Radiation Damage in Resins and Composites

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Outline

- Radiation Units and Types
- Interaction of Radiation with materials
- Classification of Plastics Materials
  - Thermoplastics and Thermosets
- Structure and Materials Selection
- Effects of Radiation
  - Mechanical, gas evolution, dimensional changes?
- Irradiation Under Load
- Electrical properties

Radiation Units

- The S.I. unit of absorbed dose is the Gray (Gy)
- An energy equivalent of one Joule absorbed in one Kilogram
- Non SI Unit – Rad; 1 Rad = 10^{-5} J/g = 10^{-2} Gy
- 1 eV = 1.602 x 10^{-19} Joules ; 1 MeV = 1.602 x 10^{-13} Joules
- barn: Unit of area (10^{-28} m^2) used in measurement of nuclear cross-sections

Radiation Types

- Neutrons - particles with energy but no charge
- Electromagnetic radiation such as γ-rays
- Charged particles - such as protons, electrons and α-particles (He^{2+})

Interaction of Radiation With Polymers

High energy particles lose energy and transfer it to polymer by:

- Ionisation - breaking chemical bonds
- Excitation -Separation of orbital electrons
- Nuclear Displacement Reactions - mainly fast neutrons - leads also to ionisation
- Nuclear Transformation - Mainly slow neutrons
- Scattering and Emission
  - Absorbed energy is degraded and appears as heat
- Energy deposition is characterised by LET

Linear Energy Transfer

- Rate of energy loss of a particle depends only on it's speed and charge and not on it's mass.
- Protons and alpha particles will react in a similar manner to electrons of the *same velocity and charge.*
- Difference in mass means that the penetration of a 20 MeV proton is comparable with that of a 10 keV electron.
- Since the LET is increased as the particle is slowed, uniform radiation conditions, apply only if the specimen is considerably thinner than the range of the incident particle.

Fast Neutrons - 1

- Fast Neutrons are intensely damaging
- Major result is production of fast protons
- Energy transfer to other atoms may break chemical bonds
- Re-coiled neutron may still have sufficient energy to break more bonds

Fast Neutrons 2

- Deposit Energy by collisions
- $E_t = \dfrac{4 \times M}{(M+1)^2} (E \cos^2 \theta)$

Nucleus	Mass	Energy Transfer (%)
Hydrogen	1	100
Carbon	12	28
Nitrogen	14	25
Oxygen	16	22

Slow Neutrons

- Most elements have larger capture x - section for slow neutrons than for fast - result is nuclear transformation reactions:
- After capture nucleus may be unstable: (capture X-section of hydrogen 80 barns)

H(1) (n,γ)D(2)　　N(14) (n,p) C(14)

2.2 MeV γ　　0.66 MeV proton

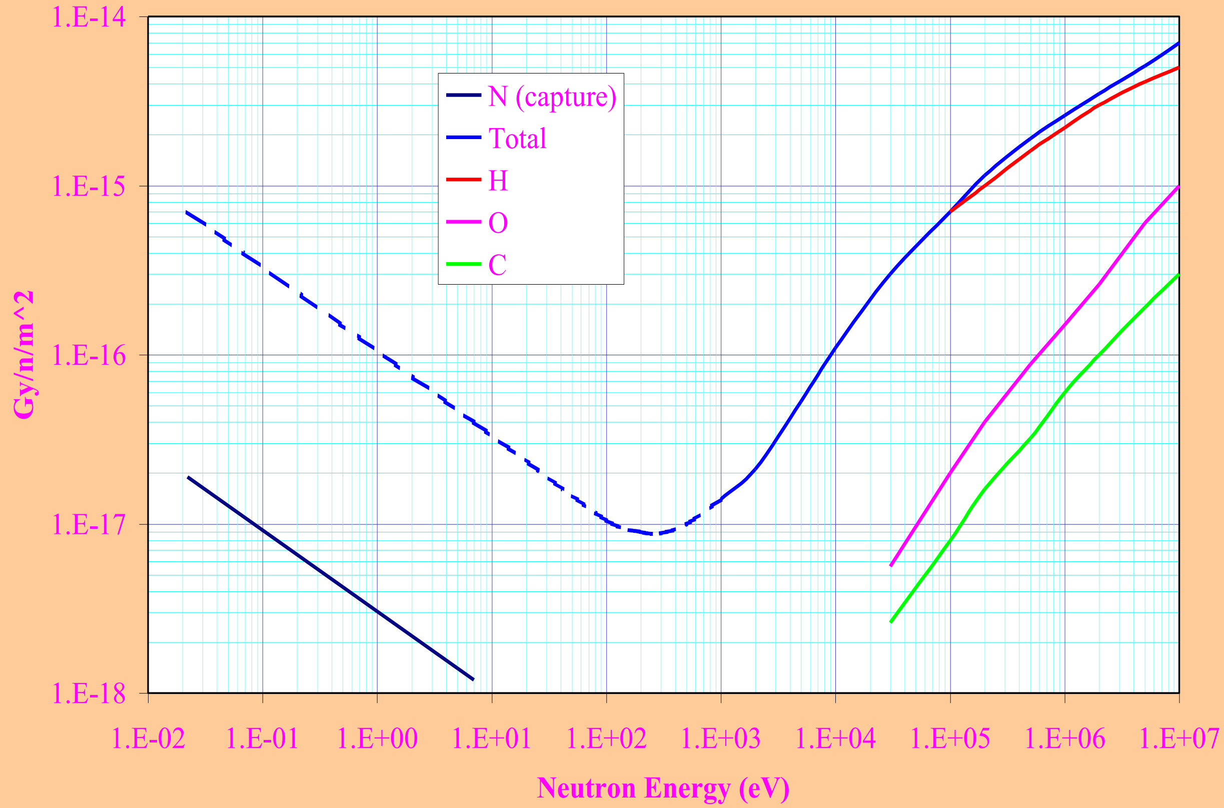
B(10) (n,α) Li(7) (B capture X-Section 700 barns)

Boron gains 1 amu and loses 4 (a high energy alpha particle) - a net loss 3 amu

Methane – A Special Case

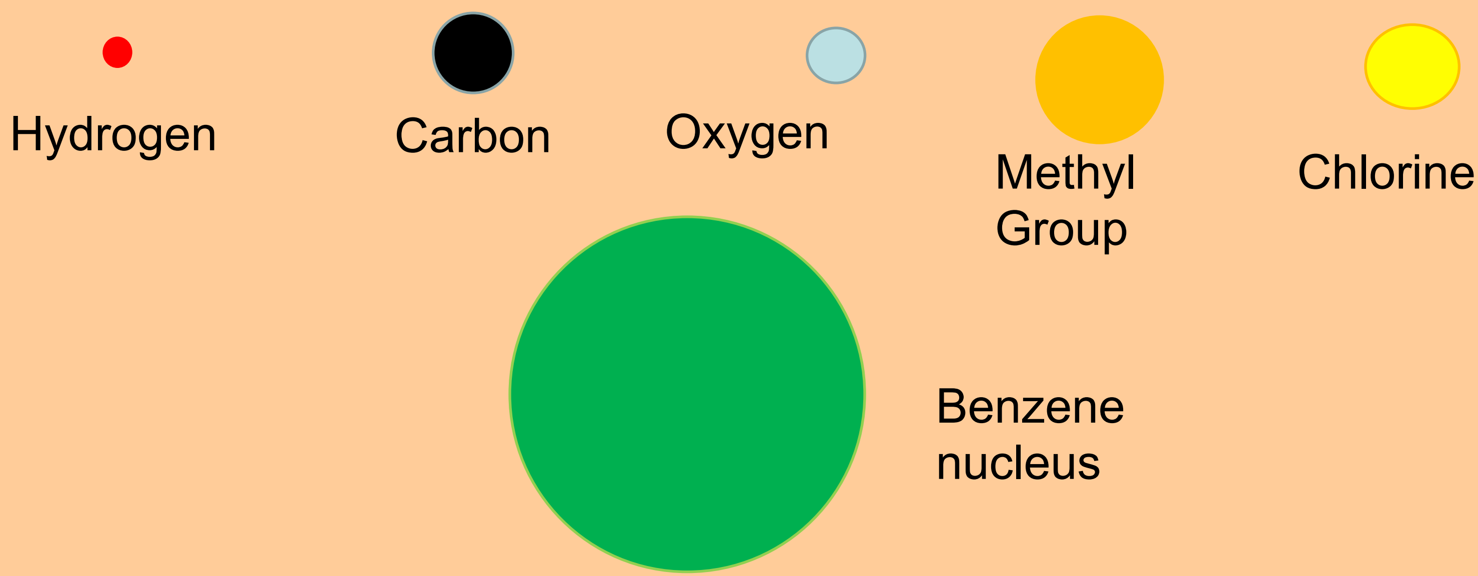
- Hydrogen rich compound most efficient way to "slow" neutrons
- Methane (CH_4) often used as a 'moderator'; fast neutron irradiation leads to hydrogen gas and 'wax' like substance – eventually carbon!
- Hydrogen gas from hydrogen abstraction
- ESR measurements show H^* & C^*H_3 in solid methane at 4K after irradiation at that temperature
- Under similar conditions H^* NOT detected in PE or other polymers
- Activated atoms lead to polymer formation and ultimately carbonization

Neutron Fluence and Dose Conversion – Energy Deposited (1st Collision)



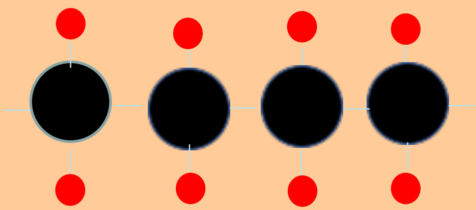
Polymer Structures
(radiation Resistance is related to structure & Composition)

Relative atomic Sizes (Approximately)!

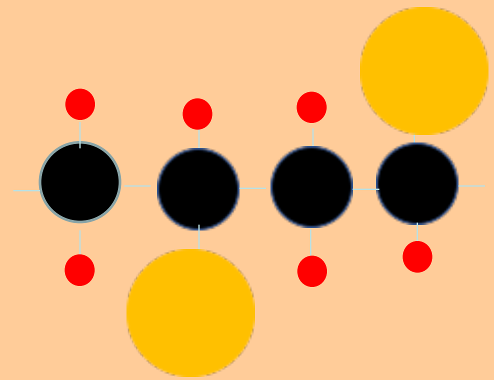


Some Thermoplastics

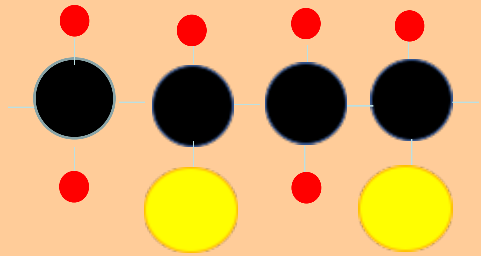
- Poly(ethylene)



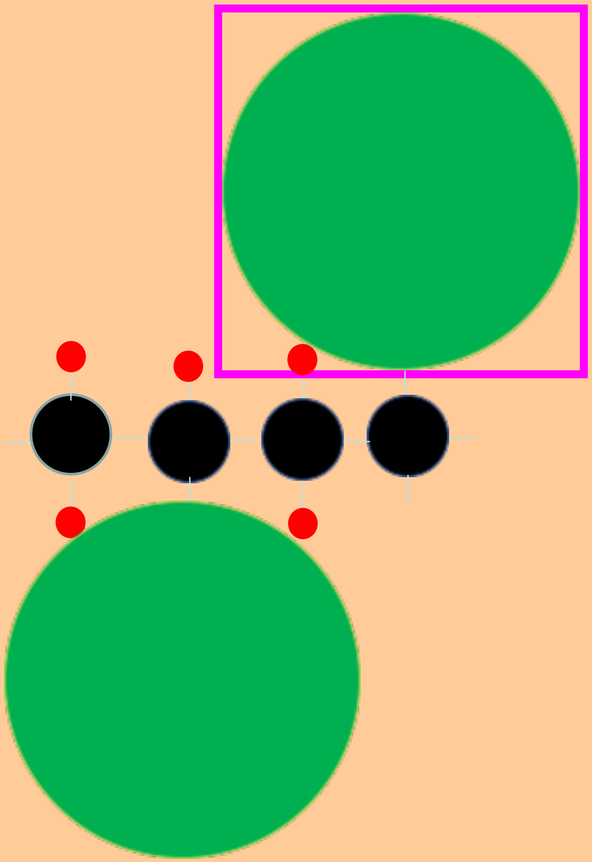
Poly(propylene)



- Poly(vinyl chloride)



Another Common Thermoplastics Material



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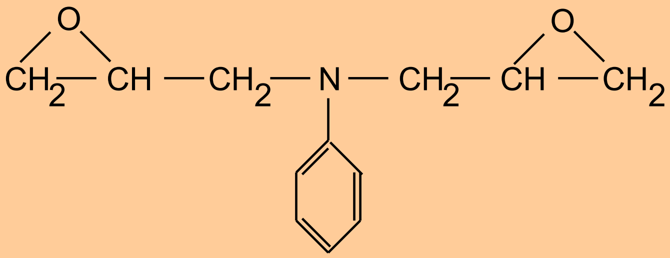
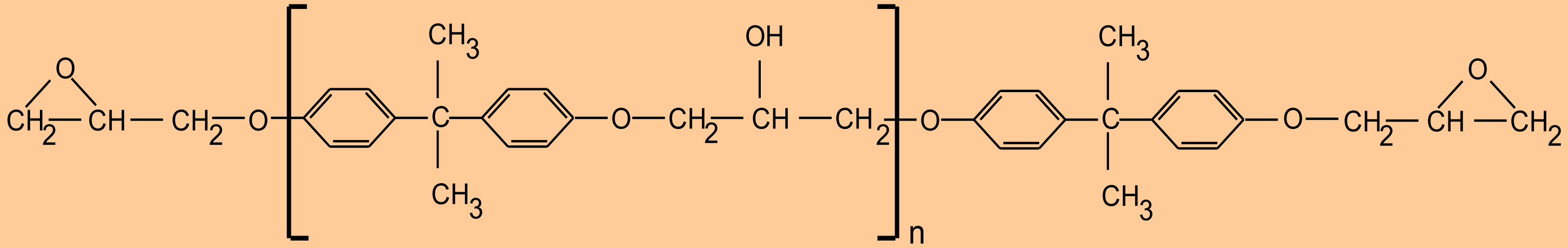
More Complex Plastics Materials

Di-Functional Resins



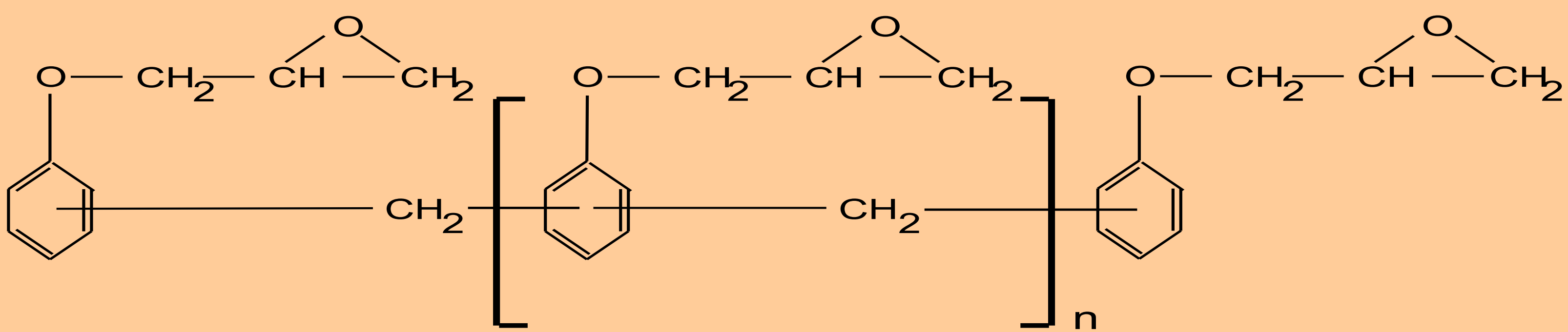
Diglycidyl Aniline

DGEBA



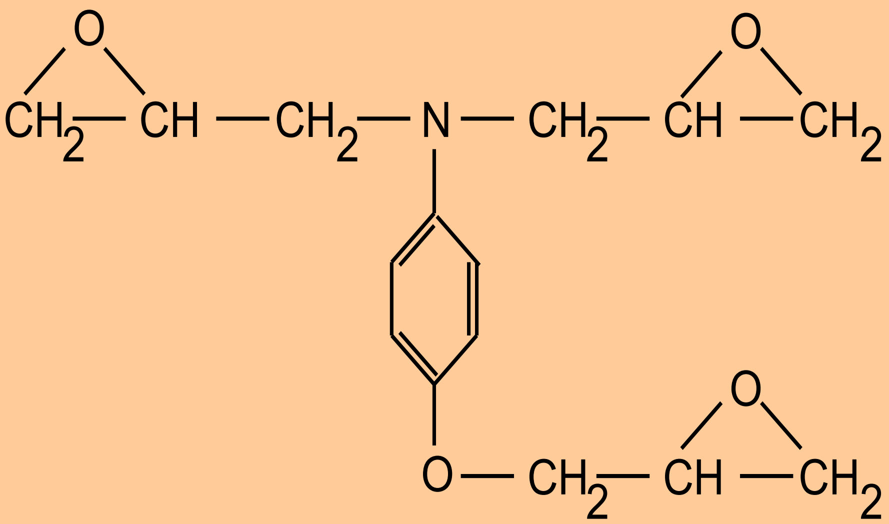
- Typical commercial DGEBA, average value for n = 0.15

Epoxy Novolak Resins



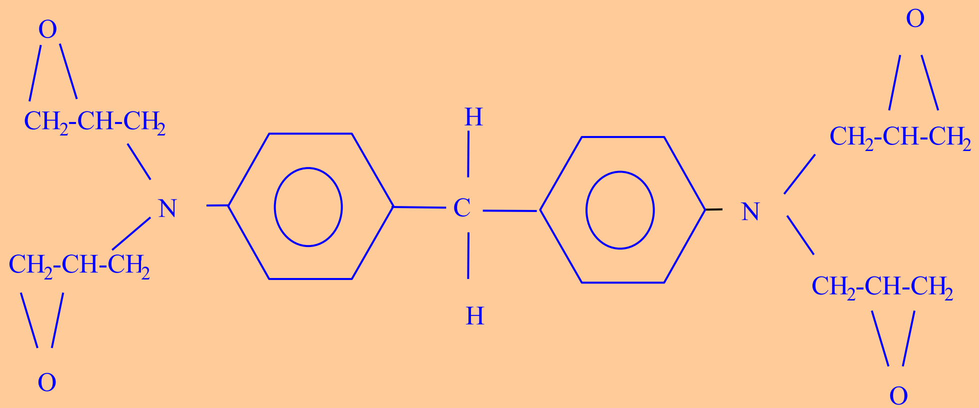
Commercial EPN Resin (n= 0.4 avg) when n = 0, Resin is (pure) DGEBF

Tri-Functional Epoxy Resins

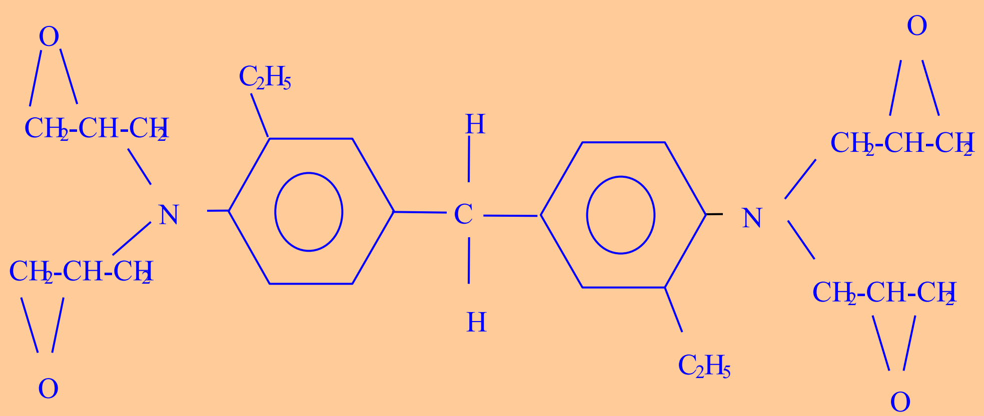


Low viscosity - brittle when cured

Tetra Functional Resins

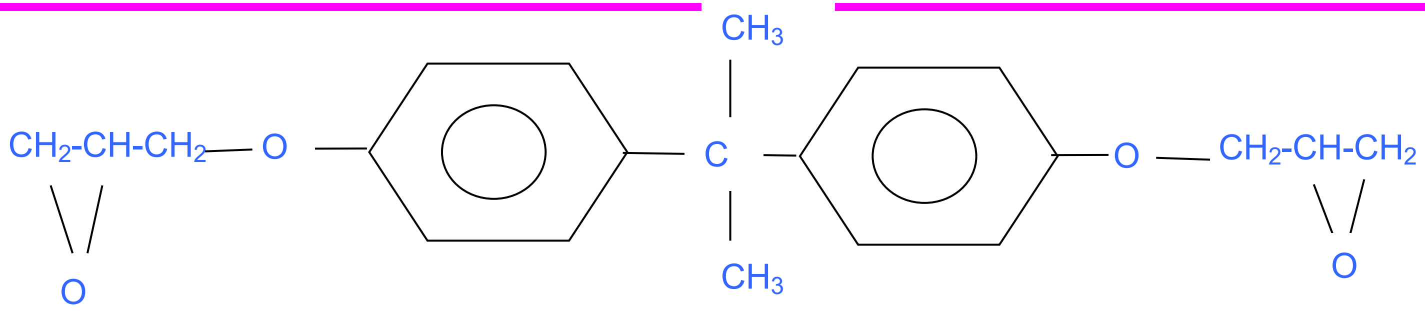


TGDM

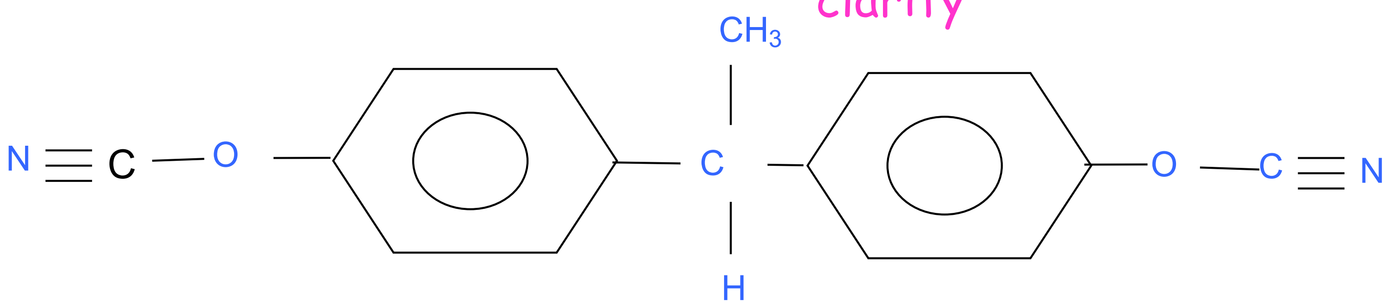


DETGDM

Cyanate Ester Resin Two Reactive Groups (Di-Functional)

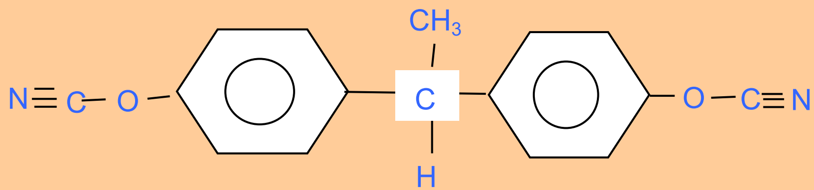


DGEBA shown pure for clarity

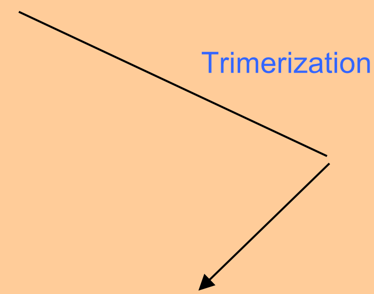


Cyanate Ester Monomer (AroCy L-10)

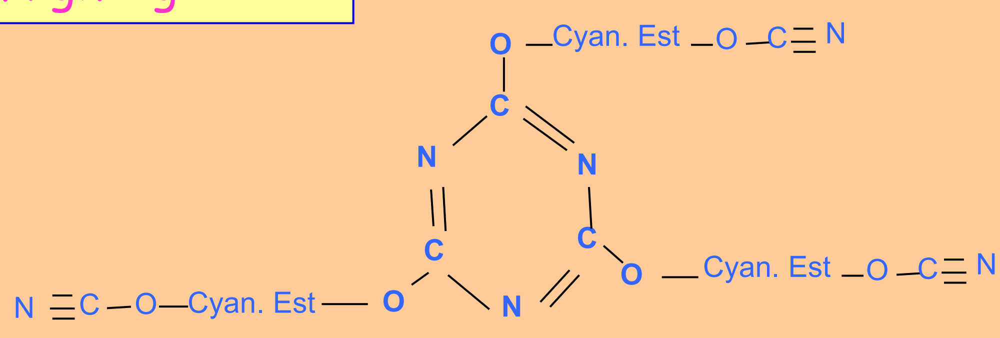
Cyanate Ester - Ring Formation



Dicyanate monomer

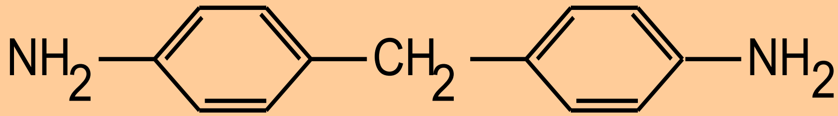


Totally cross-linked – leads to Radiation / Thermal Stability and High Tg



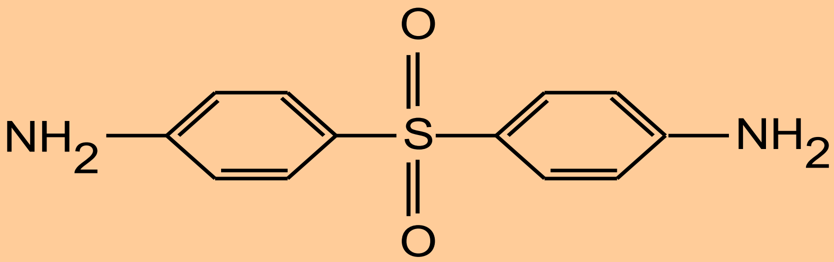
Triazine Ring

Solid Aromatic Amines



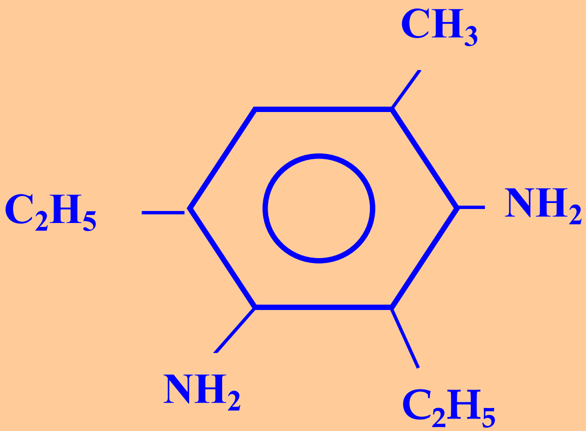
DDM (MDA)

(Suspected carcinogen)

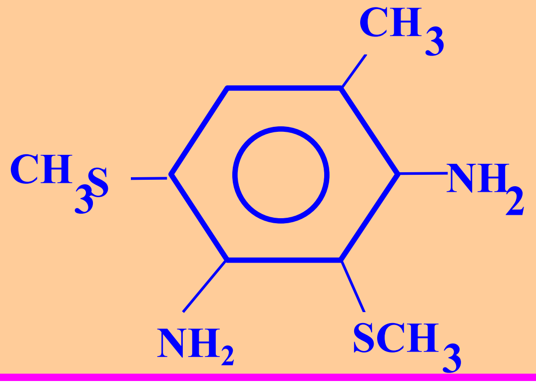


DDS

Aromatic Amines - Liquids

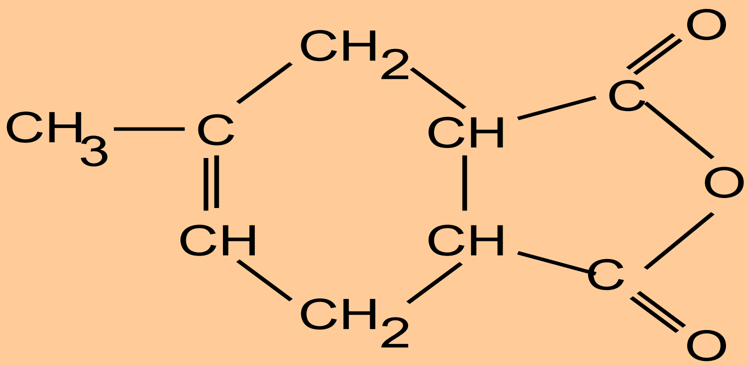


DETD Hardener AHEW 44.5



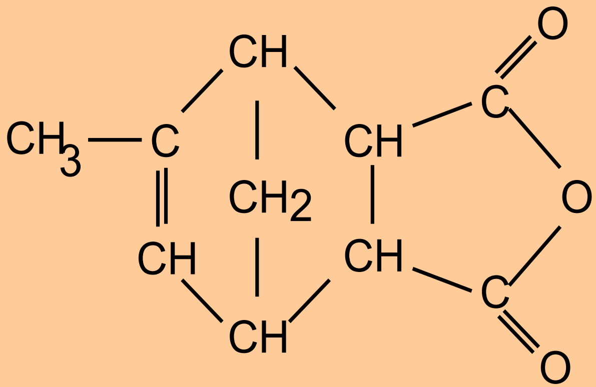
DMTD Hardener AHEW 53.5

Anhydride Hardeners



MTHPA

methyl tetra hydro phthalic anhydride



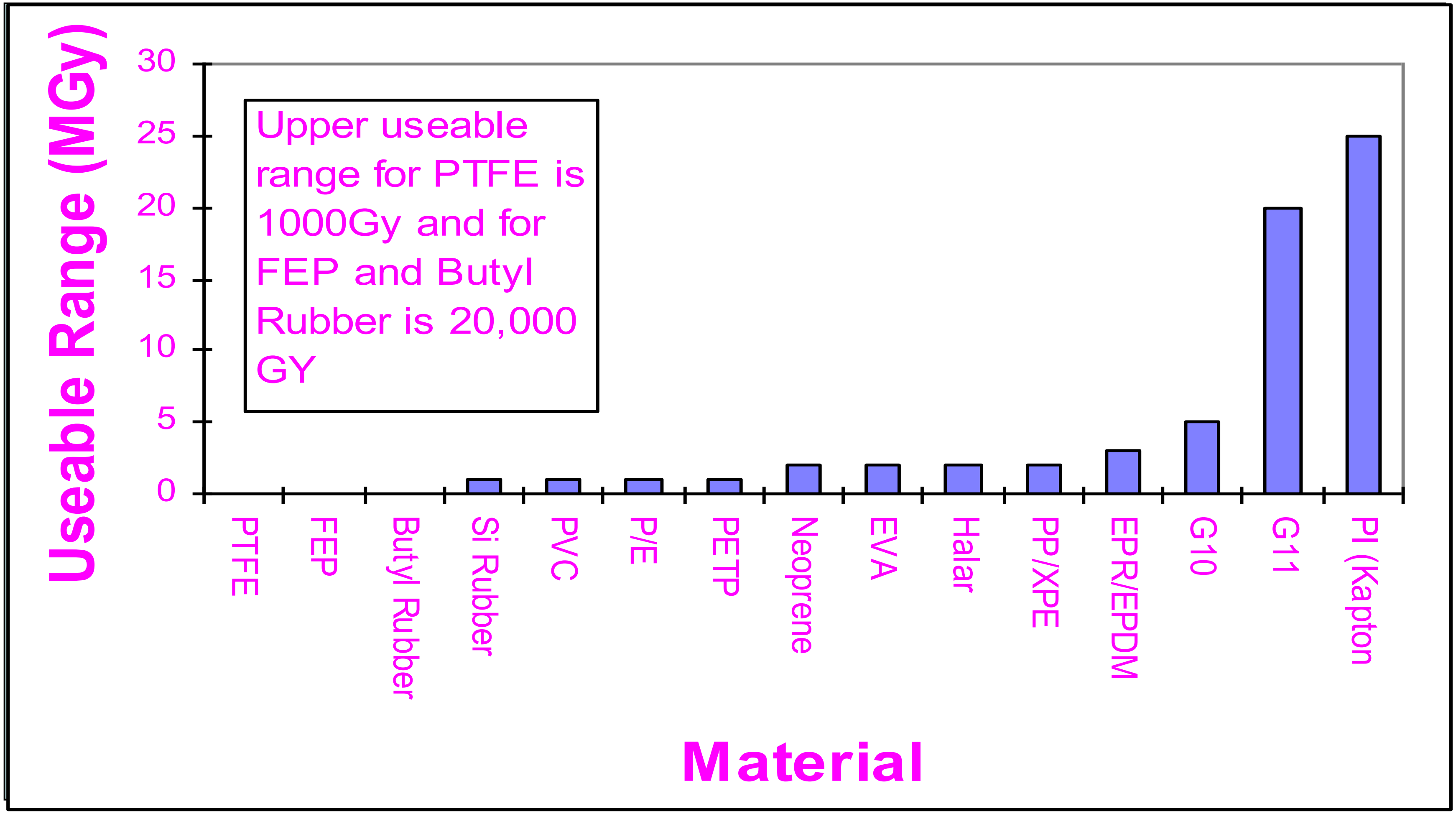
MNA

5 methyl 1,4 endomethylene cyclohexanoic anhydride

Mechanical Changes in Materials

Results & Test Methodology

Radiation Stability of Various Plastics Materials



Radiation Effects in Resins

- Changes in Mechanical properties
  - Particularly matrix dependent properties such as flexural strength and shear strength
  - Classification of "Damage"
- Radiation induced gas evolution / swelling
- Effect of Temperature

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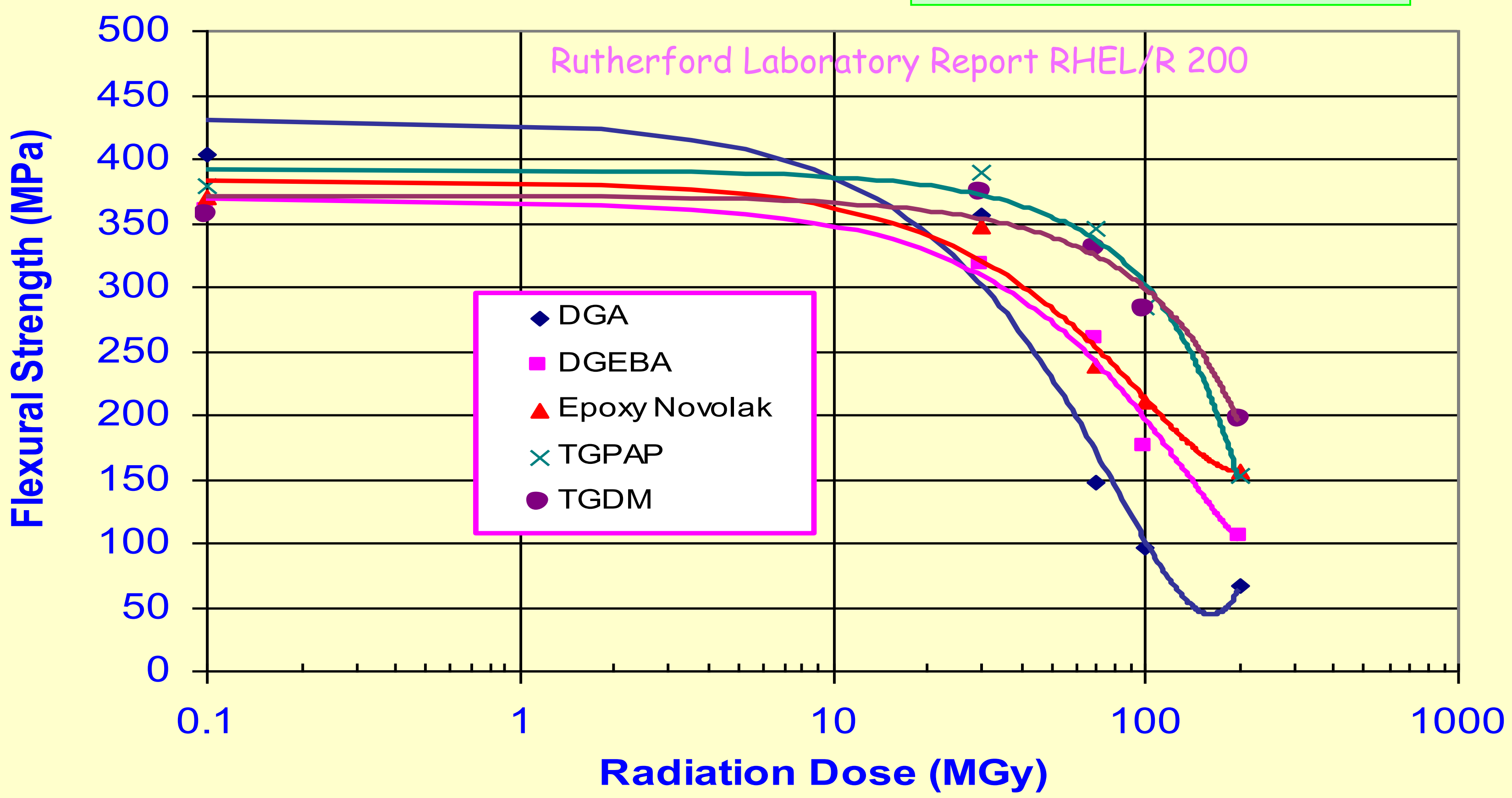
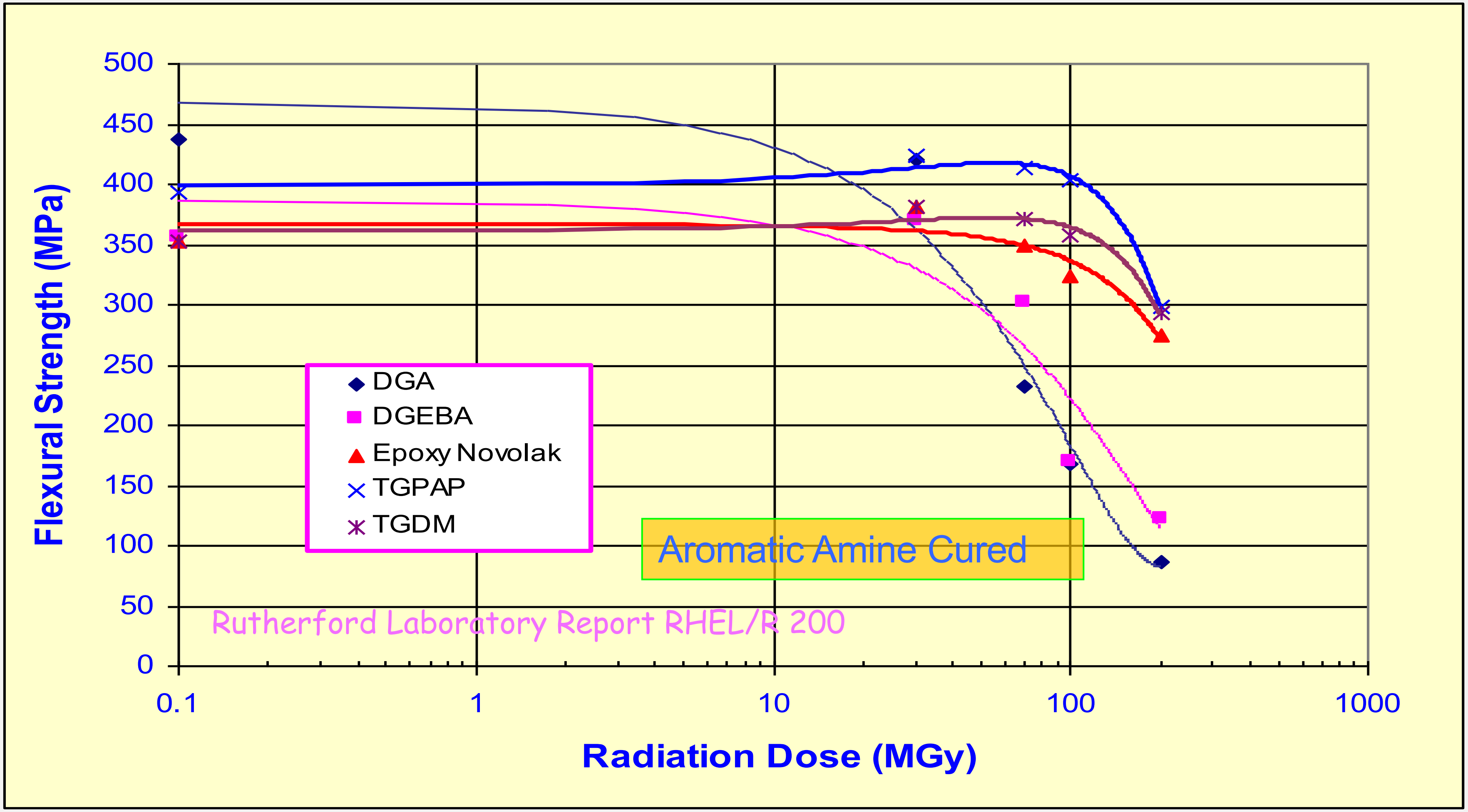
Mechanical Changes
1. Flexural Strength

Radiation Effects in Materials (1)
(Flexural Strength – Gamma Radiation – RT)

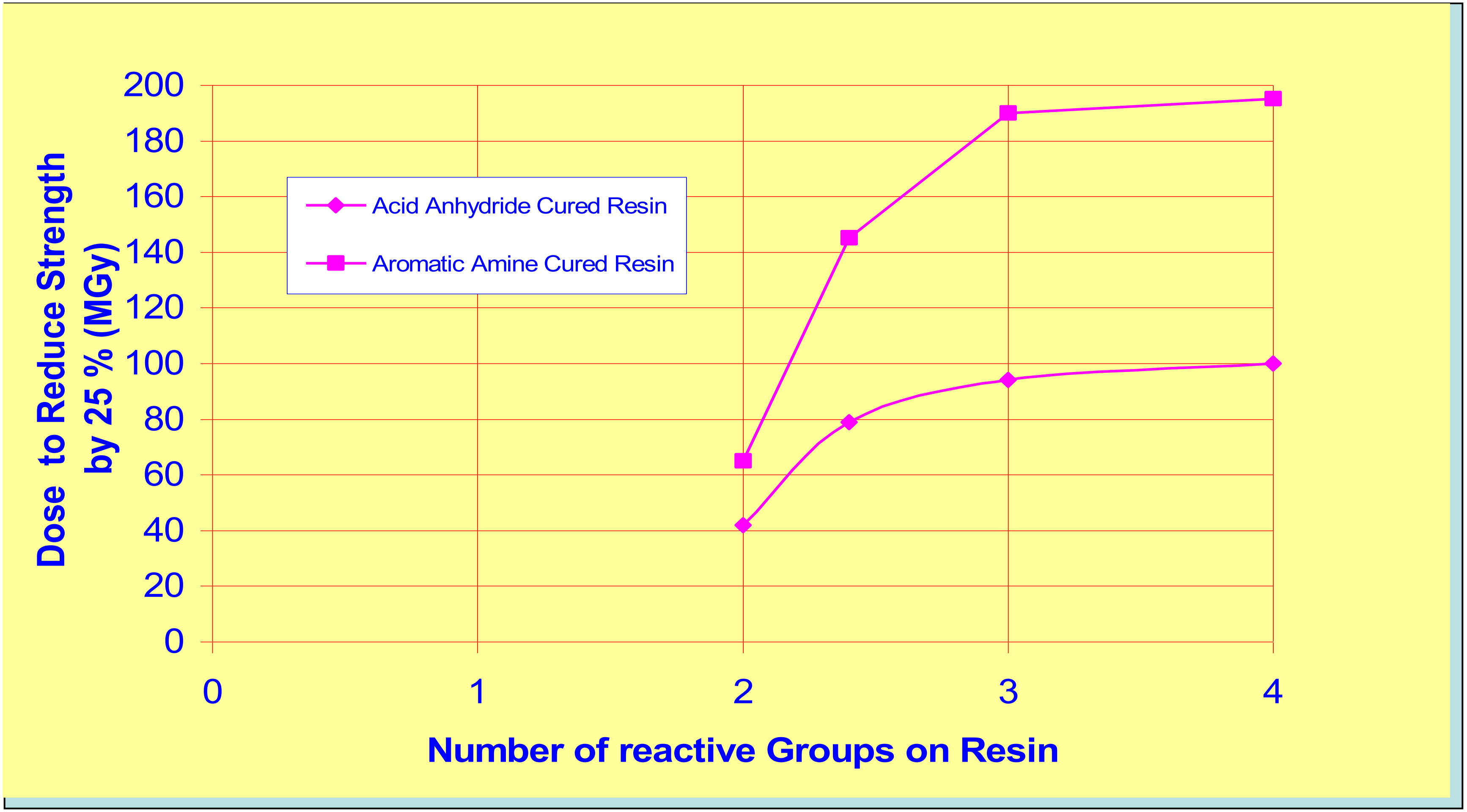
Anhydride cured Resins



Radiation Effects in Materials (2)
(Flexural Strength - Gamma Radiation - RT)

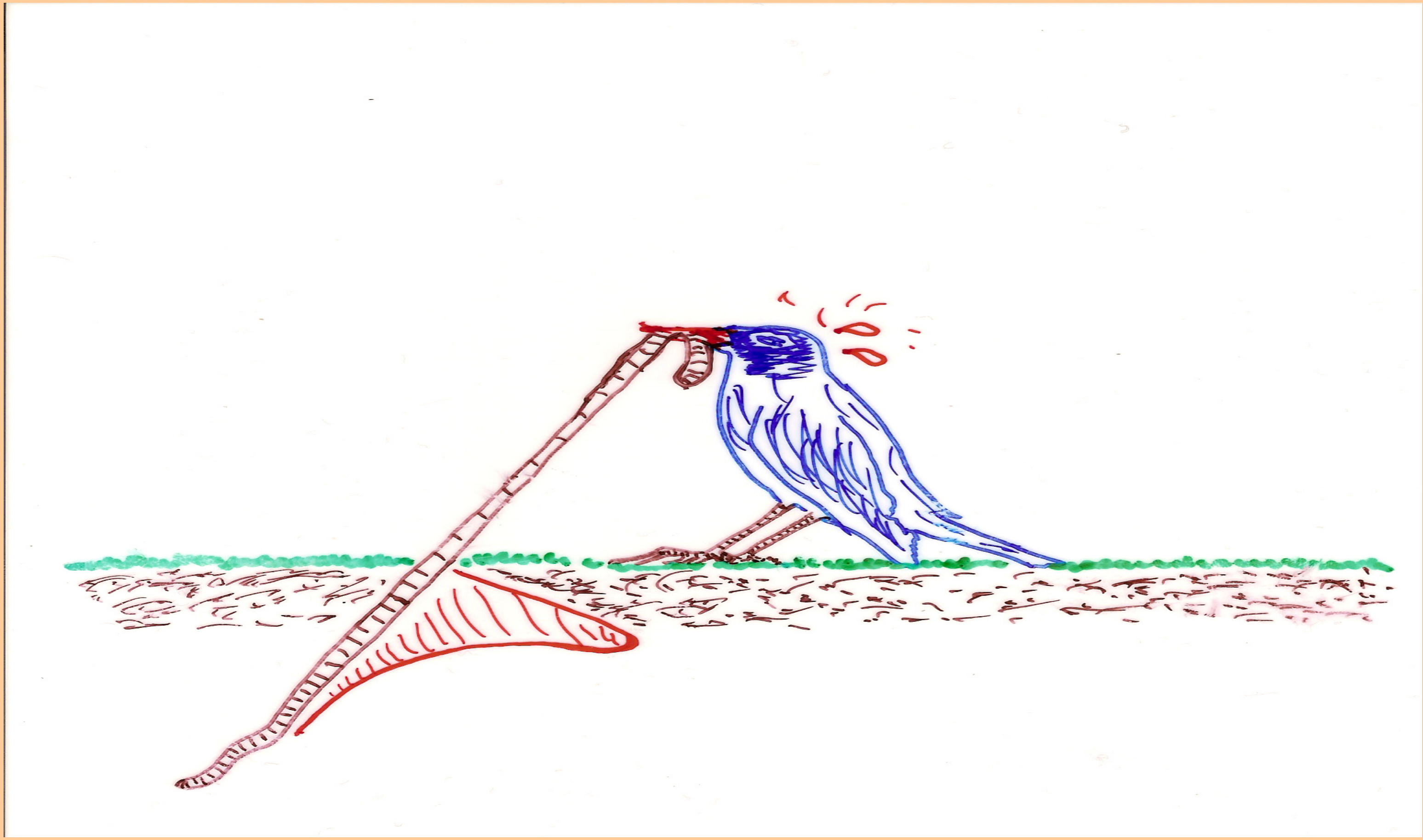


Radiation Stability and Resin Structure



Shear Testing

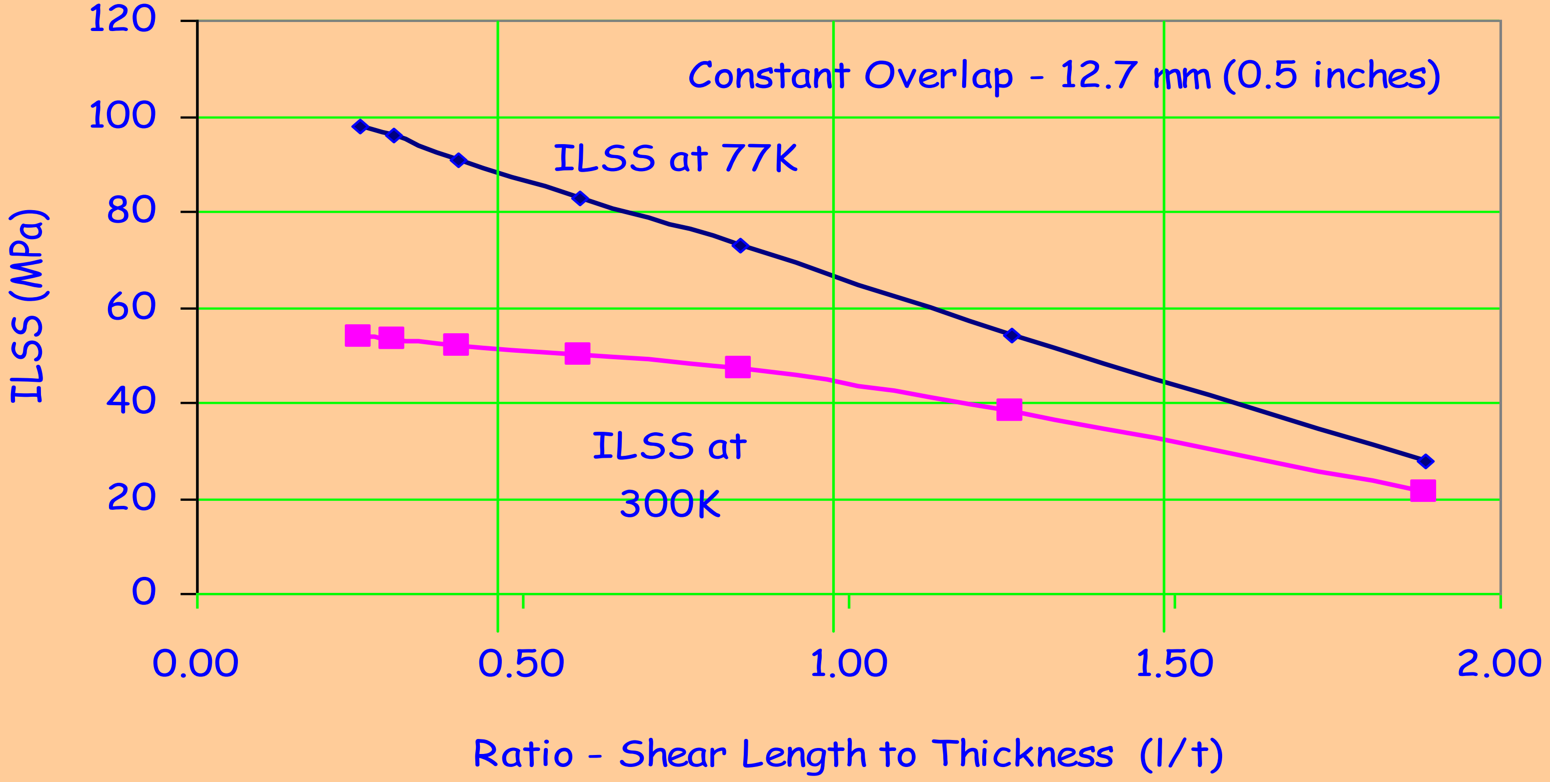
Stressful (Working) Lunch



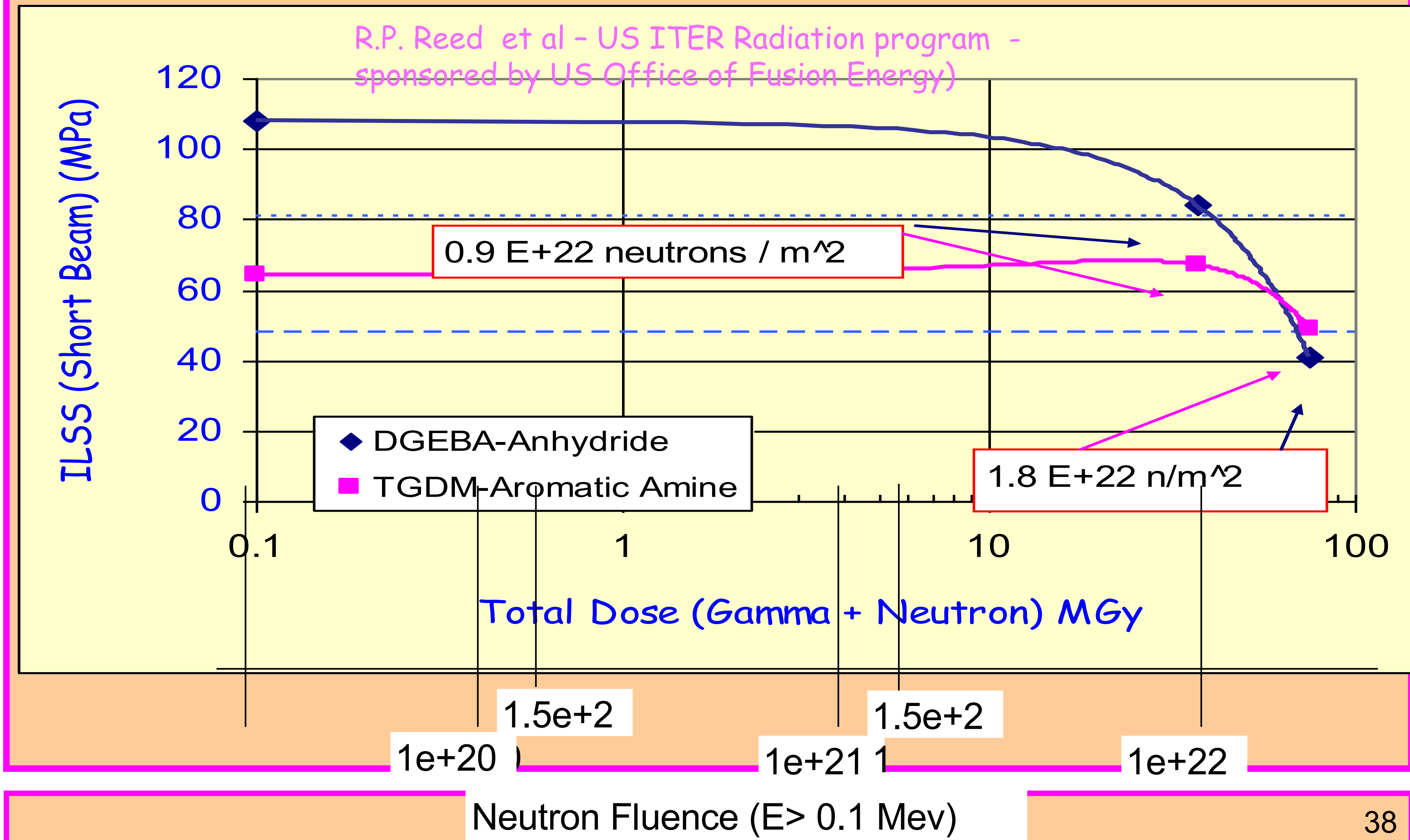
Shear Strength Evaluation

- Many methods – each has it's own problems
- Major Techniques are :
  - Guillotine – bending & stress concentrations
  - Short beam shear – variation of 3-point bending test but short span – compression on one face tension on the other
  - Shear / compression – said to be free of stress concentations – mainly used for adhesive properties

ILSS- G10
Guillotine Method



Reactor Irradiation at 5K
(Short Beam Shear)



SBS With and Without Kapton

(R.P. Reed et al – US ITER Radiation program - sponsored by US Office of Fusion Energy)

Radiation Dose (n/m2) (Mgy)	ILSS (Mpa) (SBS) No Kapton 0°	90°	ILSS (Mpa) (SBS) Kapton 0°	90	Ratio UTS/ILSS No Kapton 0°	90°	Ratio UTS/ ILSS Kapton 0°	90°
0	80	77	81	75	11	4.5	9.3	5.2
5×10^{21} (~25)	44	37	50	45	18	---	13	---
1×10^{22} (~50)	31	24	35	27	22	4.8	14	8.0

Tape Wound Samples, partly purified DGEBA – unspecified hardener

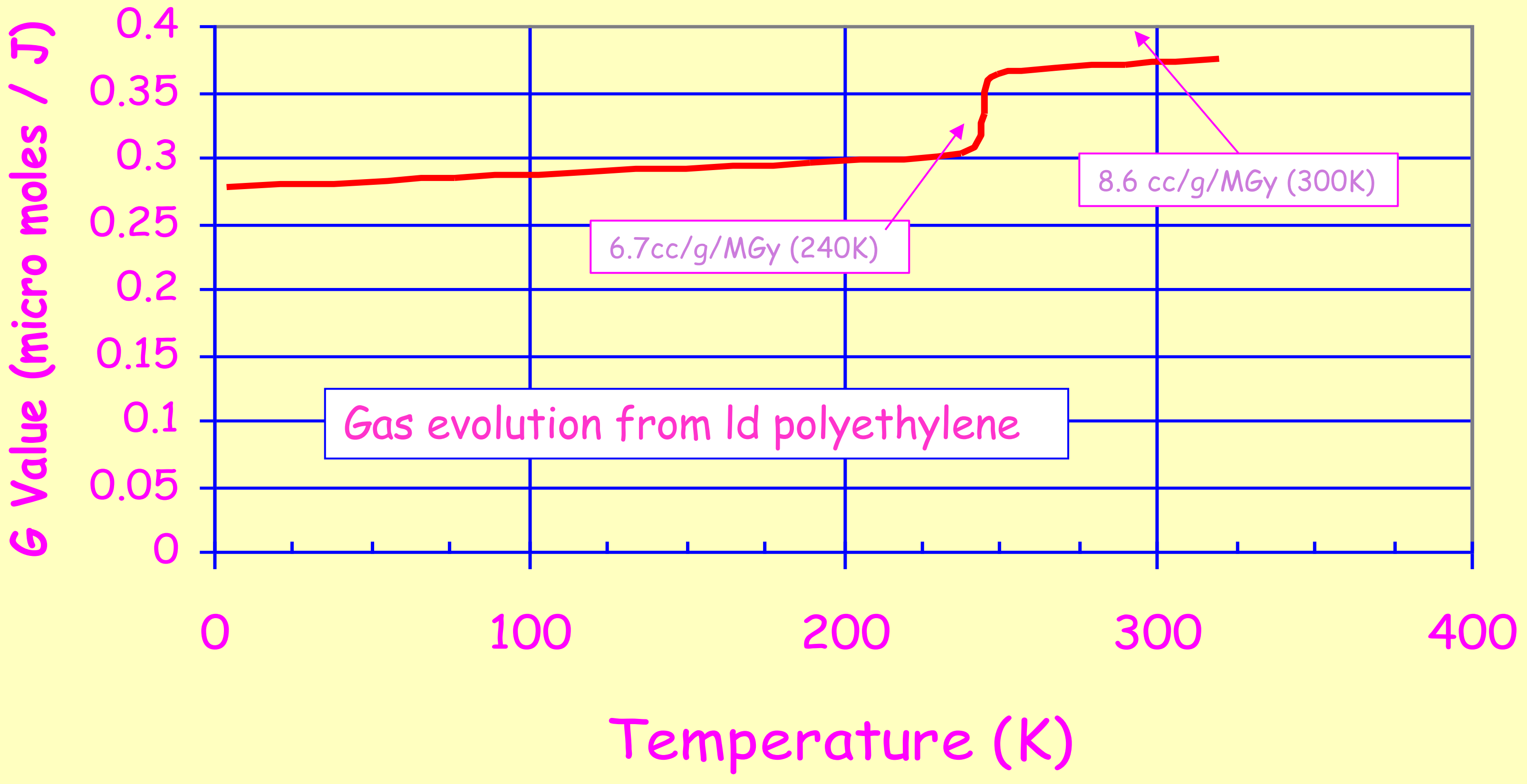
Tests in Shear Compression

- Test is 'free" of stress concentrations
- Many tests carried out RT and at 4K
- Little data on radiation stable materials
- No comparison between 4k and RT irradiation (except for samples with mica barrier) ???
- For DGEBA cured with Acid Anhydride:
  - Test at 4K – no irradiation (45 angle) 190 Mpa
  - Test at 4K irradiated at 4K* (45 angle) 26 MPa

* Reactor irradiated 1.8 x 10^{22} n/m^2 (~67 MGy)

Gas Evolution & Swelling

Radiation - Effect of Temperature



Gas Evolution & Reactor Irradiation

(Evans & Reed, Adv. Cry. Eng. Vol 42, 29 – 35)

Resin	Hardener	Gas (cc/g/MGy)
DGEBF	DETD	0.58
DGEBF	DMTD	2.32
TGPAP	DETD	0.58
DETGDM	DETD	0.91
DETGDM	DMTD	2.78
DGEBA	DDM	0.30

For Reference: DGEBF/MTHPA 1.08cc/g/MGy from Reactor Irradiation – polyethylene dosimeter

Composition of Radiation Induced Gasses

(Generalised and approximating)

- Amine Cured (aliphatic or aromatic):
  90% hydrogen, 10% carbon monoxide
- Acid Anhydride cured:
  20% hydrogen, 20% carbon monoxide, 60% carbon dioxide

Is Gas Trapped in Bulk Specimens?

(Evans & Reed, Adv. Cry. Eng. Vol 42, 29 – 35)

- **Bulk means ~ 7 mm cube**

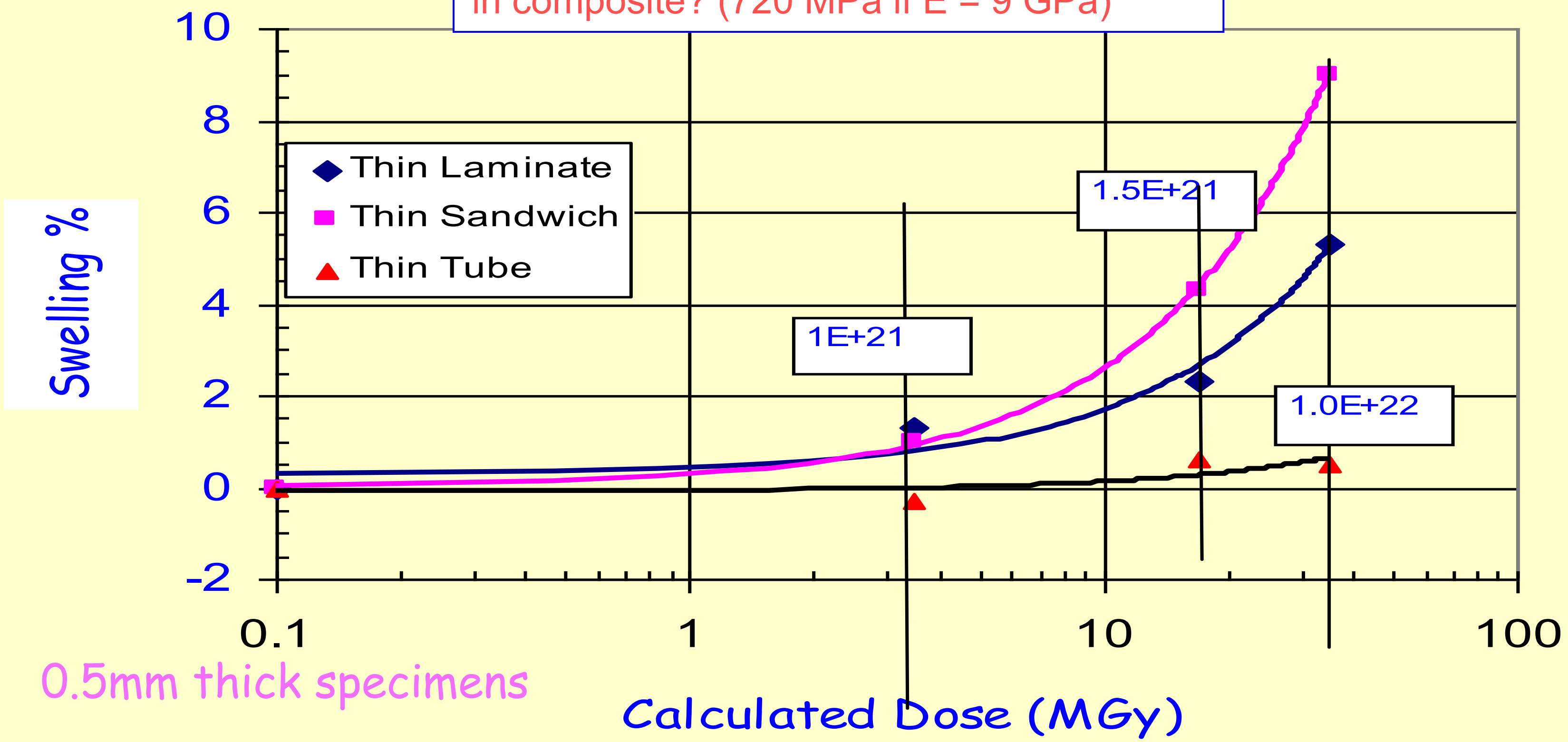
Material	Gas Production Rate Cc's / g/MGy		% Gas Trapped
	True *	Bulk**	
DGEBF/MTHPA	1.03	0.47	53
DGEBF / DETD	0.58	0.44	24
TGPAP / MTHPA	1.10	0.64	42
TGPAP / DETD	0.58	0.64	0

* Rate from powdered sample ** Rate from 7 x 7 x 7 cubes

Swelling & Reactor Irradiation at 5K

(Humer et al - Cryogenics, 40 , pp 295-301)

If glass is ~50 vol% - swelling in resin phase is double composite What is stress in composite? (720 MPa if E = 9 GPa)



0.5mm thick specimens

Swelling and Mass Loss (20 MGy) Reactor Irradiation at 5K – Unfilled Resin

(Evans & Reed, Adv. Cry. Eng. , Vol. 46, pp 211 - 218)

Resin	Hardener	Change in Properties (%) Diam	Length	Mass	Mass Change % / MGy
DGEBF	MTHPA	-0.1	0.0	-0.8	-0.04
EPN	MTHPA	0.3	0.0	-1.0	-0.05
DGEBF	DETD	0.1	0.2	-0.1	< -0.01
DGEBA	DETD	0.0	0.2	-0.1	< -0.01
TGDM	DDS	0.0	0.3	-0.1	< -0.01
TGPAP	DETD	0.0	0.0	0.0	<-0.01
DGEBA	MTHPA	-0.1	-0.2	-0.8	-0.04
TGPAP	MTHPA	0.5	-0.1	-0.7	-0.04

No Change in Young's Modulus (compression) after Irradiation

10 mm diam x 10 mm long cast and machined resin samples

The Last Word on Swelling

- Available data is very confusing – my viewis that swelling doesn't occur in epoxies or CE at dose levels reported'

- WHY – what happens to gas?
  - No new material created – gas is from atoms already present
  - Molecules possibly 'trapped' in area of formation ('cage effect')
  - Gas is 'in solution' – does not occupy a separate volume within resin

Creep and Radiation

The Real World

"---- that some discussion be focussed on integrating the insulation materials results with magnet design and operation issues. In other words, cover more than just insulation properties but also how these impinge on coil fabrication or operation.

How do properties measured on small samples relate to properties in large scale impregnated coil cross-sections under multi-dimensional loads, including combined mechanical, thermal and radiation loads ---"

Joe Minervini

(Assistant Director, MIT Plasma Fusion Center)

Irradiation at 5K – DGEBF / Anhydride

(Evans & Reed Adv. Cry. Eng. Vol 44, 183 - 190)

Neutron Fluence (E.0.1 MeV	Stress During Irradiation (MPa)	Failure Stress (MPa)
0 (control)	0	172
5 x 10^{21}	0	124
5 x 10^{21}	30	105
1 x 10^{22}	30	92

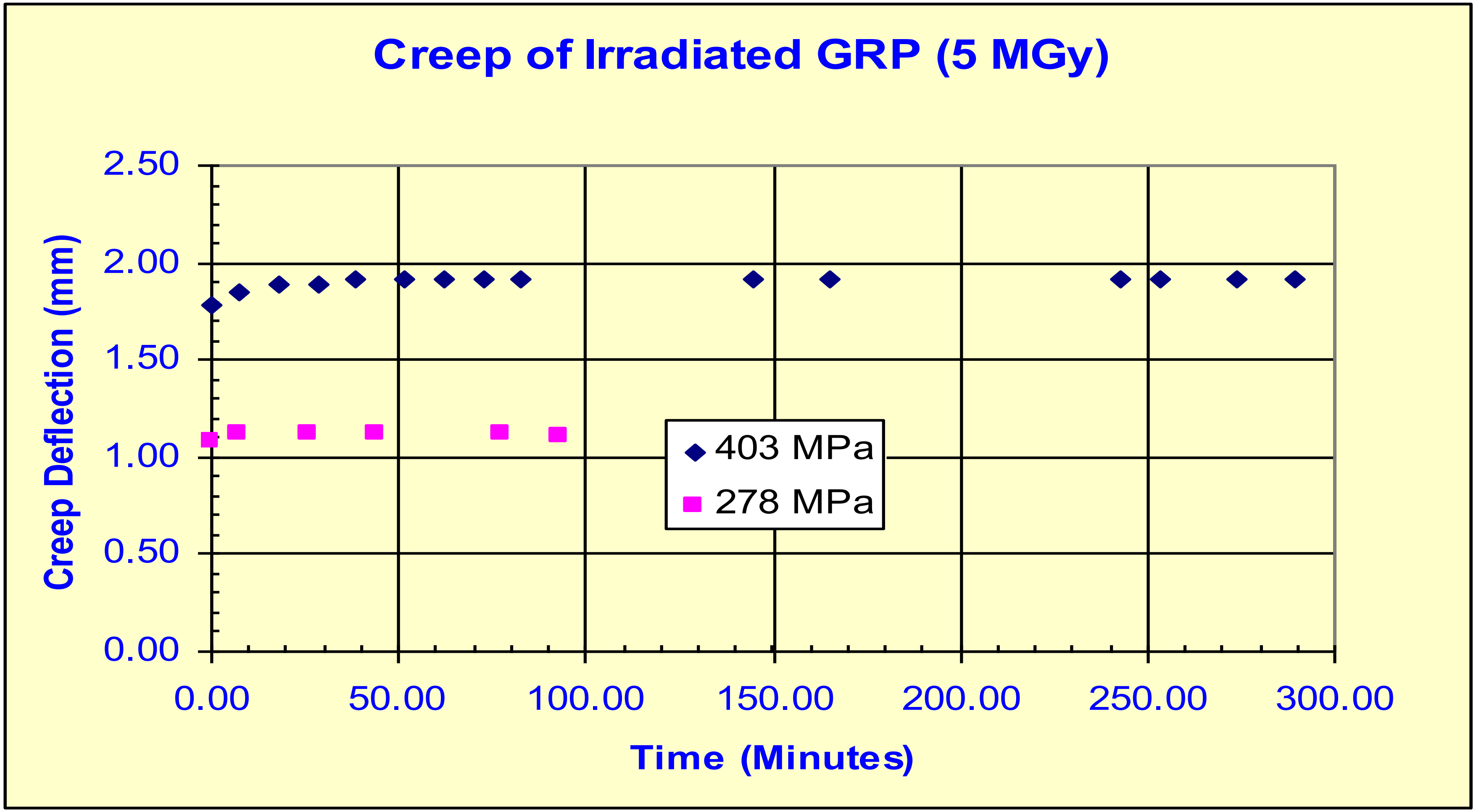
Irradiation at 5K - TGDM / Aromatic Amine

(Evans & Reed Adv. Cry. Eng. Vol 44, 183 - 190)

Neutron Fluence (E.0.1 MeV	Stress During Irradiation (MPa)	Failure Stress (MPa)
0 (control)	0	162
5×10^{21}	0	157
5×10^{21}	30	139
1×10^{22}	30	122

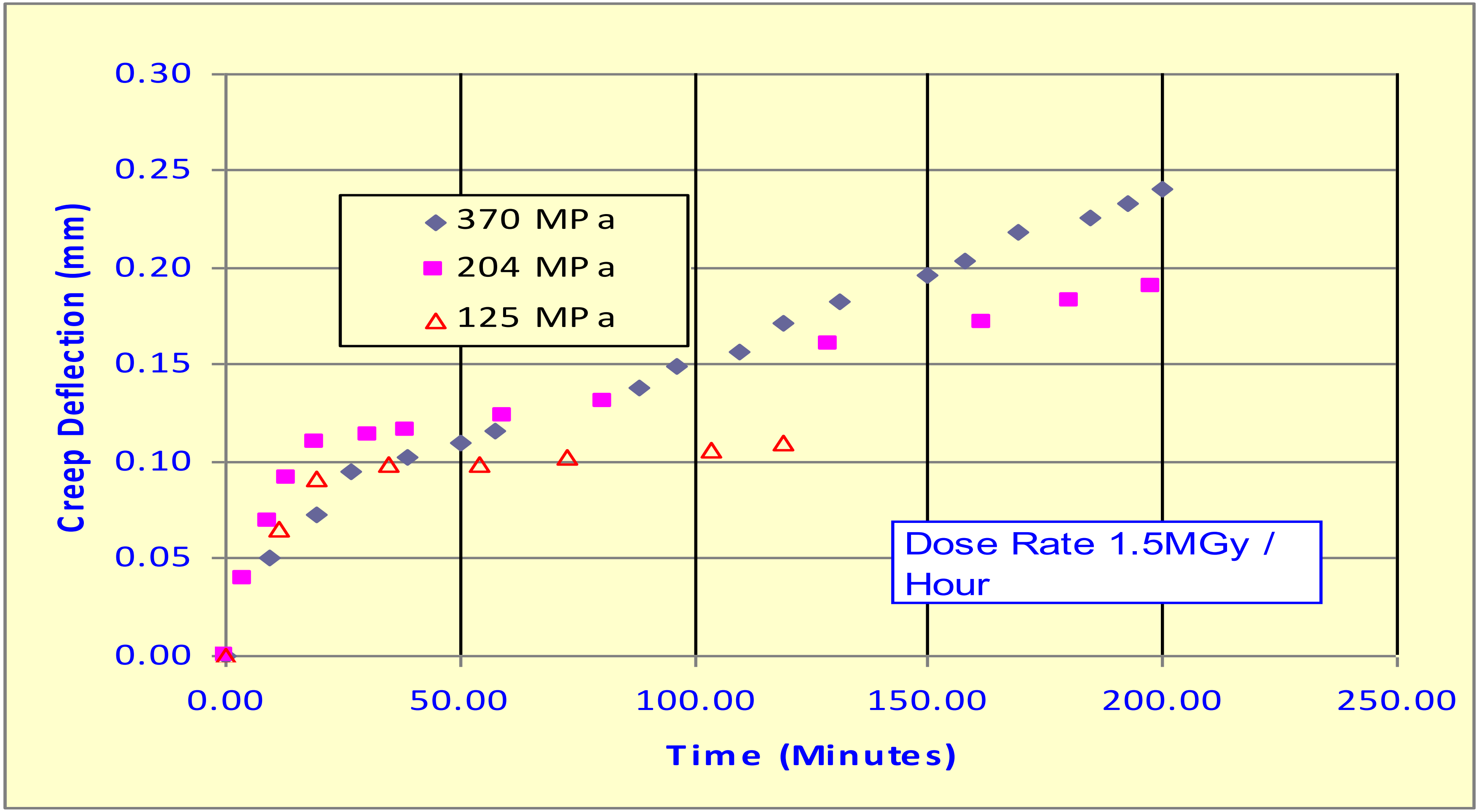
Creep at 77K of Irradiated Material

(Nishiura T et al - Cryogenics, Vol. 35, No. 11, pp 747 – 749)



Creep During Irradiation at 77K

(Nishiura T, et al - Cryogenics, Vol. 35, No. 11, pp 747 - 749)



Creep Rates

Irradiation Conditions	Stress Level (MPa)	Creep Rate (mm/minute)
Pre-Irrad*	278	$<5 \times 10^{-5}$
Pre-Irrad*	403	$\sim 9 \times 10^{-5}$
During Irrad**	125	1.5×10^{-4}
During Irrad**	204	4.5×10^{-4}
During Irrad**	370	9.0×10^{-4}

* Pre-Irradiated 5 MGY, ** Total during irradiation ~ 6MGy

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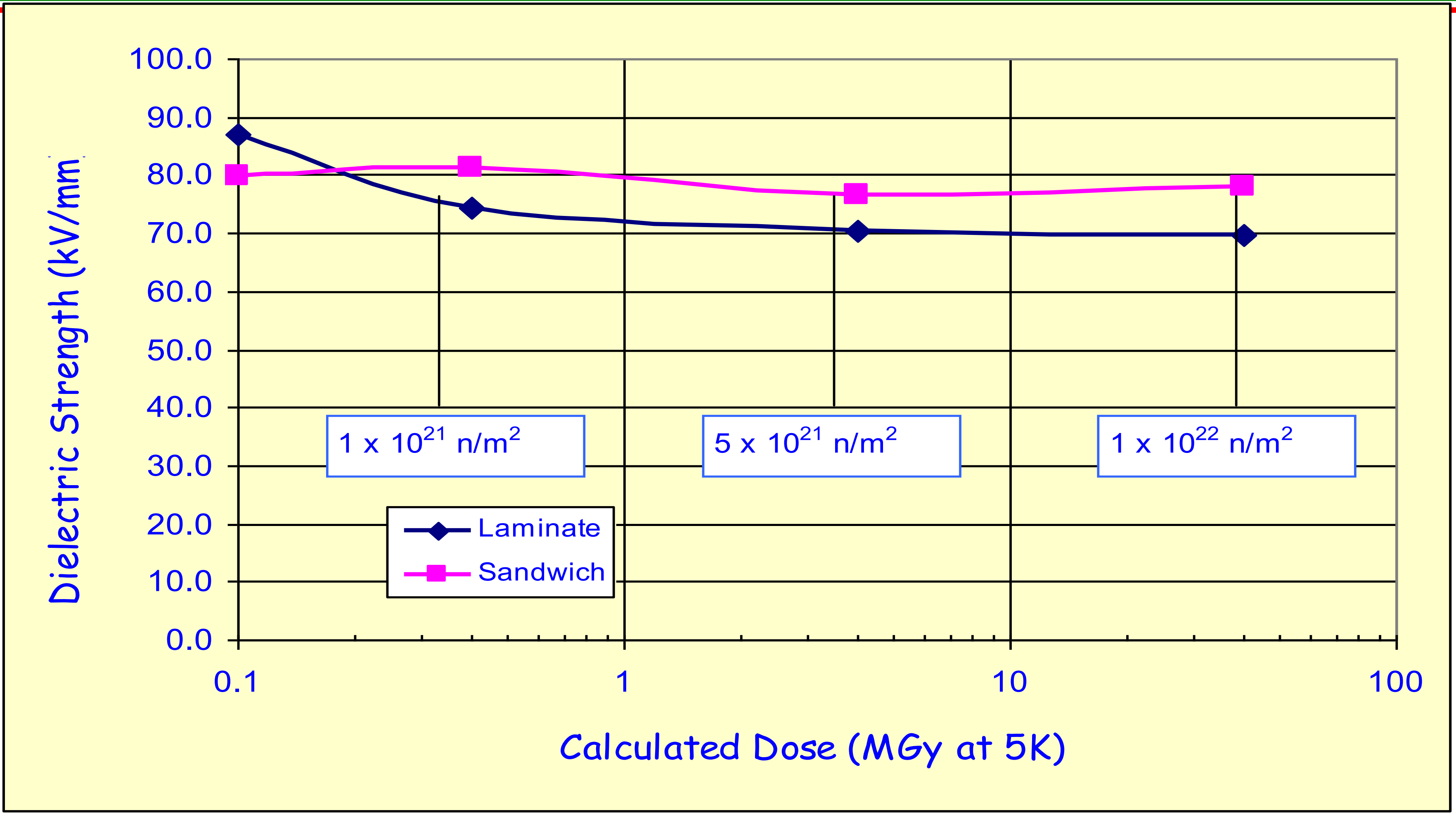
A Quick Look at Electrical Properties

Electrical Properties and Radiation



Summary

- High functionality promotes radiation stability
- Aromaticity (resin or hardener) also promotes stability
- Best Epoxies -up to 200 MGy – CE even more
- Some synergism between irradiation under stress
- Gas volumes and composition related to structure
- Results on swelling are scattered and confusing – on balance no swelling up to 100 MGy
- No significant change in electrical properties – up to ~ 100 MGy – no apparent relationship with structure