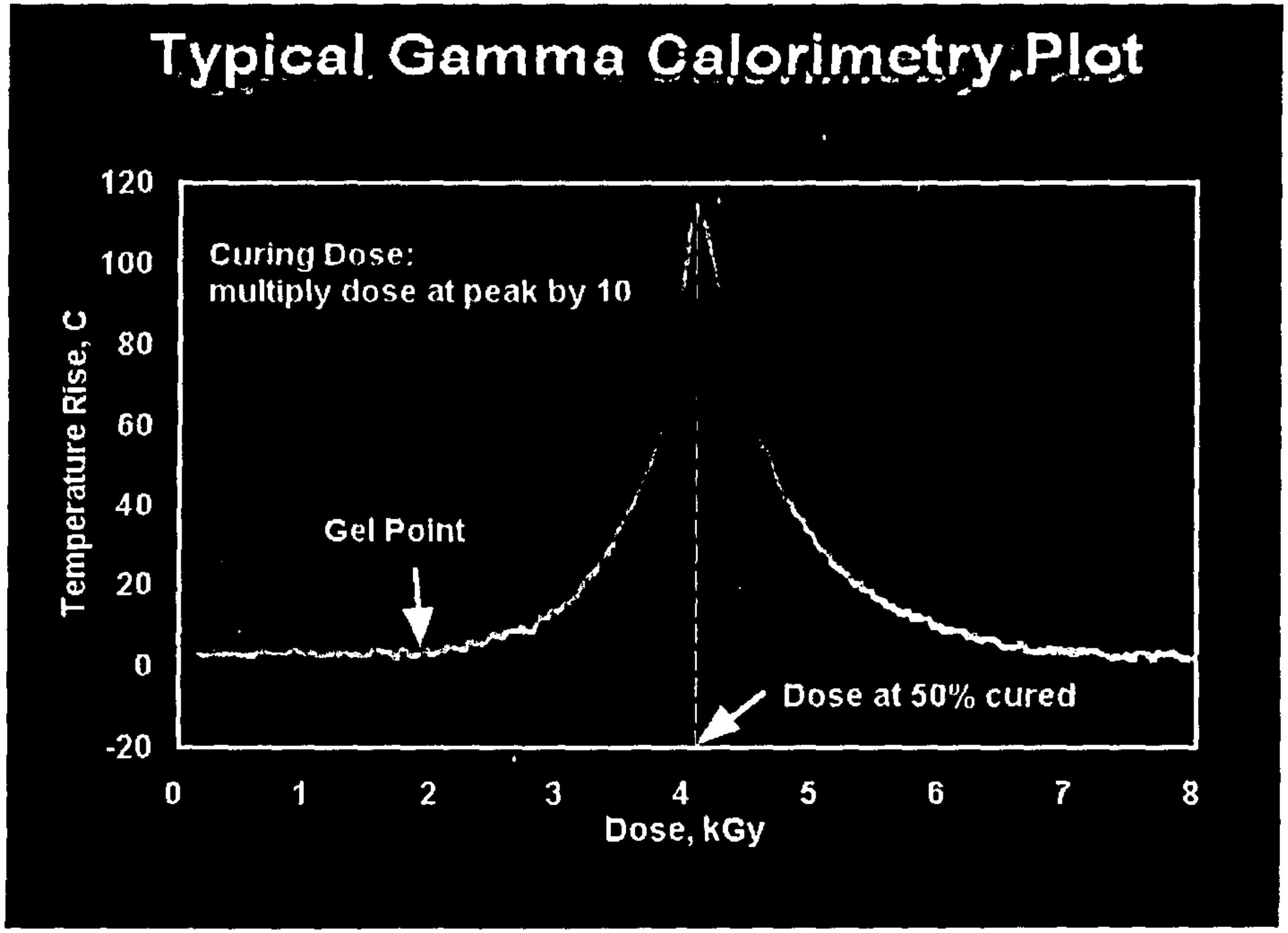
Relative Product Characteristics for Selected Resins

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	

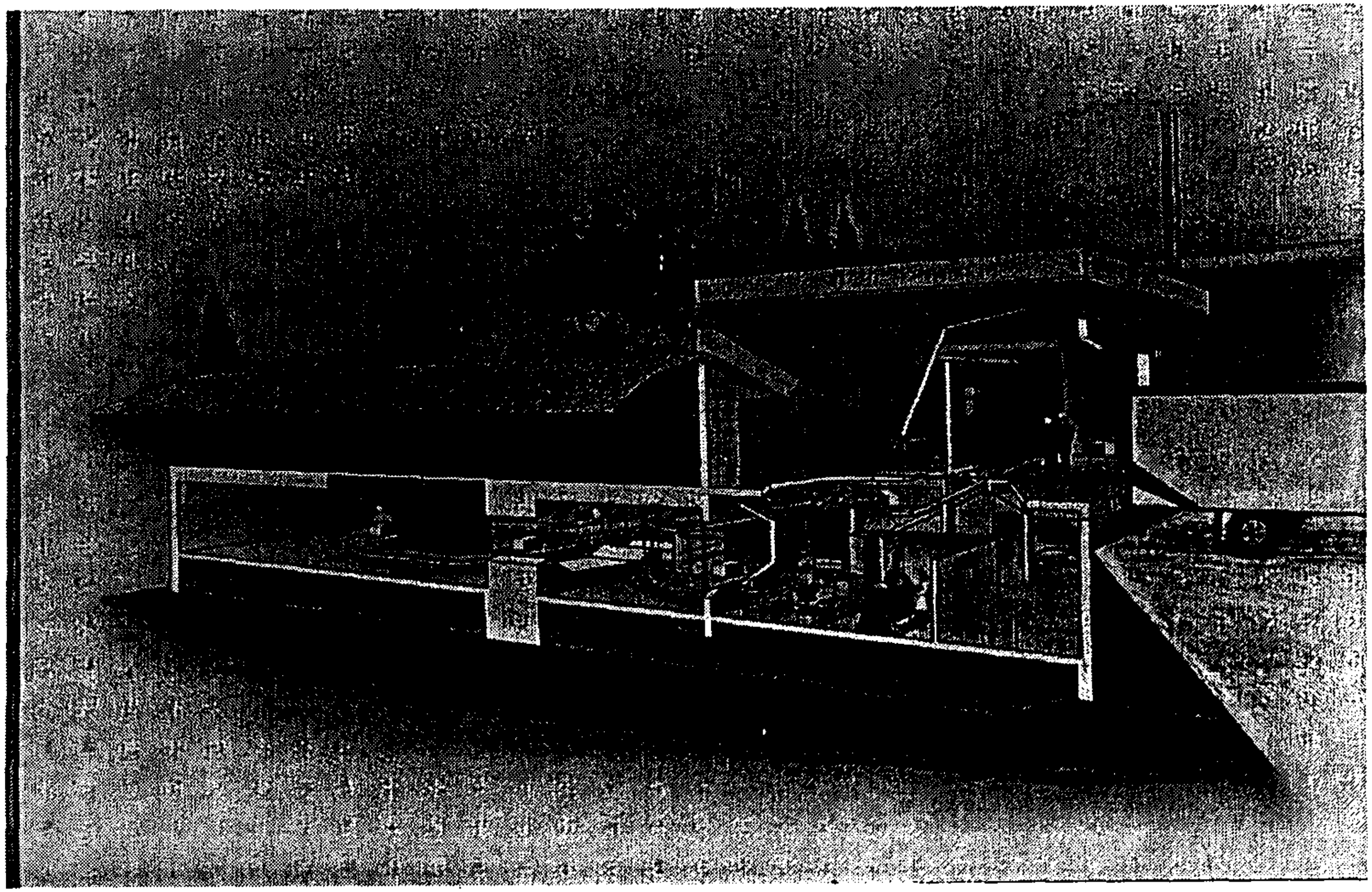
X-imparts specified property to the cured polymer

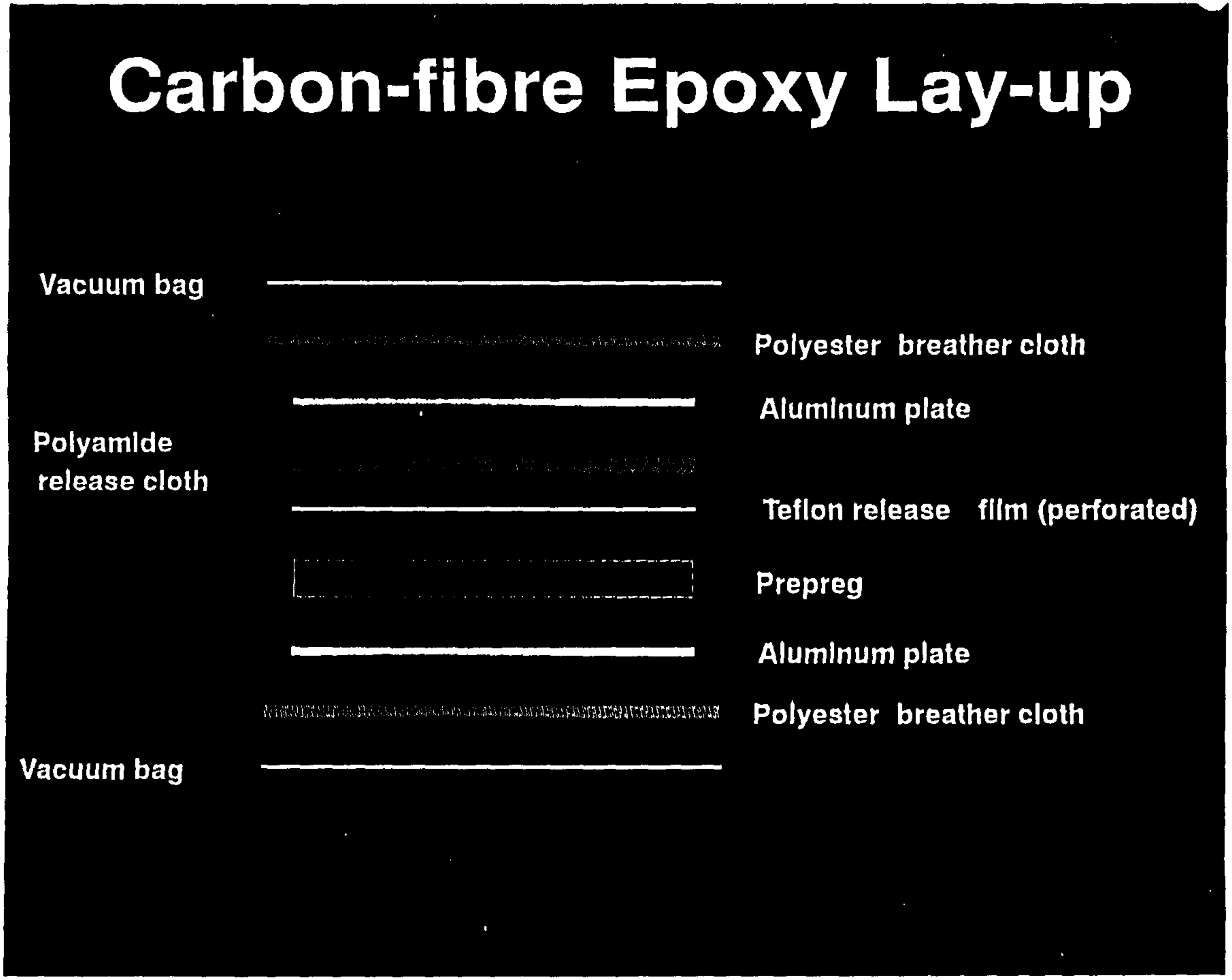
Gamma Calorimetry



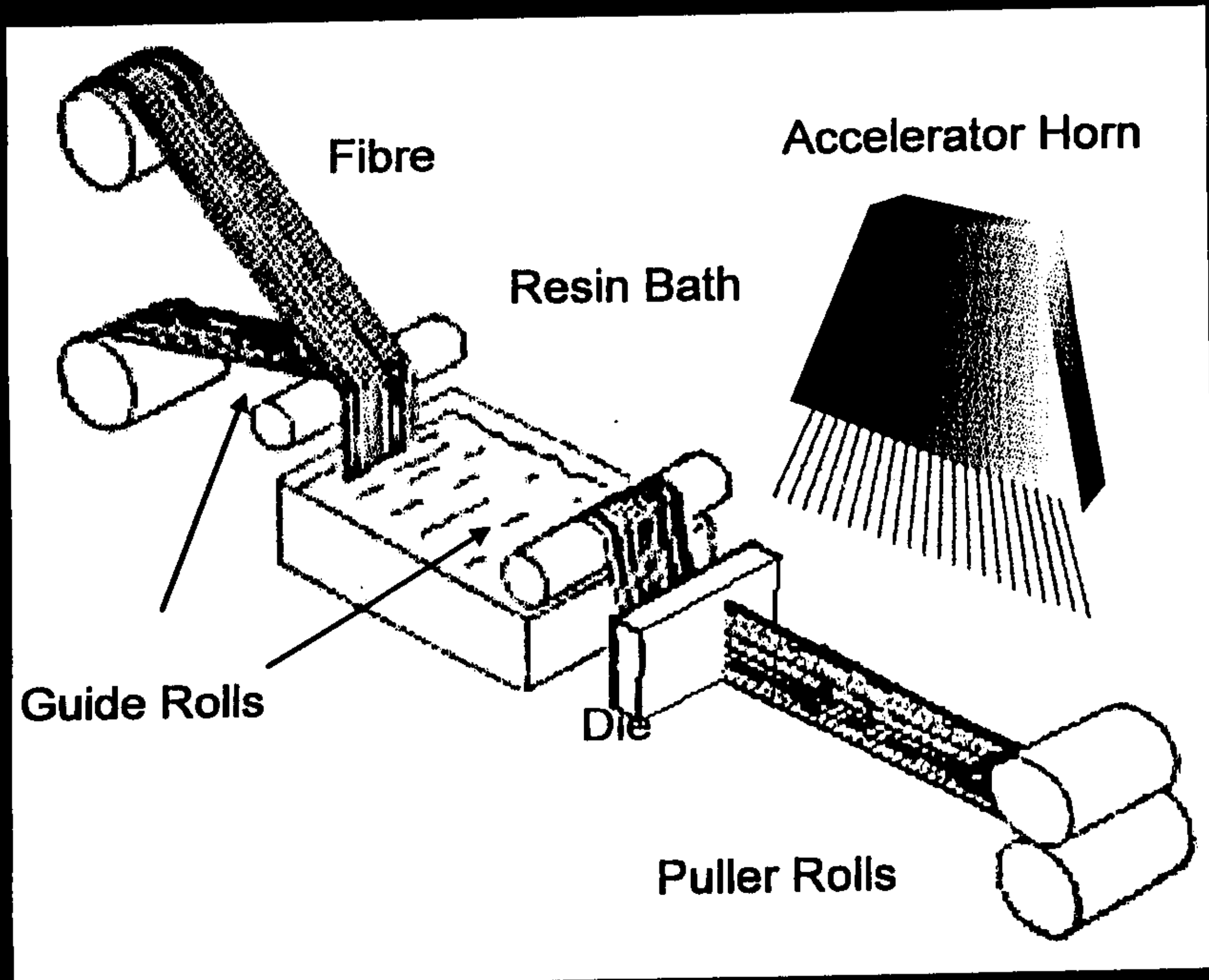

Typical Gamma Calorimetry Plot
Curing Dose:
multiply dose at peak by 10
Gel Point
Dose at 50% cured
Temperature Rise, C
120
100
80
60
40
20
0
-20
0
1
2
3
4
5
6
7
8
Dose, kGy

Whiteshell Irradiator I-10/1



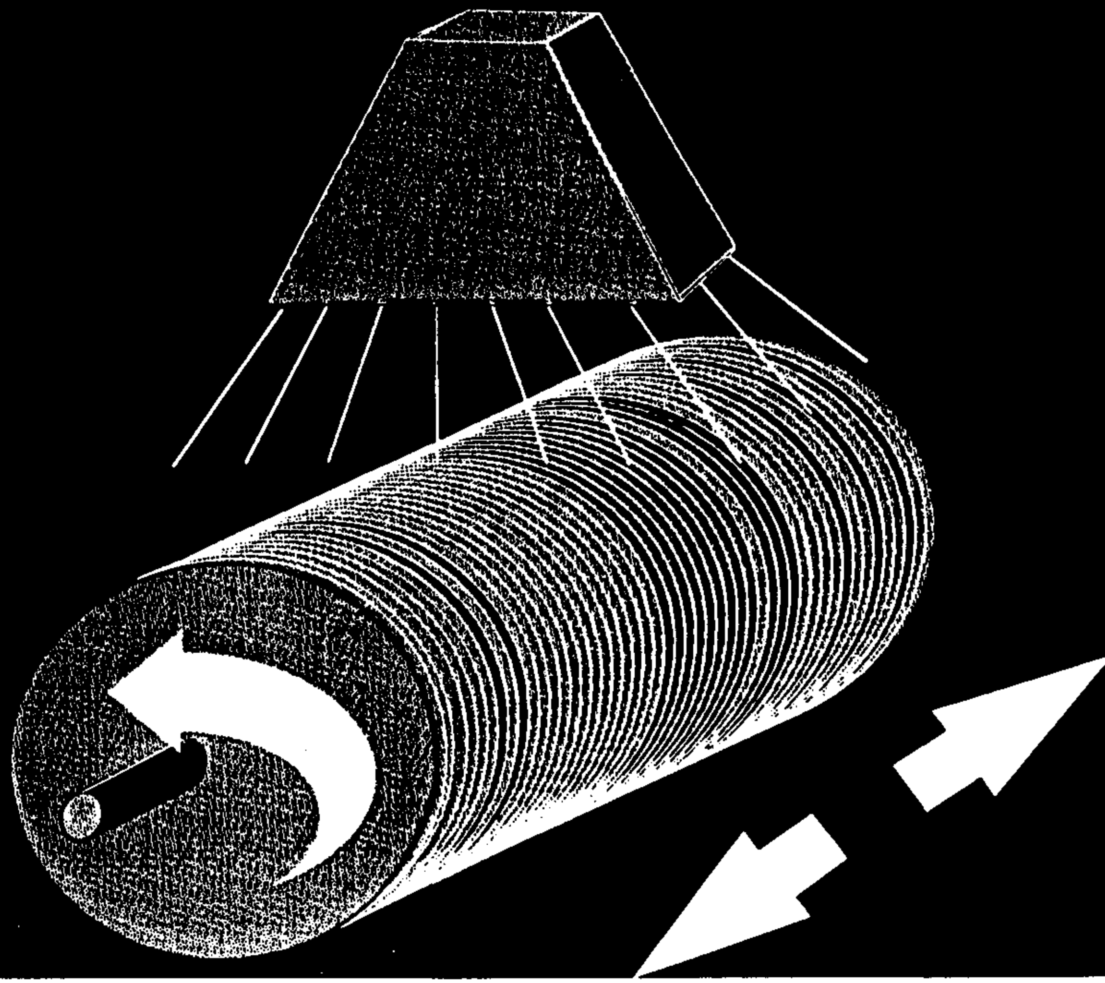

Carbon-fibre Epoxy Lay-up
Vacuum bag
Polyester breather cloth
Aluminum plate
Polyamide release cloth
Teflon release film (perforated)
Prepreg
Aluminum plate
Polyester breather cloth
Vacuum bag

Pultrusion

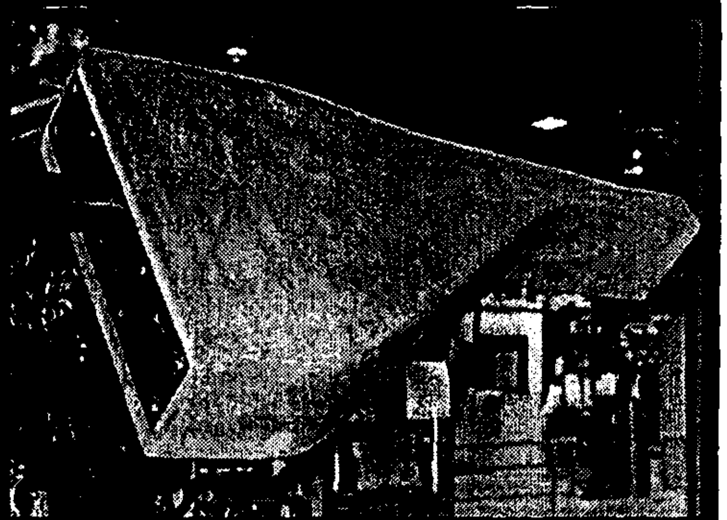

Fibre
Accelerator Horn
Resin Bath
Guide Rolls
Die
Puller Rolls

Filament Winding

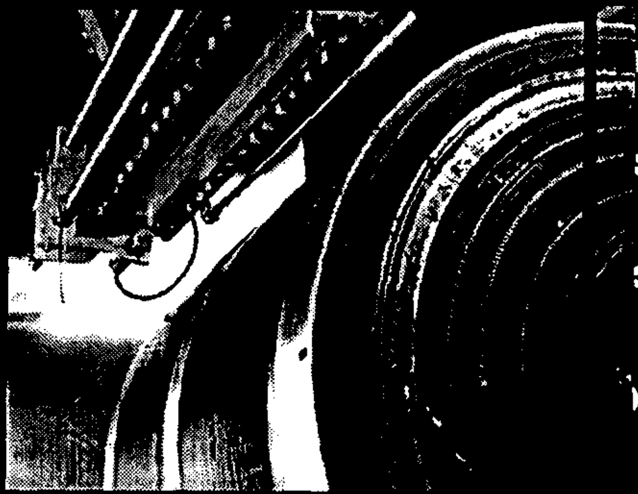
AECL
Accelerators



Typical EB Process



- Material selection
  * Resins * Fibers
  * Interface chemistry
  *Adhesives



- Consolidation
- Fabrication
  * Layup * Tape placement
  * VARTM * Filament winding
- EB Cure/QA

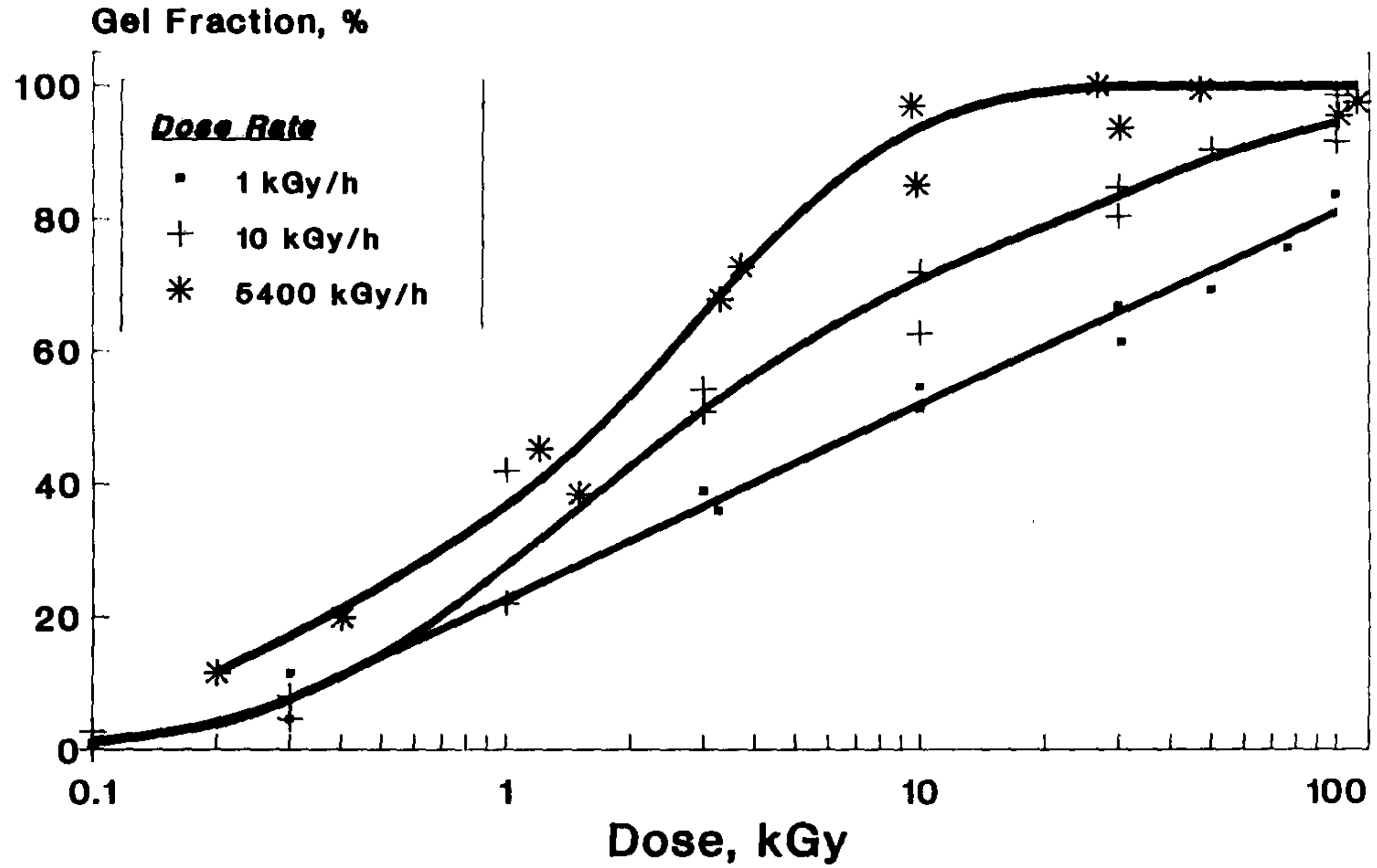
Typical Mechanical Properties

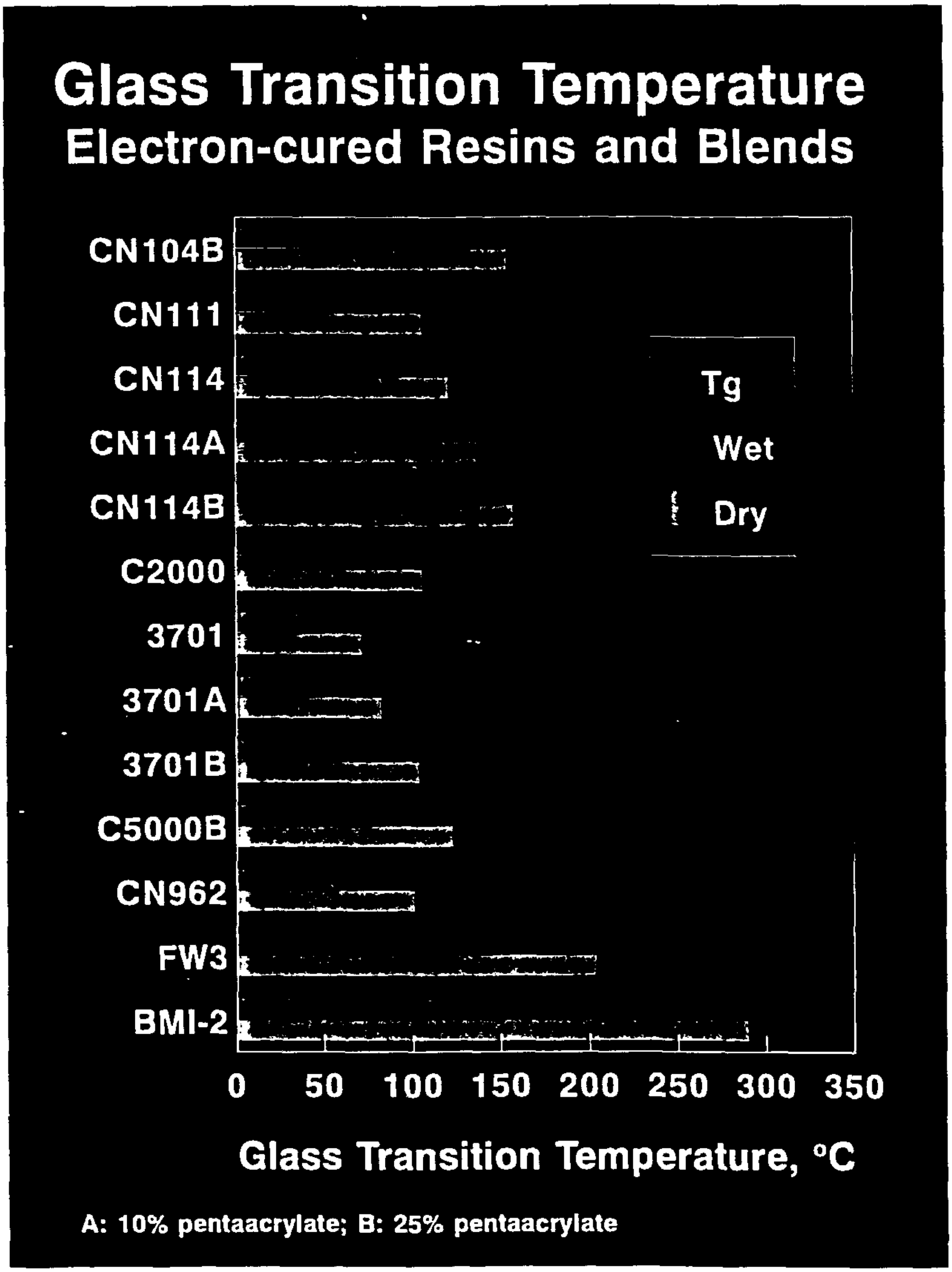
EB-Cured Carbon Fabric Laminates

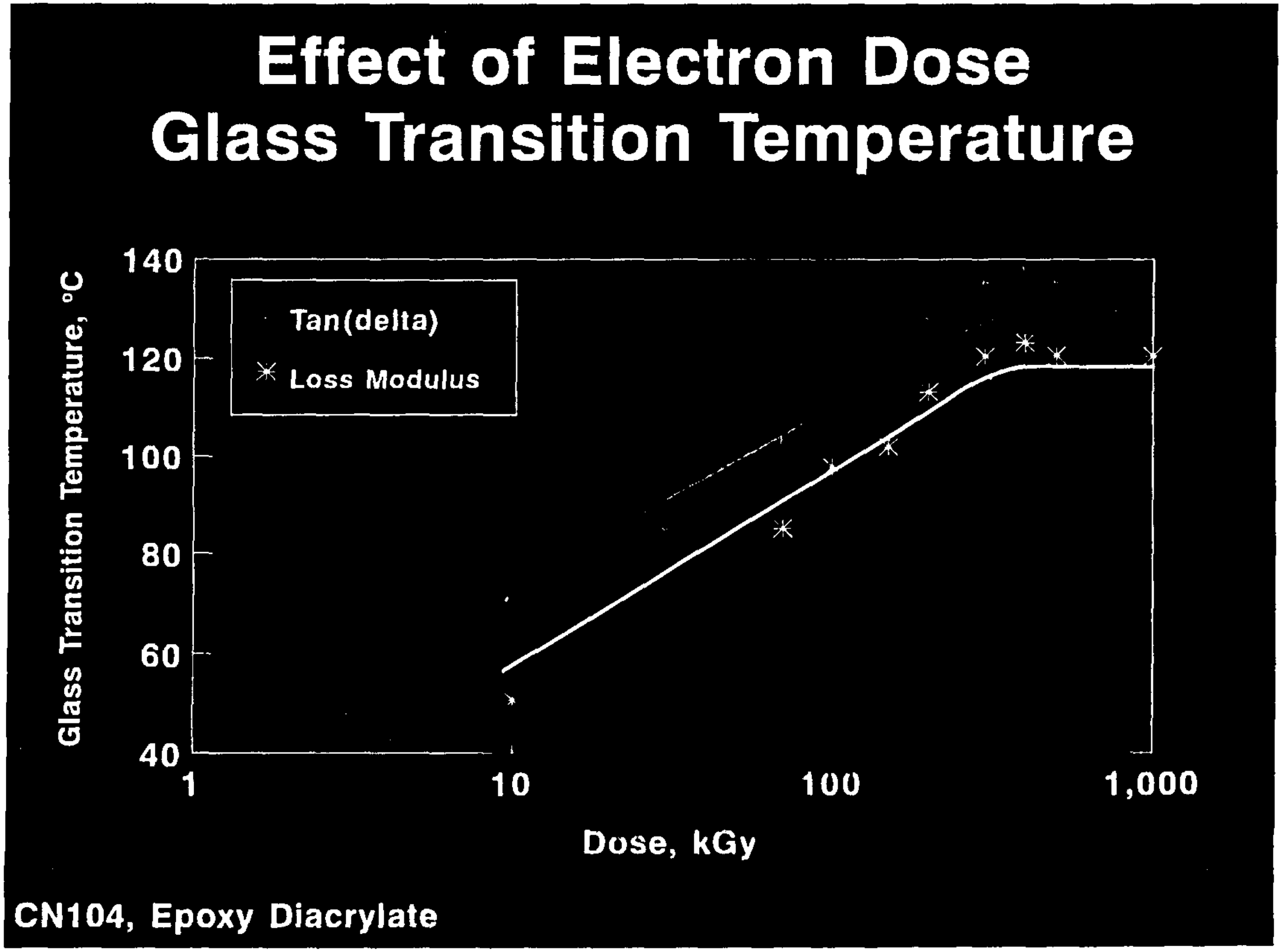
Property	Minimum Specifications		Sample Properties	
	Average	Value	Average	Minimum Value
Tensile:				
Strength, MPa	465	400	600	565
Modulus, GPa	57	53	60	50
Compression:				
Strength, MPa	460	300	460	390
Modulus, GPa	50	40	70	55

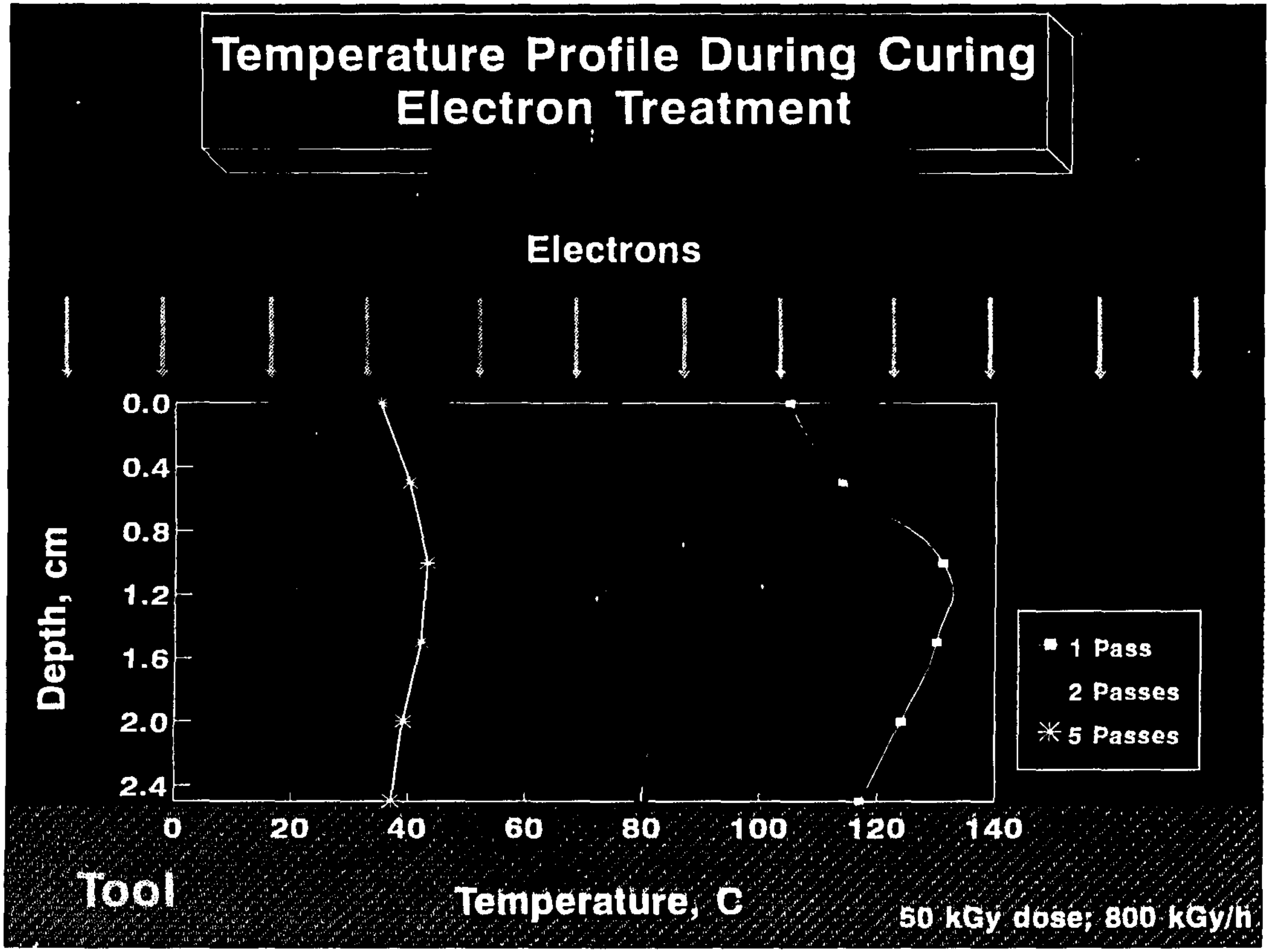
14-ply; same orientation; tested at 20°C

Gel Fraction
C3000 (Epoxy diacrylate)

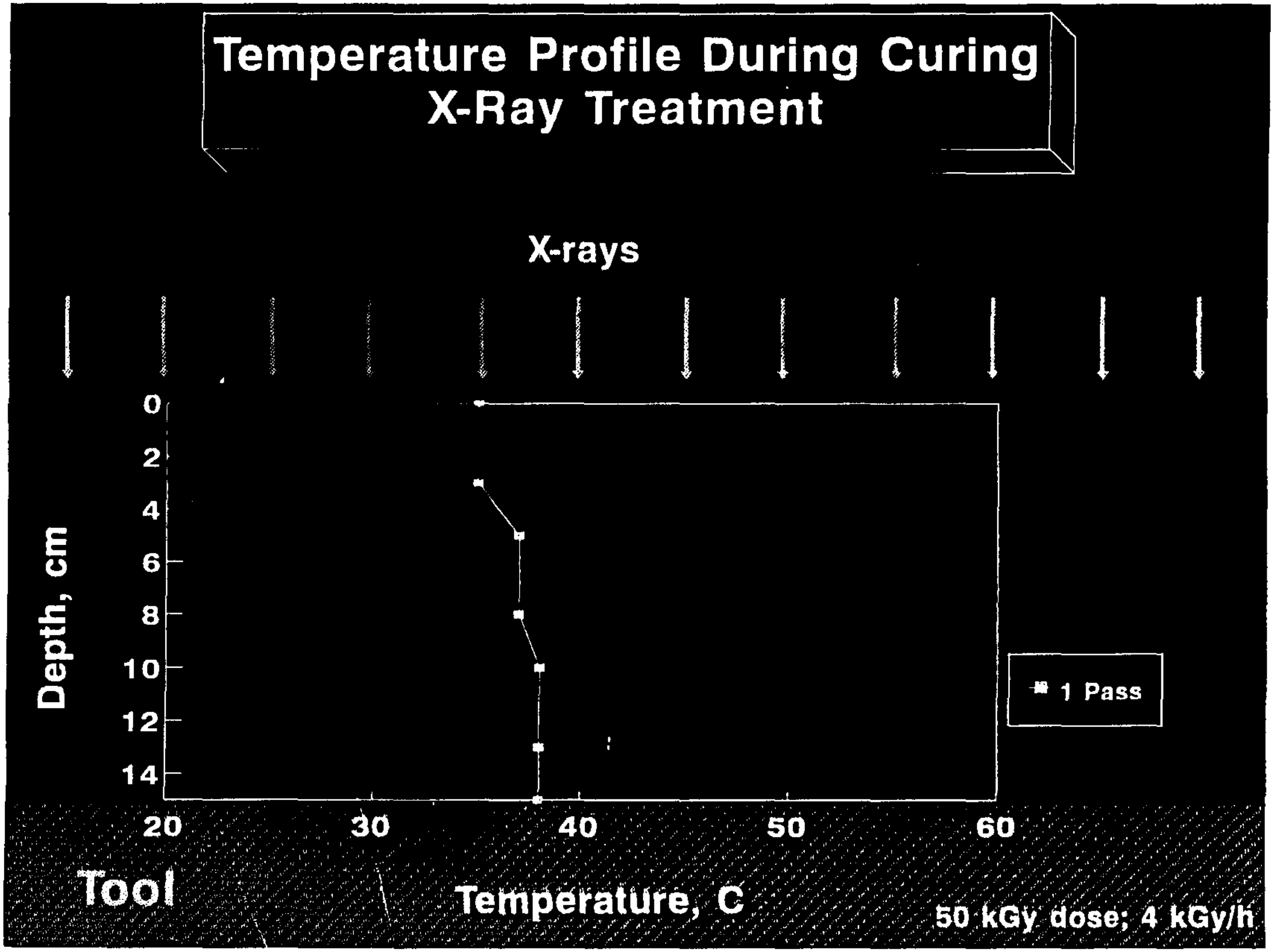



Glass Transition Temperature
Electron-cured Resins and Blends
CN104B
CN111
CN114
CN114A
CN114B
C2000
3701
3701A
3701B
C5000B
CN962
FW3
BMI-2
Tg
Wet
Dry
0 50 100 150 200 250 300 350
Glass Transition Temperature, °C
A: 10% pentaacrylate; B: 25% pentaacrylate


Effect of Electron Dose
Glass Transition Temperature
Glass Transition Temperature, °C
140
120
100
80
60
40
Tan(delta)
Loss Modulus
1
10
100
1,000
Dose, kGy
CN104, Epoxy Diacrylate



Temperature Profile During Curing
Electron Treatment
Electrons
0.0
0.4
0.8
1.2
1.6
2.0
2.4
Depth, cm
0
20
40
60
80
100
120
140
Tool
Temperature, C
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
1 Pass
Tool
Temperature, C
50 kGy dose; 4 kGy/h

Amount of Volatiles Released from Selected Matrix Polymers During Curing

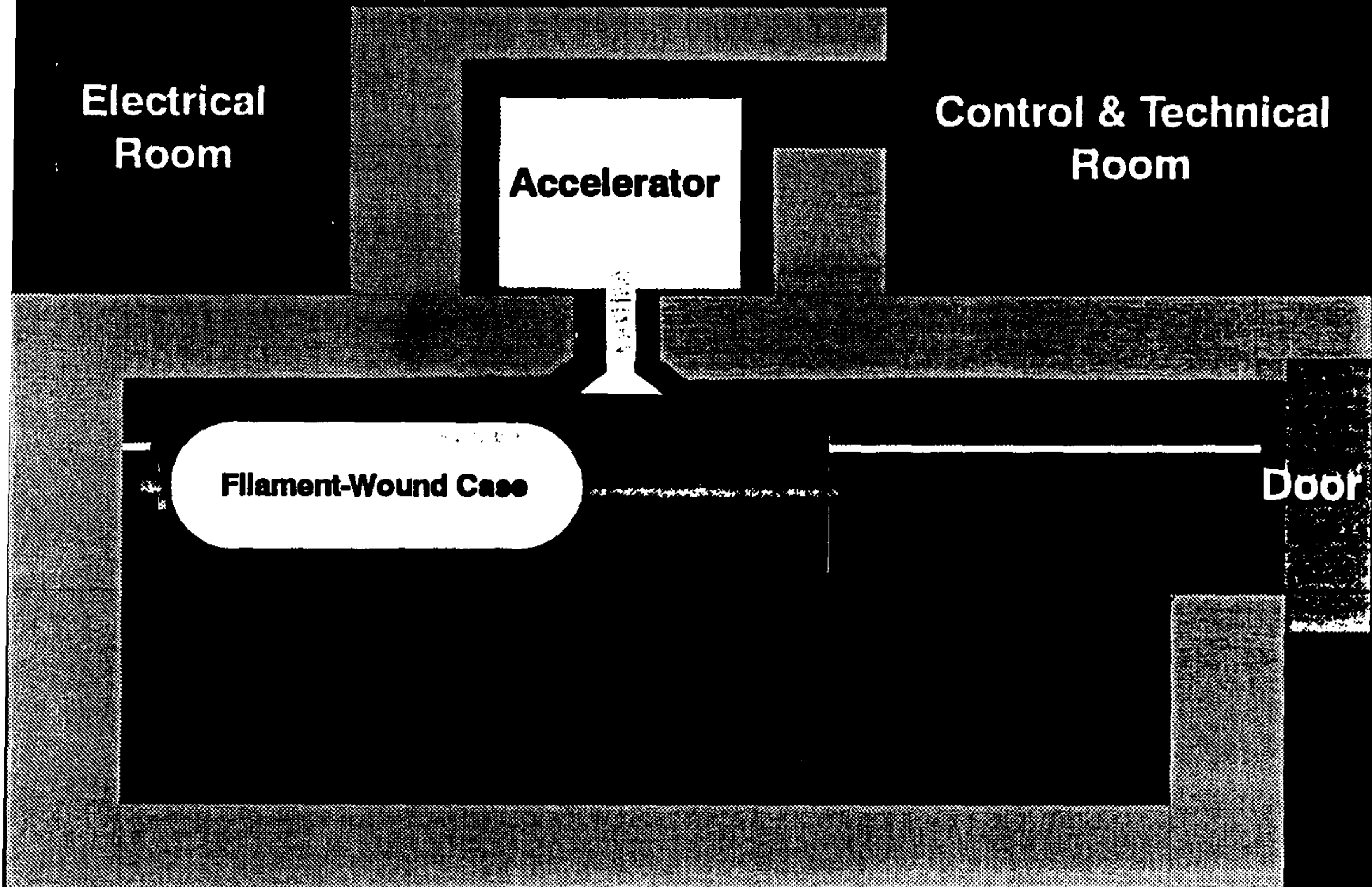
Curing Method	Material	Curing Cycle @25°C	Volatiles (mg/g)
Electron	CN-104	50-100 kGy	< 0.005
Electron	CN-114	50-100 kGy	< 0.005
Electron	Derakane 470-36	50 kGy	0.75*
Catalyst	Derakane 470-36	20 min	3.0
Thermal	Hysol epoxy RE-2039	2 hr @ 150°C	3.45
Thermal	PMR-15	300°C	1.38

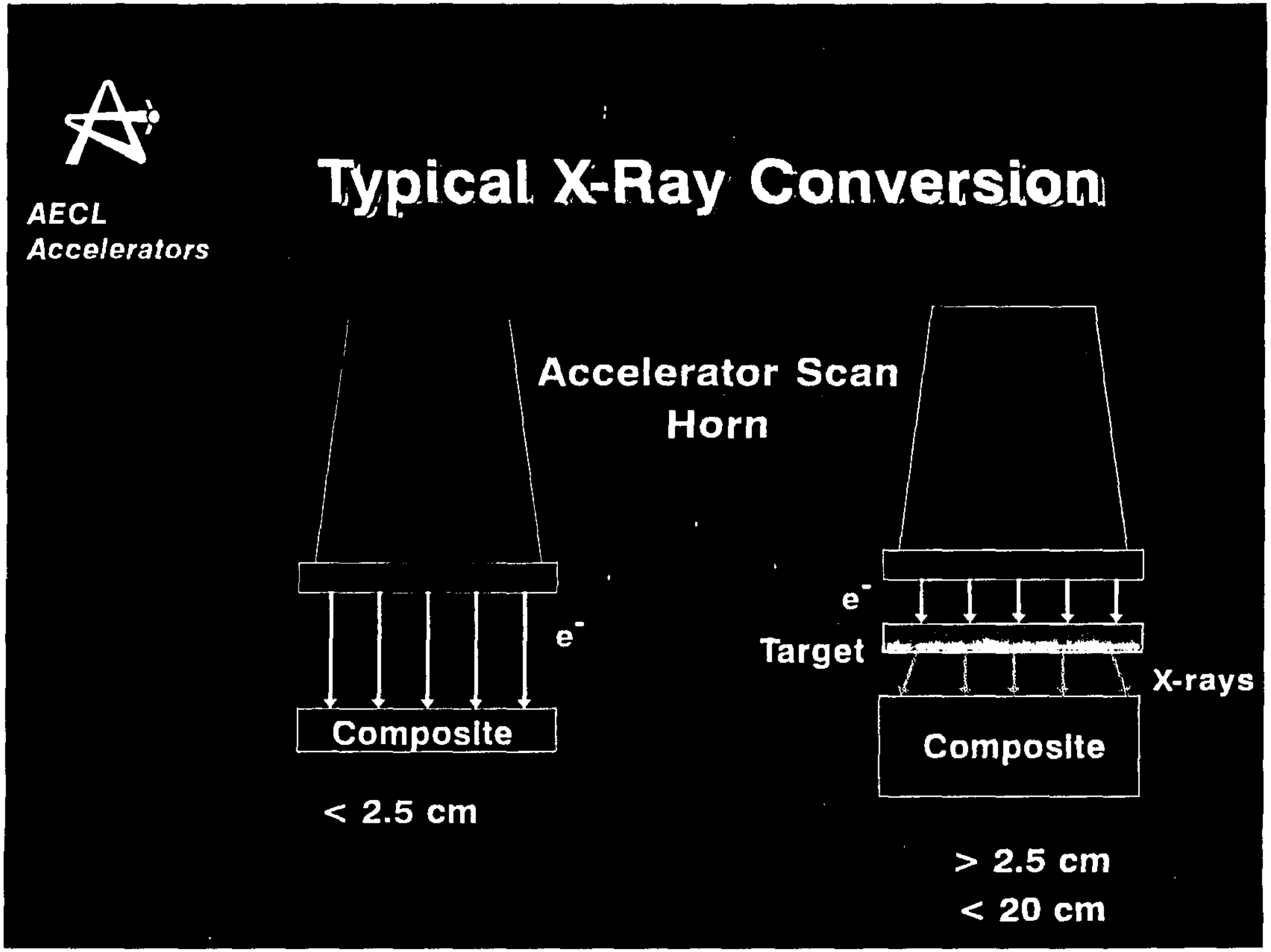
* blank = 0.78

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
Accelerator Scan
Horn
e-
Composite
< 2.5 cm
e-
Target
X-rays
Composite
> 2.5 cm
< 20 cm

CRADA

Cooperative Research & Development Agreement

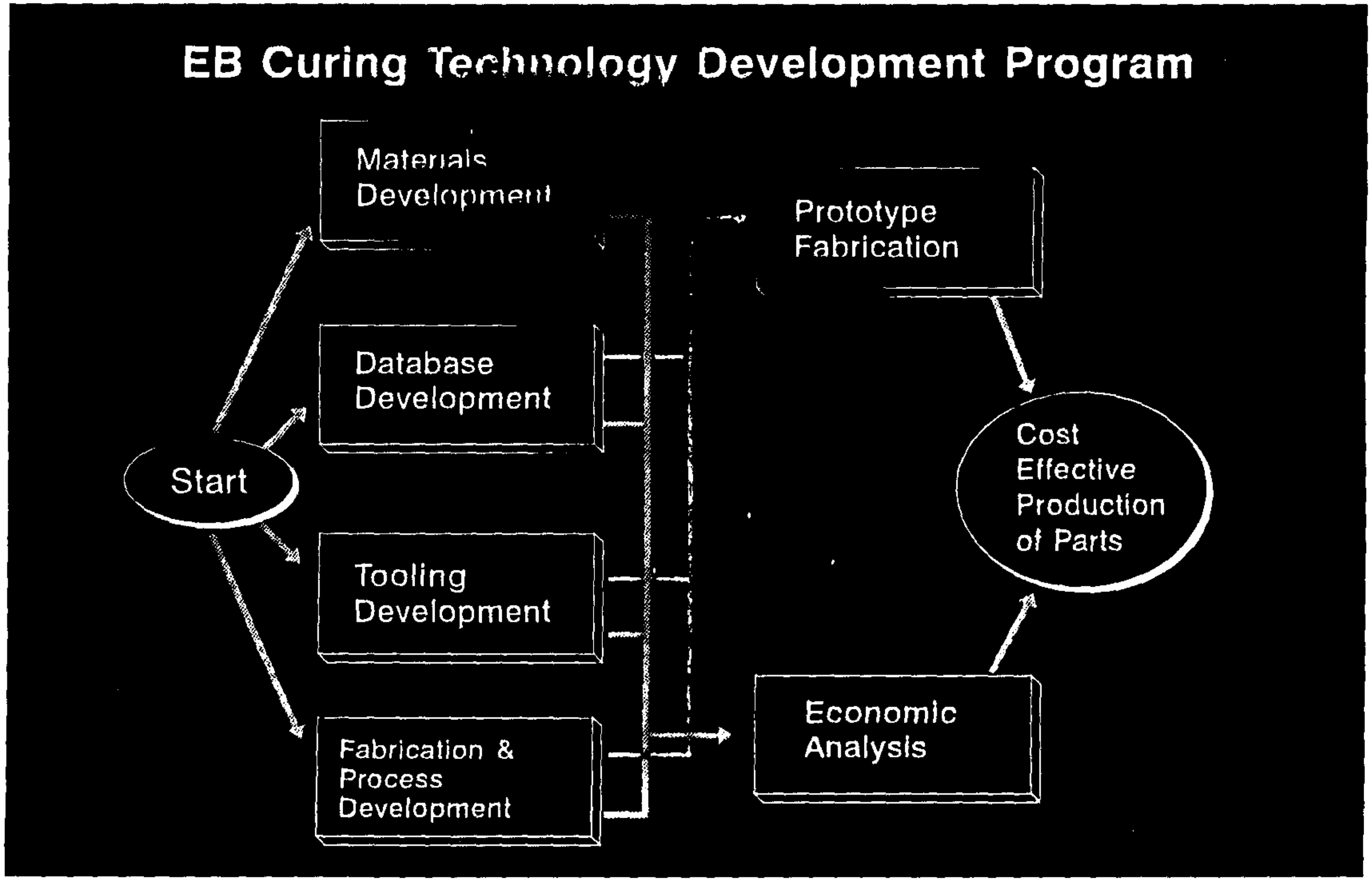
- Objective
  to conduct R&D to better understand and utilize electron beam polymer matrix composite curing technology

- 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
Materials Development
Database Development
Start
Tooling Development
Fabrication & Process Development
Prototype Fabrication
Economic Analysis
Cost Effective Production of Parts

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

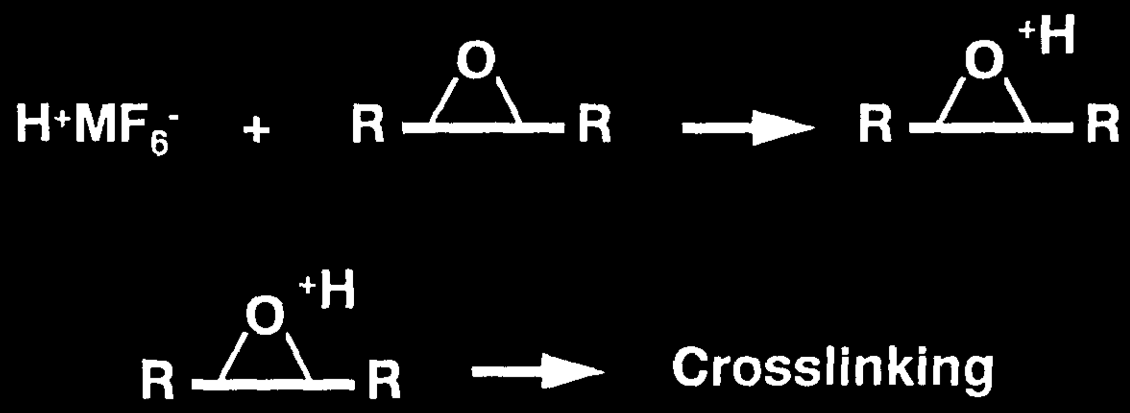
Optimizing Properties of EB-Curable Fiber Reinforced Composites

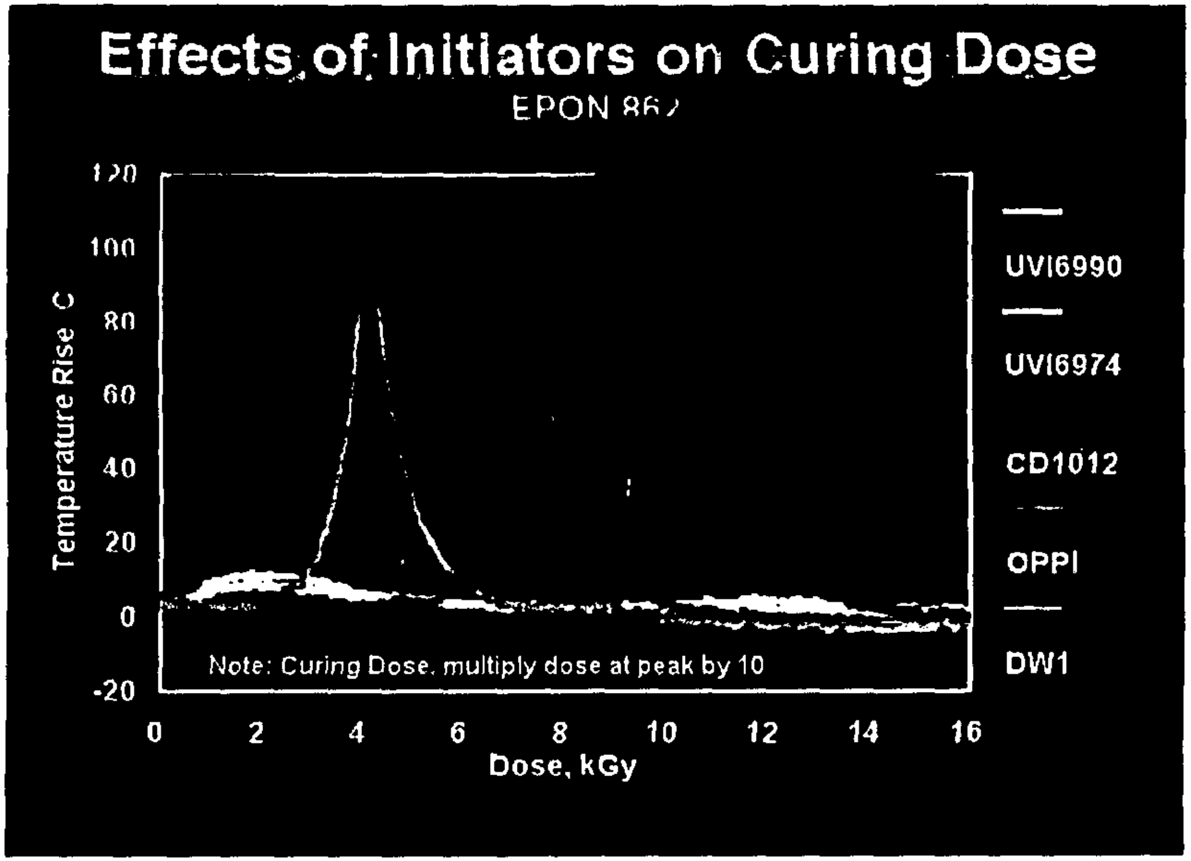
- Most Efficient Cationic Initiator
- Initiator Concentration
- Curing Dose
- Dose Rate and Radiation Type
- Epoxy Mixture for end-use
- Fiber Sizing
- Processing Conditions

Cationic Intiators

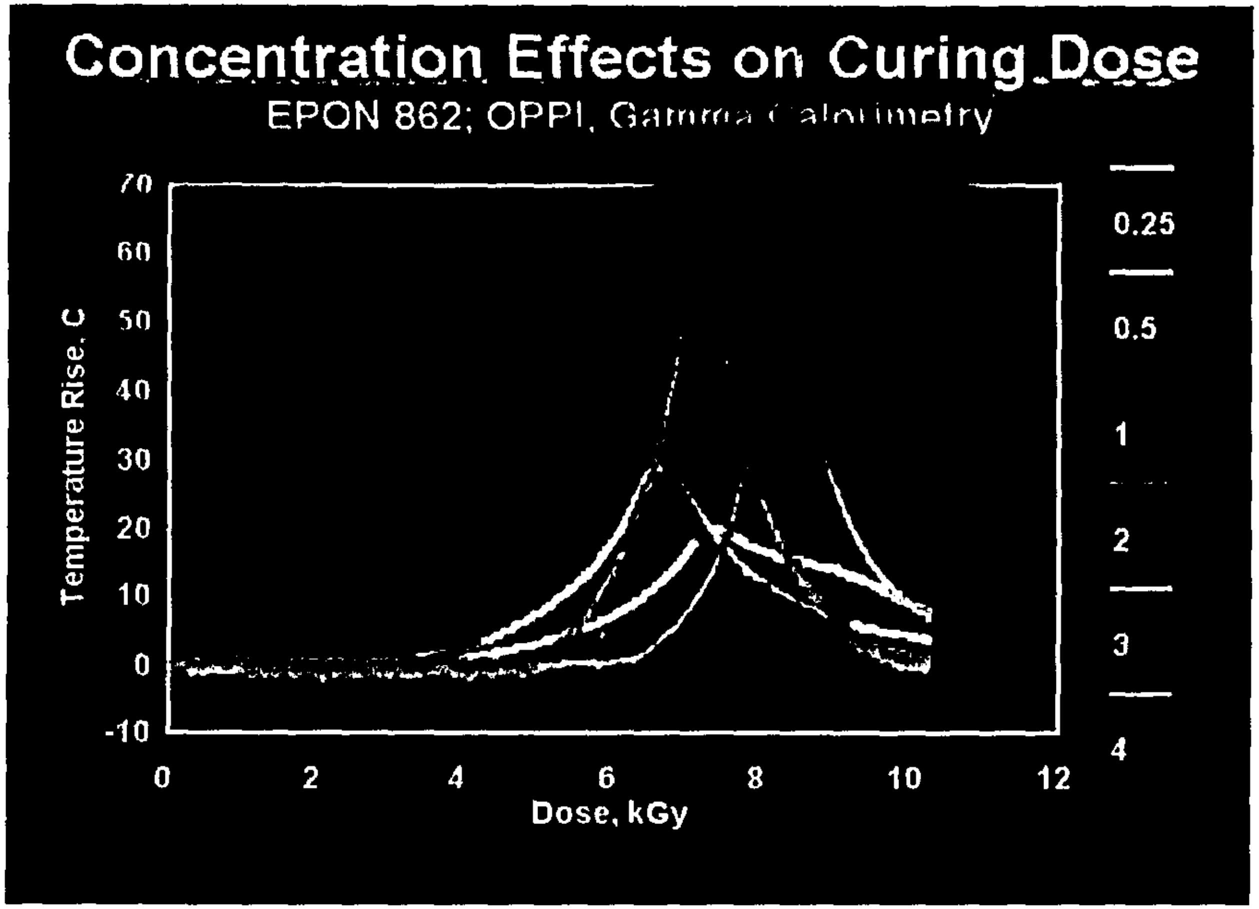
$SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$

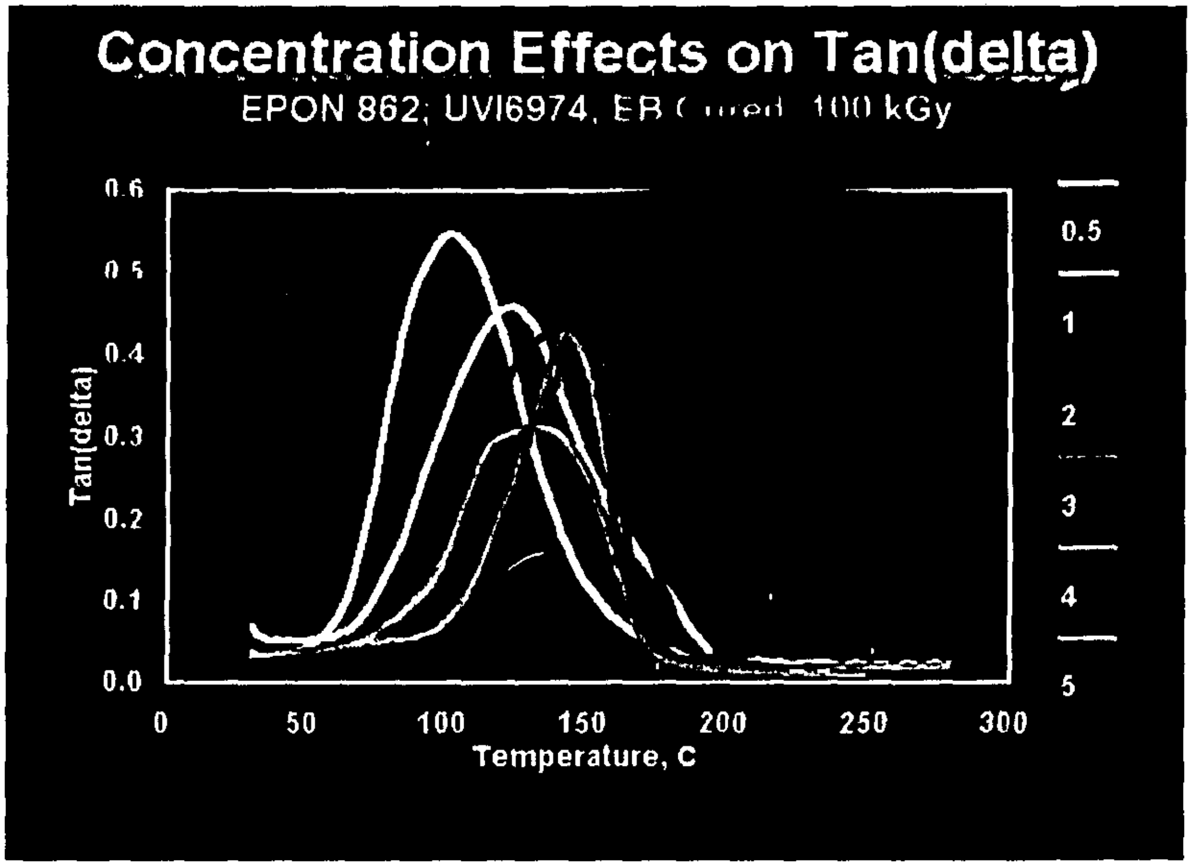
$$Ar^+MF_6^- \xrightarrow{e^-,\ e^-(x),\ \gamma,\ UV} H^+MF_6^-$$





Effects of Initiators on Curing Dose
EPON 862
Temperature Rise C
Dose, kGy
Note: Curing Dose, multiply dose at peak by 10
UVI6990
UVI6974
CD1012
OPPI
DW1
120
100
80
60
40
20
0
-20
0
2
4
6
8
10
12
14
16


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
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

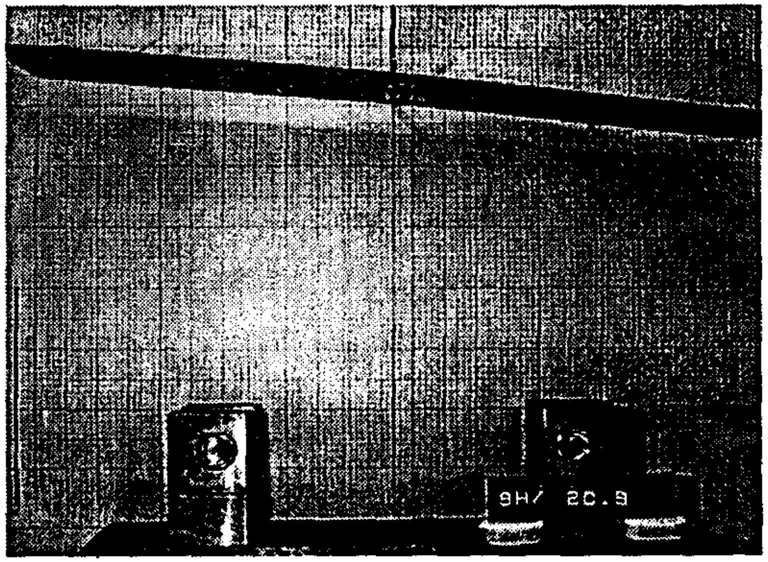
Curing and Rheological Properties

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

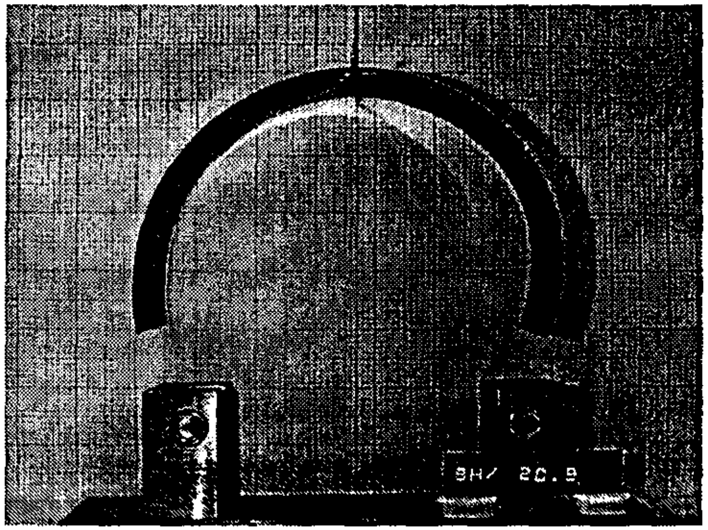
Curing and Rheological Properties

- 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



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



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

Features of EB-Curable Resins

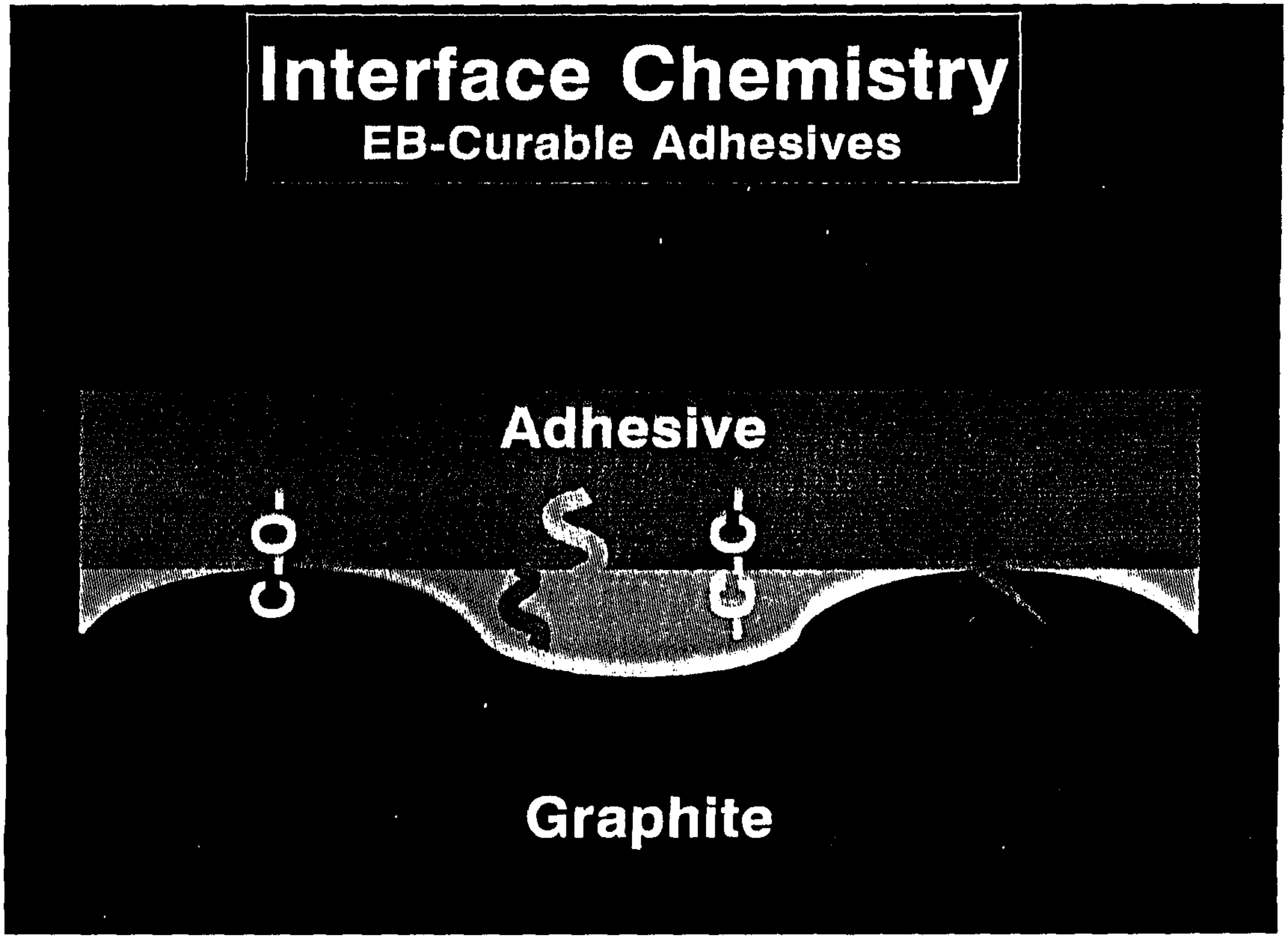
Features	EB-Curable Epoxy	Thermosetting Epoxy
Mechanical Properties	high-performance	high-performance
Manufacturing Costs	moderate	high
Prepreg Storage/Handling	extended life @ 20°C	limited life @ 0°C
Environmental Concerns	low	moderate to high
Shrinkage on Curing (%)	2-3	4-6
Volatile Emissions (%)	<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

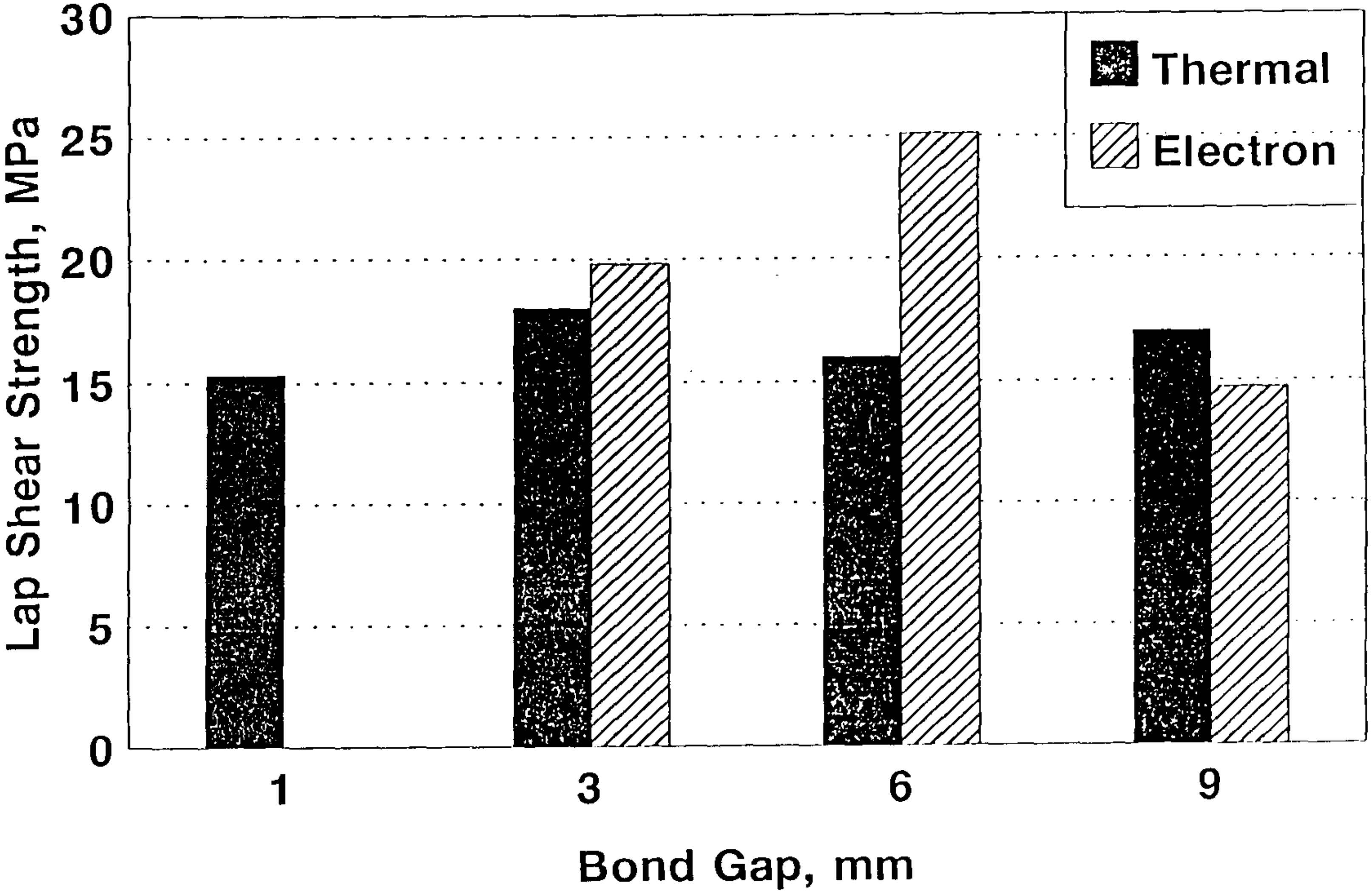
Features	EB-Curable Epoxy	Thermosetting Epoxy
Thickness Limit	50 mm (EB) 200 mm (X-ray)	20 mm
Tooling Materials	metals, wood, ceramics, plastics, waxes, foams	metals, ceramics, graphite
Tooling Costs	low-moderate	moderate-high
Cure Time (10-mm-thick)	seconds-minutes	hours
Energy Requirements	low to moderate	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

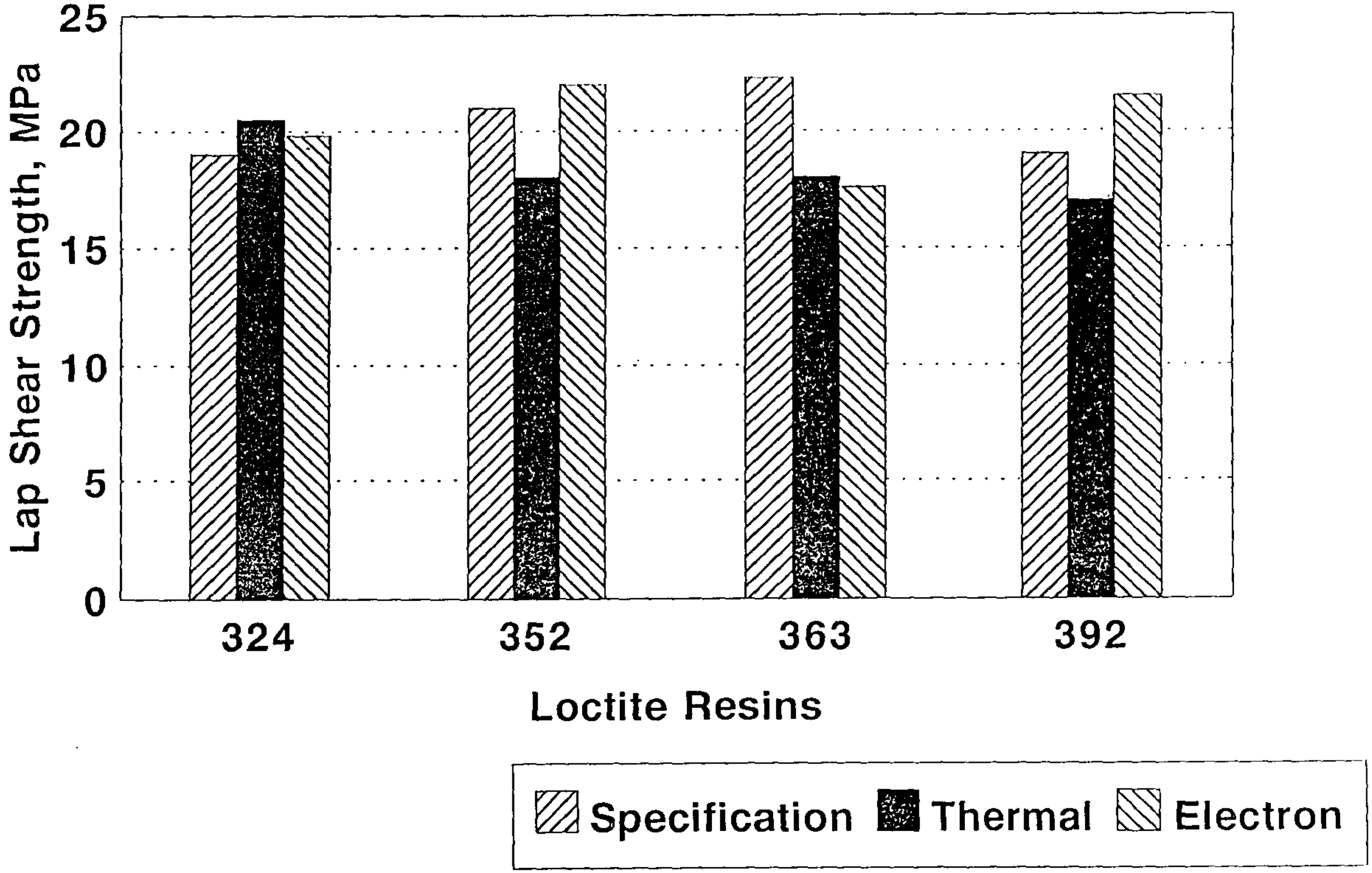


ctite 363; sanded; 50 kGy dose

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



ım 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