Analytical Techniques for Assessing the Effects of Radiation on UHMWPE

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Outline

- Common analytical techniques used in the industry
  - Pre-irradiation
  - Post-irradiation
- Case studies

Analytical Test Techniques

- Prior to Irradiation
  - Powder
  - Consolidated Resin
- Post-Irradiation
  - Puck, Rod, or Slab
  - Machined Component

Prior To Irradiation

- Electron microscopy
  - SEM, TEM
- Molecular weight analysis
  - GPC, dilute solution viscometry, light scattering
- Chemical analysis
  - Net ash, trace element, FTIR, DSC

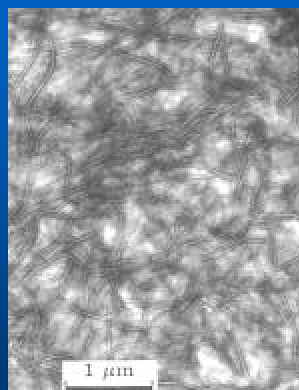
Post-Irradiation

- Mechanical Analysis
  - Tensile, compression, fatigue, J-integral, small punch
- Crosslink density
  - sol-gel, transient swelling
- Differential scanning calorimetry
  - crystallinity, melting point
- FTIR
  - TVI, VI, OI, IR-crystallinity

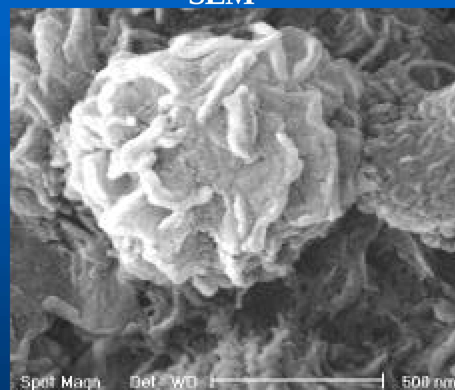
Pre-Irradiation Analysis

Electron Microscopy

TEM



SEM



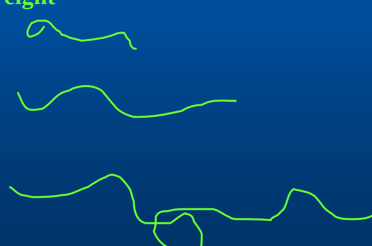
-Chlorosulfonic acid
-Uranyl acetate

-Gold coating
-ESEM

Molecular Weight Analysis

- Polymers are a distribution of chain lengths (molecular weights)

#chains	Molecular Weight
n_1	M_1
n_2	M_2
n_3	M_3

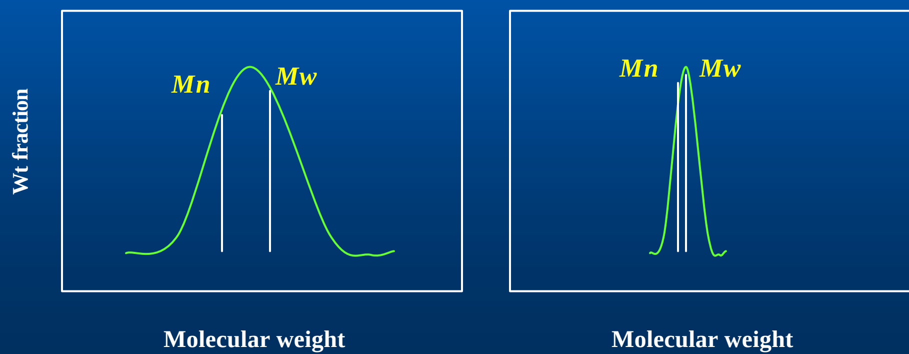


Moments of distribution

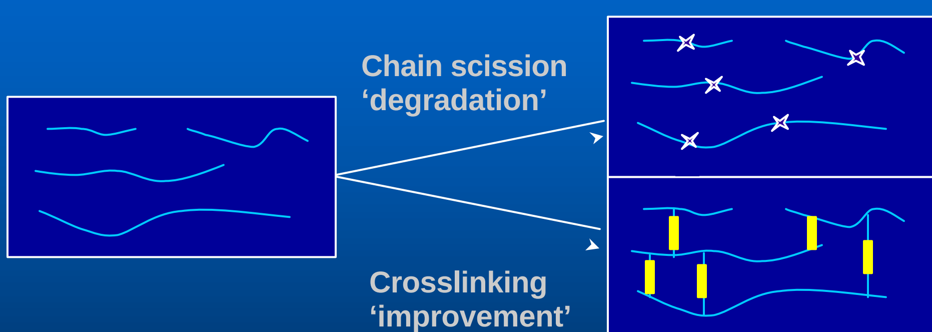
$$M_z = \frac{\sum_{i=1}^{m} n_i M_i^{z}}{\sum_{i=1}^{m} n_i M_i^{z-1}}$$

Molecular Weight Analysis

$$M_n = \frac{\sum_{i=1}^{m} n_i M_i}{\sum_{i=1}^{m} n_i} \qquad M_w = \frac{\sum_{i=1}^{m} n_i M_i^{\,2}}{\sum_{i=1}^{m} n_i M_i} \qquad PDI = \frac{M_w}{M_n}$$



Nomenclature in Radiation Chemistry



G value = # of events (yield) per 100eV or radiation energy

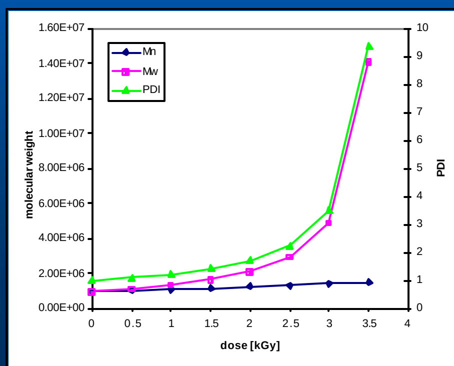
100 eV = 1.602×10^{-17} kGy.g

Radiation Effects on Molecular Weight

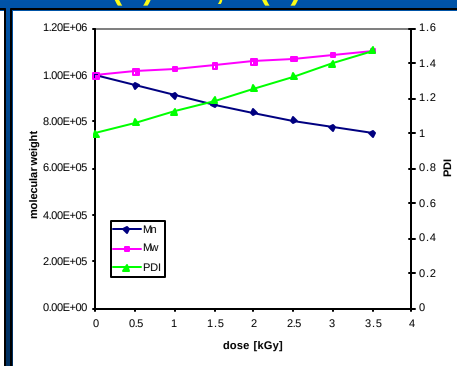
$$M_n^{-1} = M_{n,0}^{-1} + [G_s - G_x] D / 100 N_{av}$$

$$M_w^{-1} = M_{w,0}^{-1} + [G_s / 2 - 2G_x] D / 100 N_{av}$$

G(X)=1.4, G(S)=0.5



G(X)=0.5, G(S)=1.4

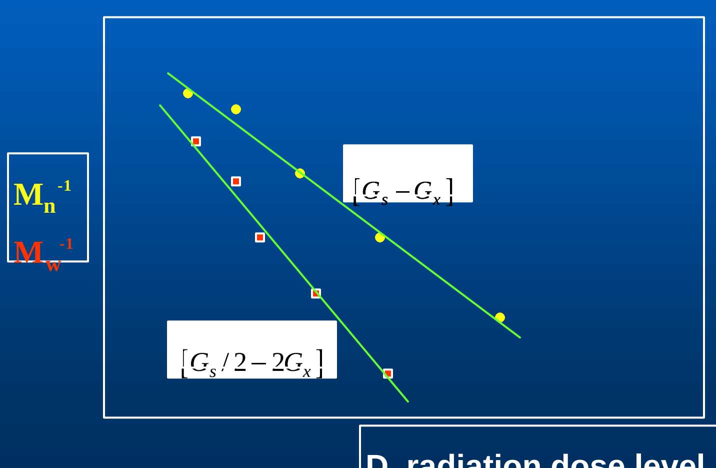


Guven, O., "Crosslinking and Scission in Polymers"

Measuring G-Values

$$M_n^{-1} = M_{n,0}^{-1} + [G_s - G_x] D / 100 N_{av}$$

$$M_w^{-1} = M_{w,0}^{-1} + [G_s / 2 - 2G_x] D / 100 N_{av}$$



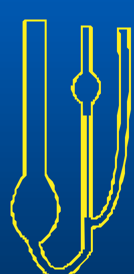
How to Measure Molecular Weight

- Dilute Solution Viscometry
  - Viscosity-averaged Molecular Weight
- Gel Permeation Chromatography
  - Gives molecular weight distribution

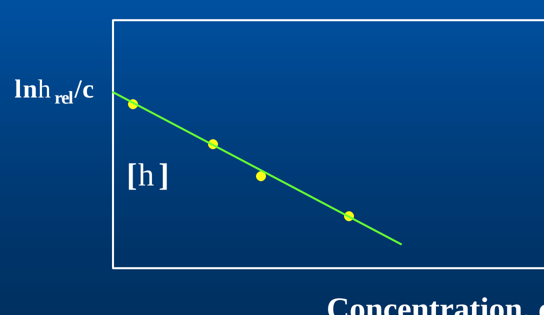
Dilute Solution Viscometry

Measures size of polymer chain
Empirically related to molecular weight for linear polymers
ASTM D2857, F4020

$$\eta_{rel} = \eta/\eta_0 \approx t/t_0$$
$$[\eta] = [(\ln \eta_{rel})/c]_{c=0}$$



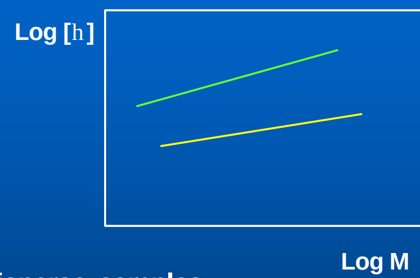
Ubbelohde



Huggins, J. Am. Soc. (1942)

Relating to Molecular Weight

$[h] = K'M^a$



Yields M_v (10-20 below M_w)

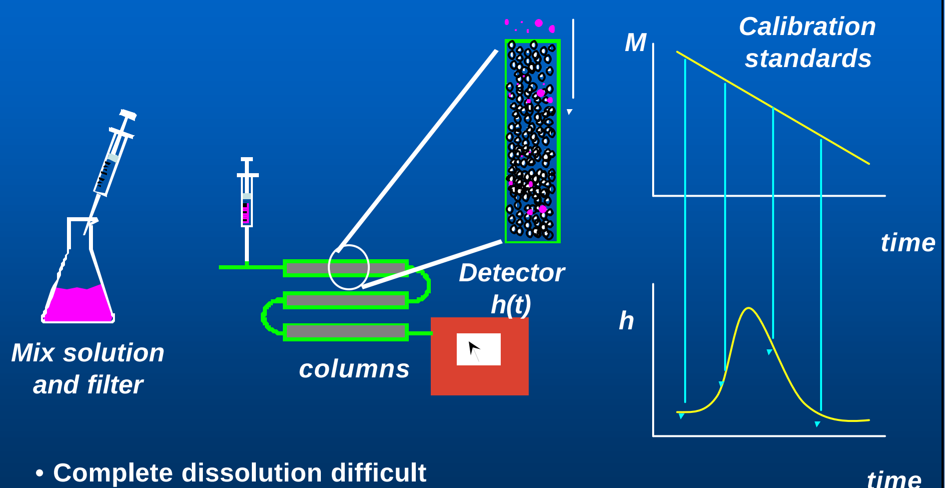
K' **and** ***a***

- determined empirically from monodisperse samples
- of known molecular weight
- function solvent system used

Polyethylene in decahydronapthalene (135C) $M_{vnom} = 5.37 \times 10^4 [h]^{1.37}$

Polymer Handbook, Brandrup, ed.

Gel Permeation Chromatography

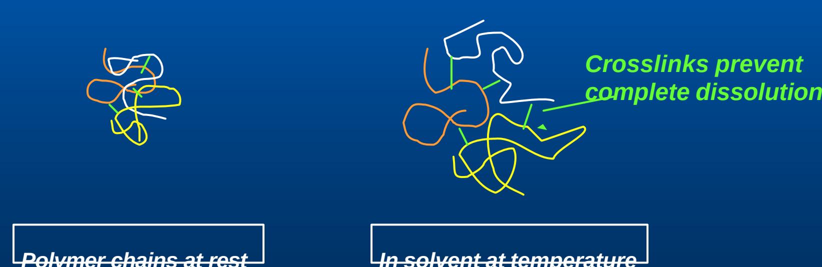


- Complete dissolution difficult
- Lose high molecular weight components

Post-Irradiation Analysis

Swelling Studies

- Used to characterize degree of crosslinking in polymer networks
- Competition between free energy of mixing and free energy of elasticity



Swelling Theory

- Flory, *Principals of Polymer Chemistry* (1953)
- Assumes a tetrafunctional network
  - free ends do not contribute to elastic (retractive) forces

$$\Delta F_m = kT\left[n_1 \ln u_1 + c_1 n \mu_2\right]$$
$$\Delta F_{el} = \left[kTn_e/2\right]\left[3a_s^2 - 3 - \ln a_s^3\right]$$

$$n_d = (-\ln(1-q^{-1}) + q^{-1} + c\,q^{-2})/V_1 q^{-1/3}$$

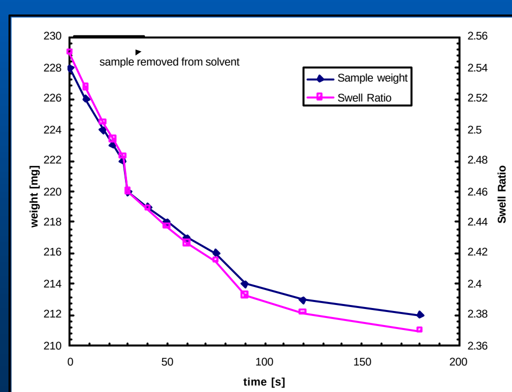
Measure swell ratio $q = \left[\frac{V_f}{V_0}\right] = \left[\frac{H_f}{H_0}\right]^3$

Swelling Studies

Per ASTM D2765

- **Gravimetric approach**

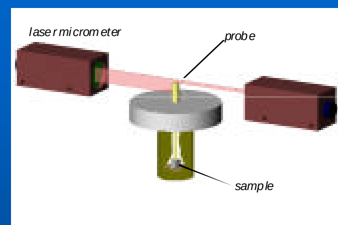
- **Solvent loss**
- **Handling of hazardous hot solvent**

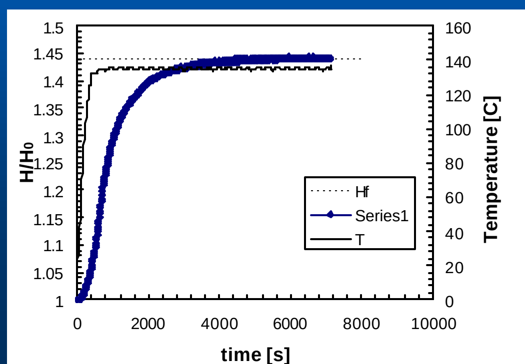


Swelling Studies

Per new ASTM standard

- **In Situ measurements**
- **Transient and steady state results**
- **Round Robin in progress**

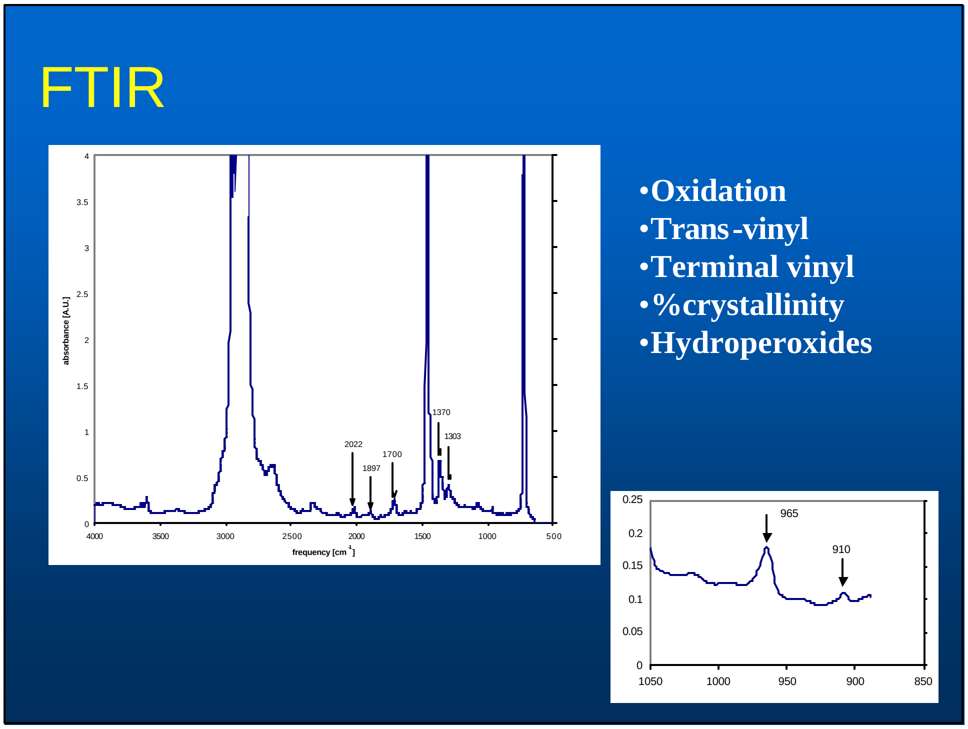


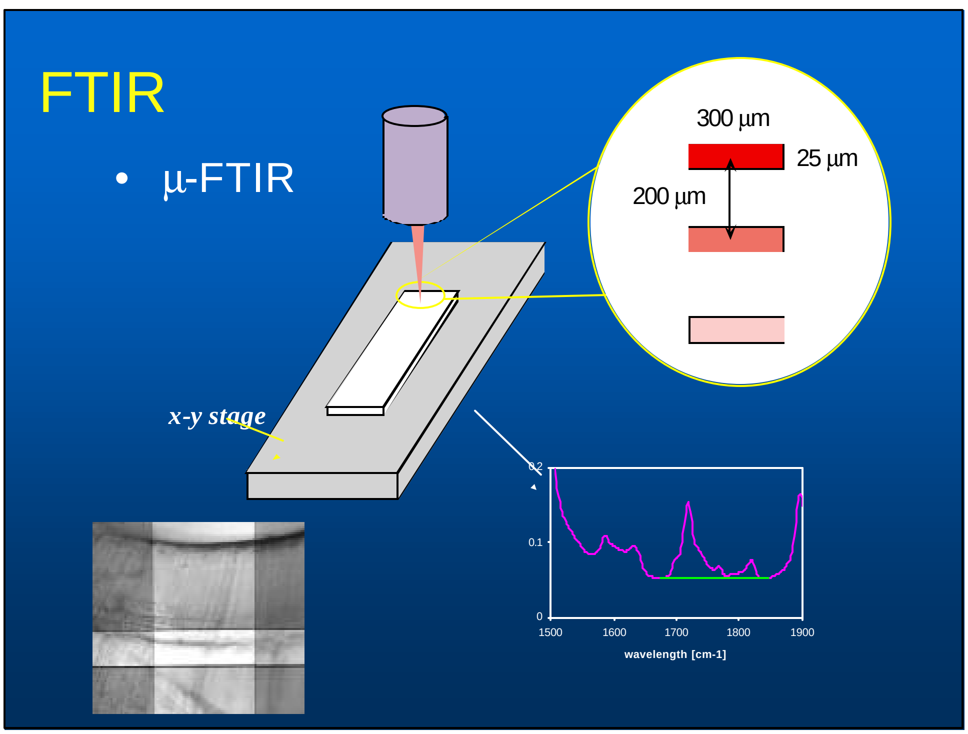


FTIR

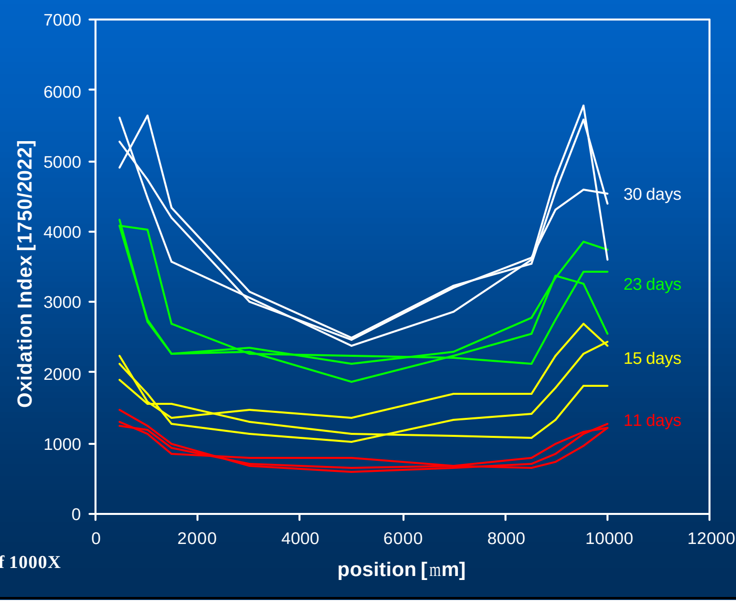
- Oxidation Index (1700 cm^{-1})
- Trans vinyl groups (965 cm $^{-1}$)
- Terminal vinyl groups (910 cm $^{-1}$)
- ir crystallinity (1303 cm $^{-1}$)

- Good spatial resolution (20 μm)


FTIR
•Oxidation
•Trans-vinyl
•Terminal vinyl
•%crystallinity
•Hydroperoxides
absorbance [A.U.]
frequency [cm-1]
2022
1897
1700
1370
1303
965
910


FTIR
• µ-FTIR
x-y stage
300 µm
25 µm
200 µm
wavelength [cm-1]

Sterilized (nitrogen), bomb-aged



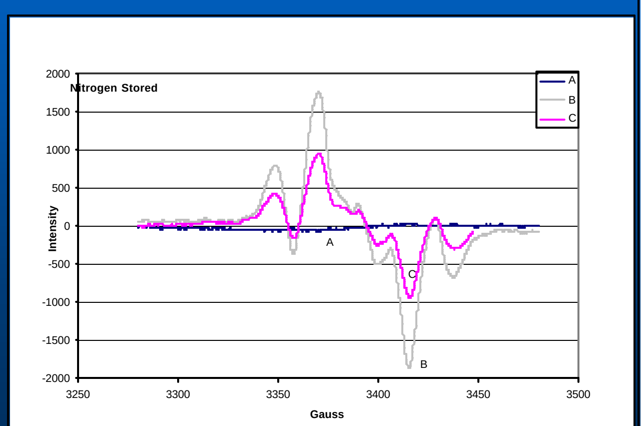
Factor of 1000X

Electron Spin Resonance

Detects residual free radicals in system

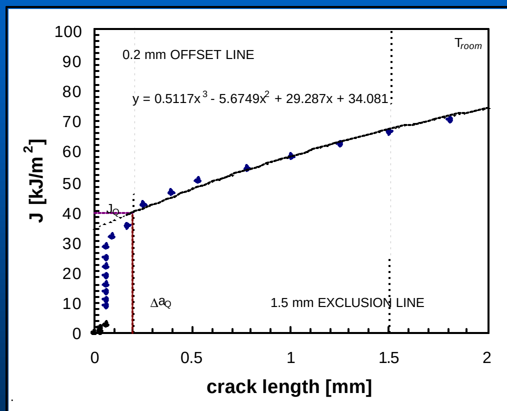
A-C: 30-100 kGy

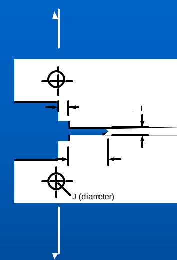
Multiple peaks indicate free radicals resulting from peroxide disassociations



Mechanical Analysis

J-Integral Testing: Crack Propagation





- **Specimens usually in plane stress conditions**
- **Extensive stress whitening (microcavitation)**
- **Not a good test for ductile materials**

ASTM J-813

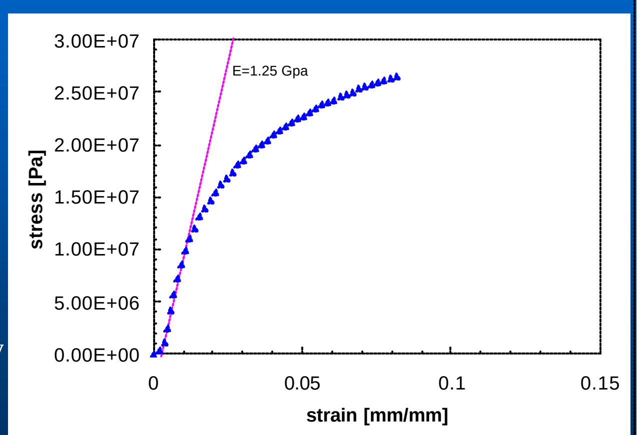
Mechanical Analysis

Uniaxial compression

33% modulus reduction with temp 25 to 37C

50% modulus reduction with radiation

Very sensitive to compliance in grip, sample slippage, sample uniformity



Other Mechanical Techniques

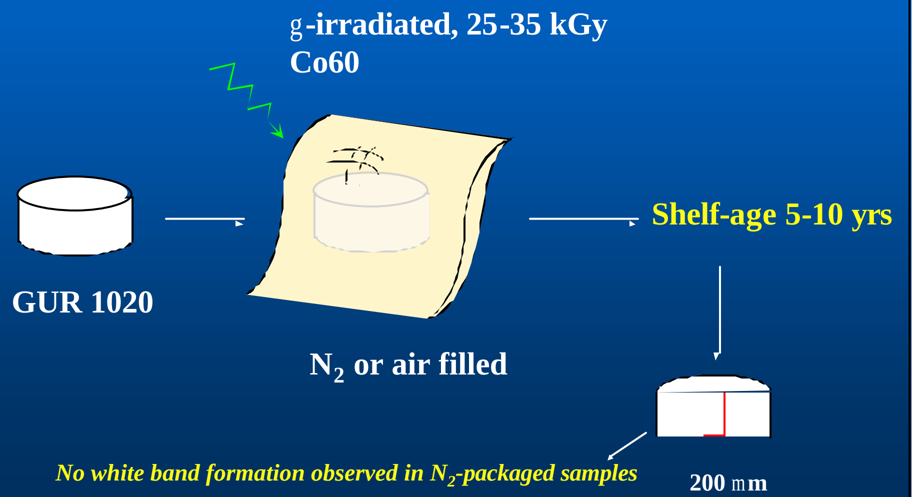
- Tensile testing (ASTM D2990, D638)
- Fatigue (ASTM E647)
- Small Punch (Kurtz et al. 1999)

Case Study 1: Effects of Nitrogen Packaging on Shelf-Storage

Used micro-FTIR to examine oxidation index of shelf-stored gamma sterilized UHMWPE inserts sterilized in nitrogen packaging

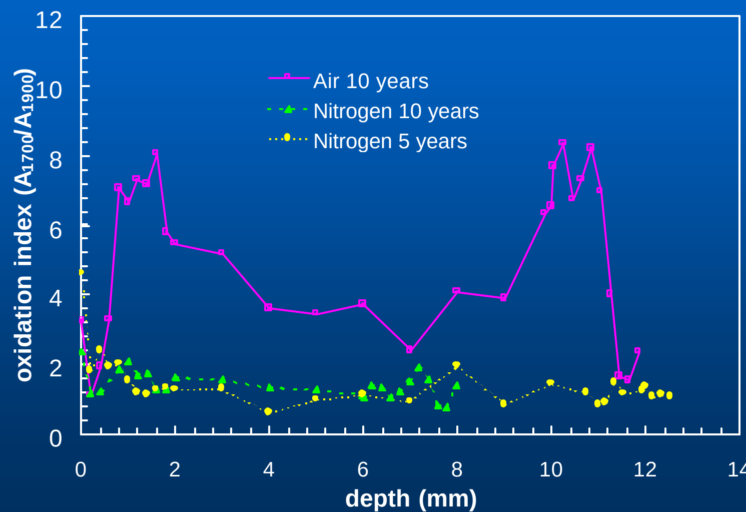
Silvio Schaffner, Sulzer Orthopedics

Procedure



Air-sterilized

Nitrogen sterilized



Case Study II: Effects of MWD on Crosslinking

- Used GPC to determine molecular weight distribution before crosslinking
- Swelling data to determine crosslink density after chemical and radiation crosslinking

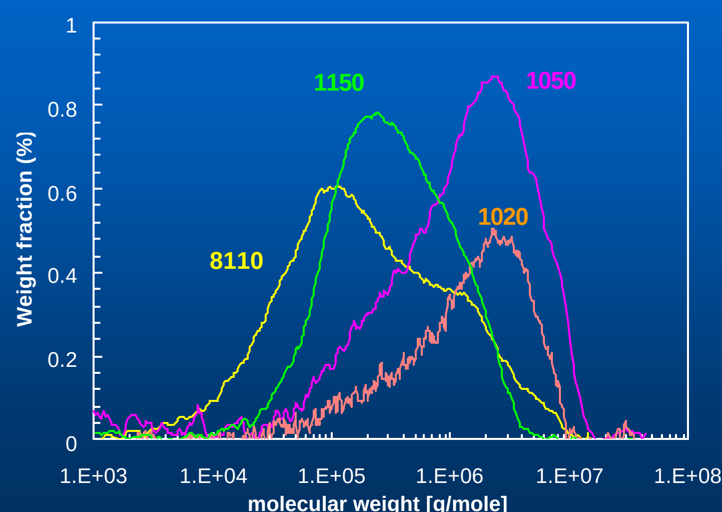
A. Edidin, Stryker Howmedica Osteonics
S. Kurtz, Exponent

UHMWPE

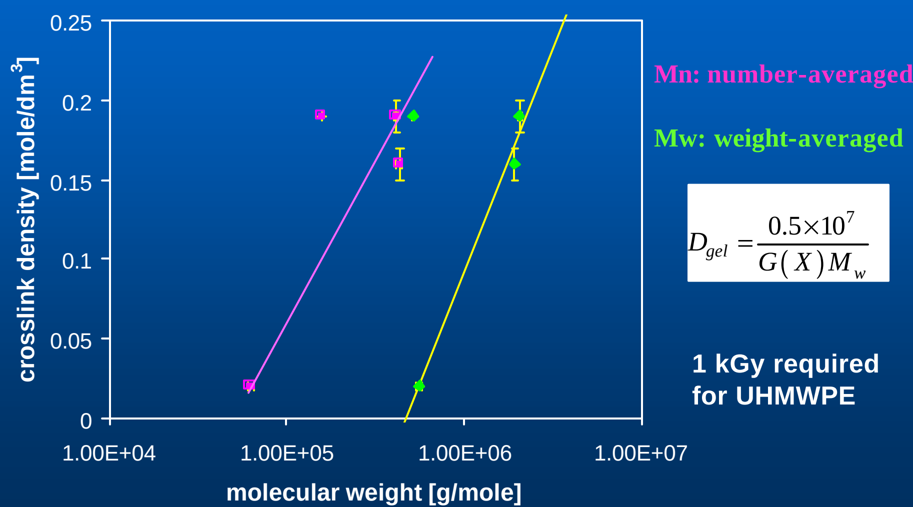
- Ticona (TX)

Material	Density (g/cc)	M_v, g/mol	IV (dl/g)
8110	0.95	500,000	4.45
1020	0.93	2-4 million	20
1050/1150	0.93	4-6 million	28

Molecular weight distributions

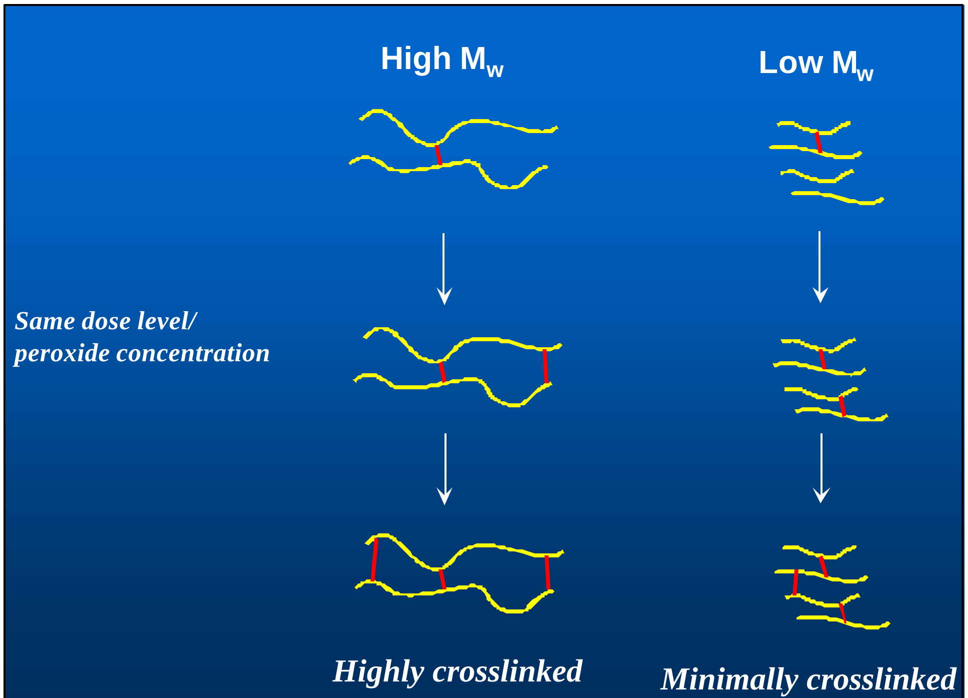


Crosslink density dependence on Molecular Weight



$$D_{gel} = \frac{0.5 \times 10^{7}}{G(X)M_w}$$

1 kGy required for UHMWPE



Conclusions

- Suite of testing procedures
- Pre- and Post-irradiated UHMWPE
- Proper test design and data interpretation useful for manufacturing and R&D

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Go to www.campoly.com for application notes on these subjects