

Mechanical properties, fatigue and wear  
resistance of an easily crosslinkable polyethylene  
with a Mw of 500 kg/mol

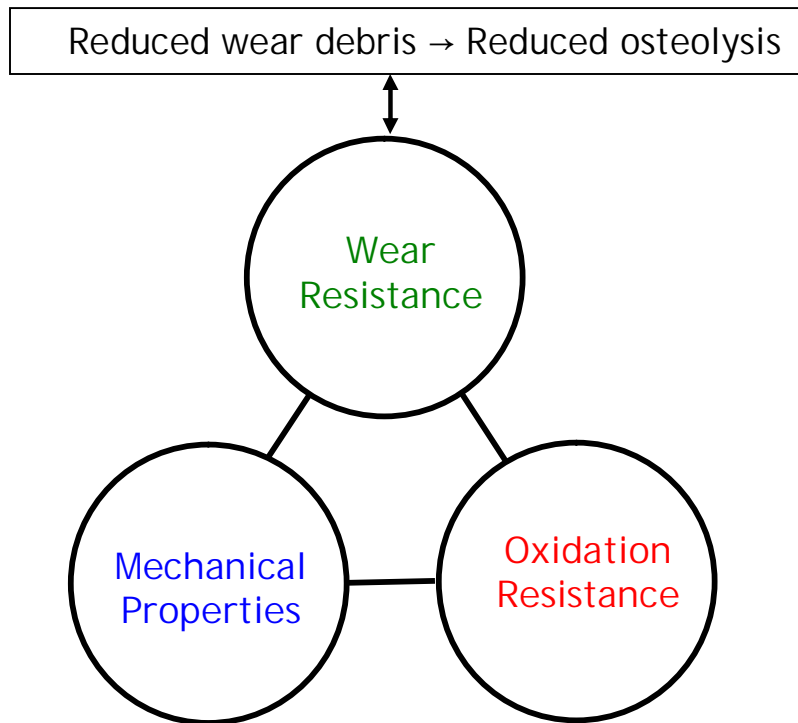
Easy-XL™ polymer

UHMWPE Conference Philadelphia

DSM Biomedical  
Harold Smelt

September 22<sup>nd</sup>, 2011

# Demands for UHMWPE in total joint replacements



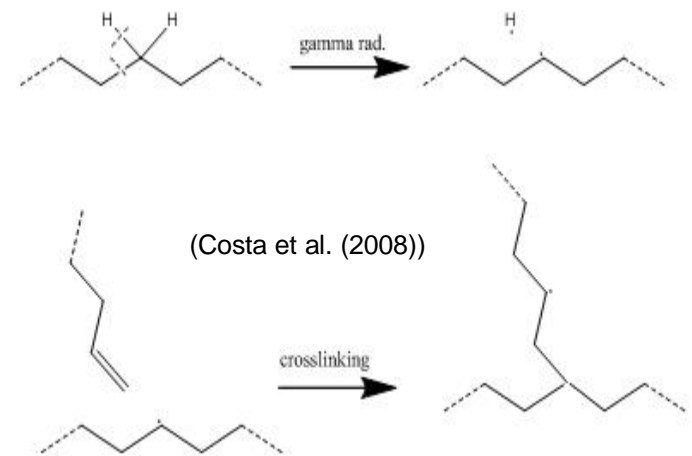
1. Wear resistance has significantly improved by solid state irradiation cross-linking
2. To improve oxidative stability, highly cross-linked materials are heat treated to neutralize remaining free radicals
3. This however affects mechanical properties

The UH paradigm: Gomez-Barrena, E et al. *Acta Orthopaedica* 2008, 79 (6), 832.

Future materials should have improved properties on all 3 aspects

# Improve cross-link efficiency

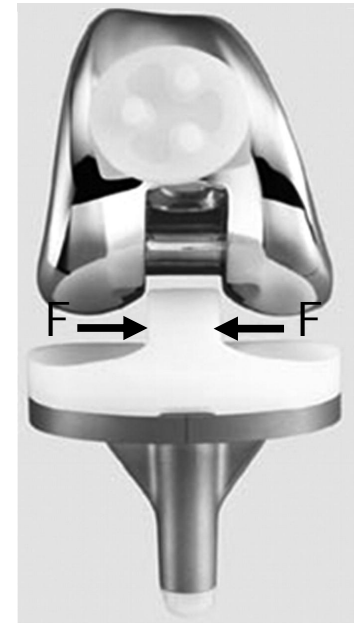
- The consumption of vinyl double bonds has been found to be proportional to the absorbed irradiation dosage (Bracco et al. 2005).
- Although the crosslink level increases with irradiation dosage, it reaches a plateau for dosages beyond 100 kGy when the majority of vinyl double bonds have been consumed (Brunella et al., 2007).



By introducing more vinyl double bonds, the crosslink efficiency can potentially be improved

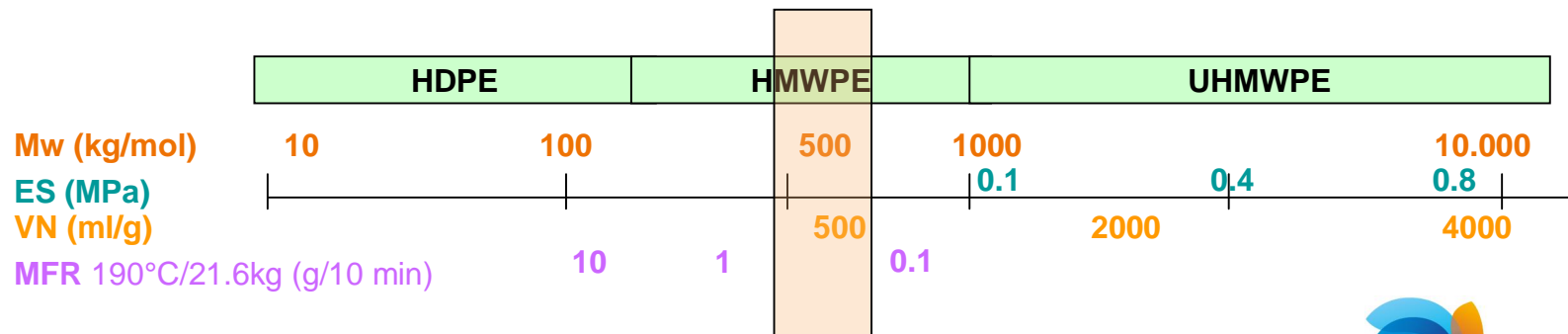
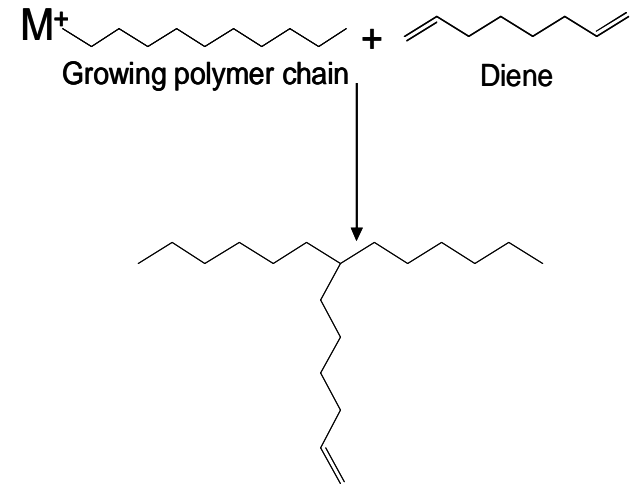
# Improve mechanical properties

- For achieving a high yield stress, low creep and high fatigue resistance, a high crystallinity is desirable  
(Champion et al, 1994; Kurtz, 1999; Baker et al, 2000; Oral et al, 2009)
- In particular, reducing Mw increases crystallinity
- For conventional UHMWPE, reducing Mw was not an option, as such materials could not be cross-linked efficiently enough to maintain both adequate wear and oxidation resistance.
- A reduced Mw grade may become a viable option, by incorporating additional vinyl double bonds to facilitate network formation during cross-linking.



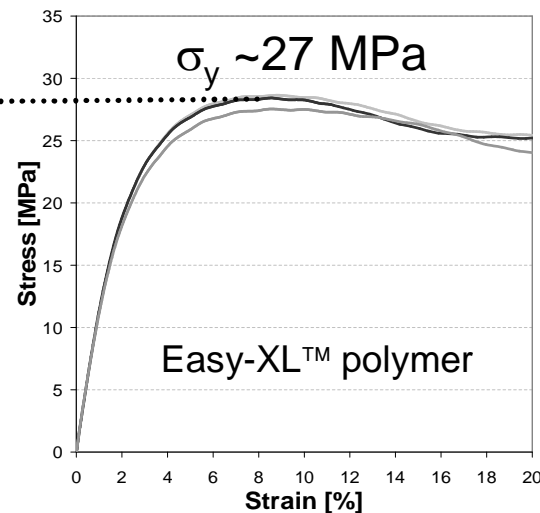
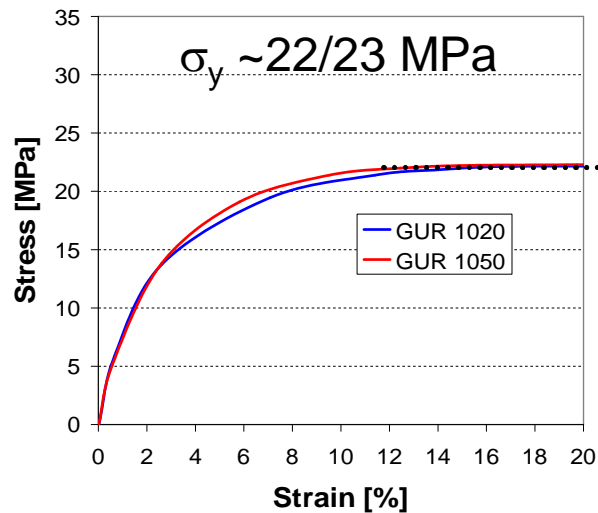
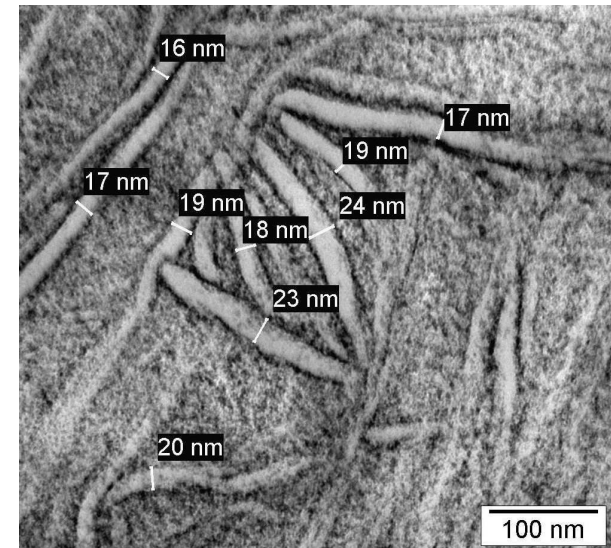
# Design philosophy for Easy-XL™ polymer

- Copolymerization of ethylene and octadiene
  - Using a Ti containing ZN catalyst
  - 22 vinyl double bonds/100.000 carbon atoms versus max 4 for conventional UHMWPE's
- Molecular weight of 0.5 million g/mol
  - Viscosity number of 500 ml/g
  - Melt index (190°C/21.6 kg) of 0.2 g/10 min

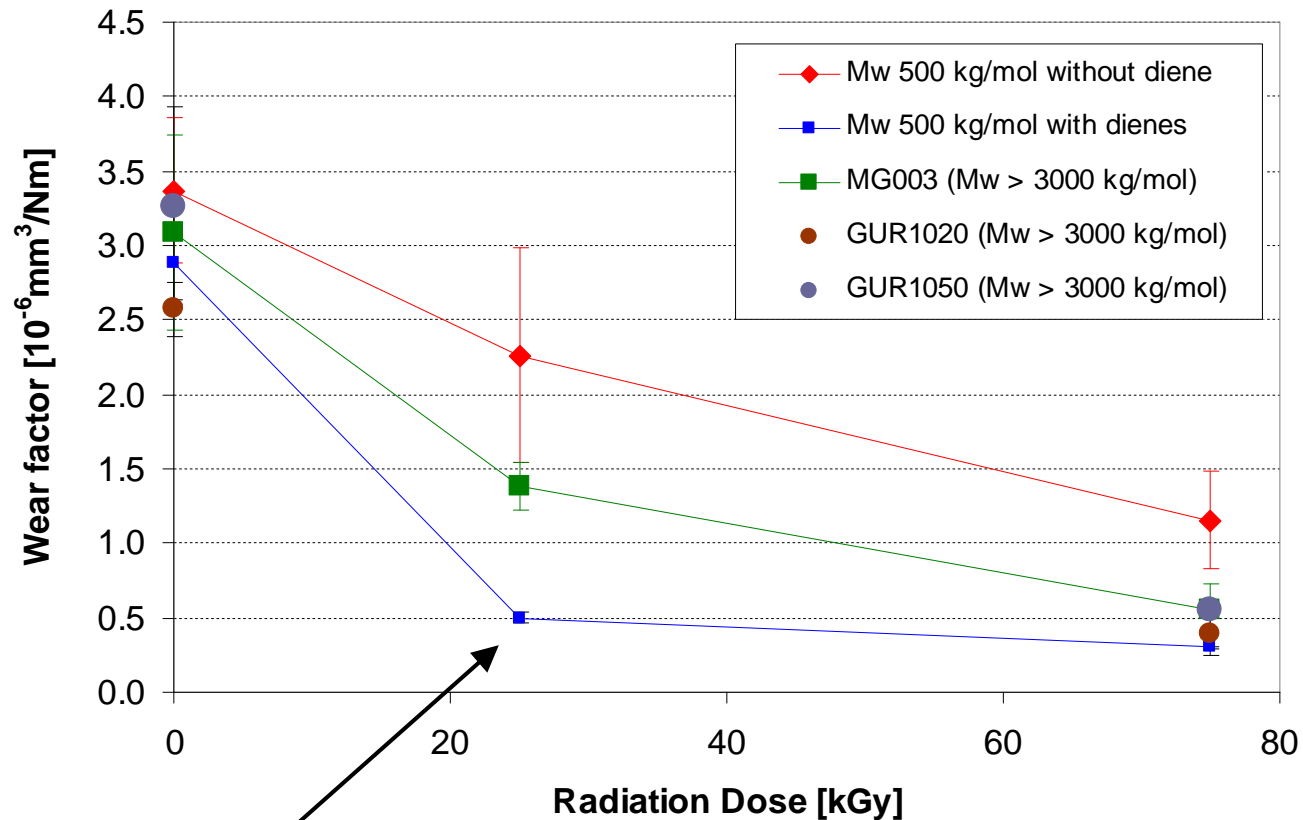


# Properties as molded

- Crystallinity 68%
- Lamellar thickness  $\pm 20$  nm
  - non cross-linked; no thermal treatment
- Yield strength 27 MPa
- Elongation at break  $> 450\%$



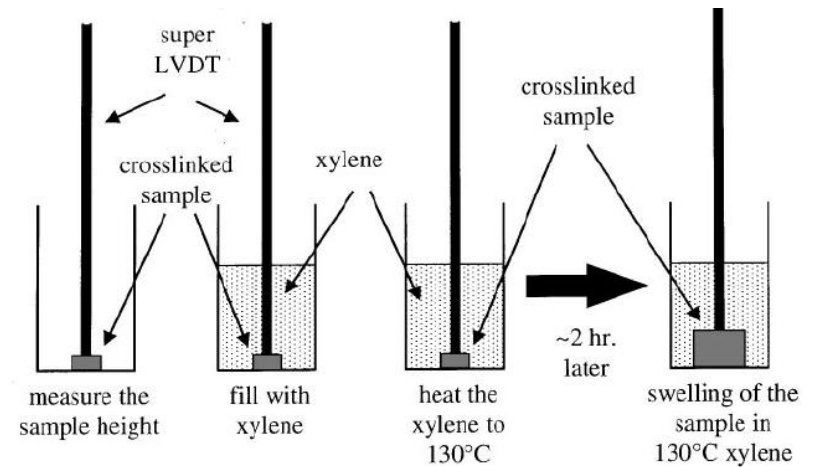
# POD wear versus irradiation dosage



- Results showed that 25 kGy irradiation resulted in a POD wear resistance comparable to highly XL materials ( $\geq 75$  kGy)

# Swell ratio versus wear resistance

- At equal low wear resistance, a difference in swell ratio was observed
  - 4.5% for Easy-XL polymer (25 kGy)
  - 2.5% for conventional UHMWPE (75 kGy)



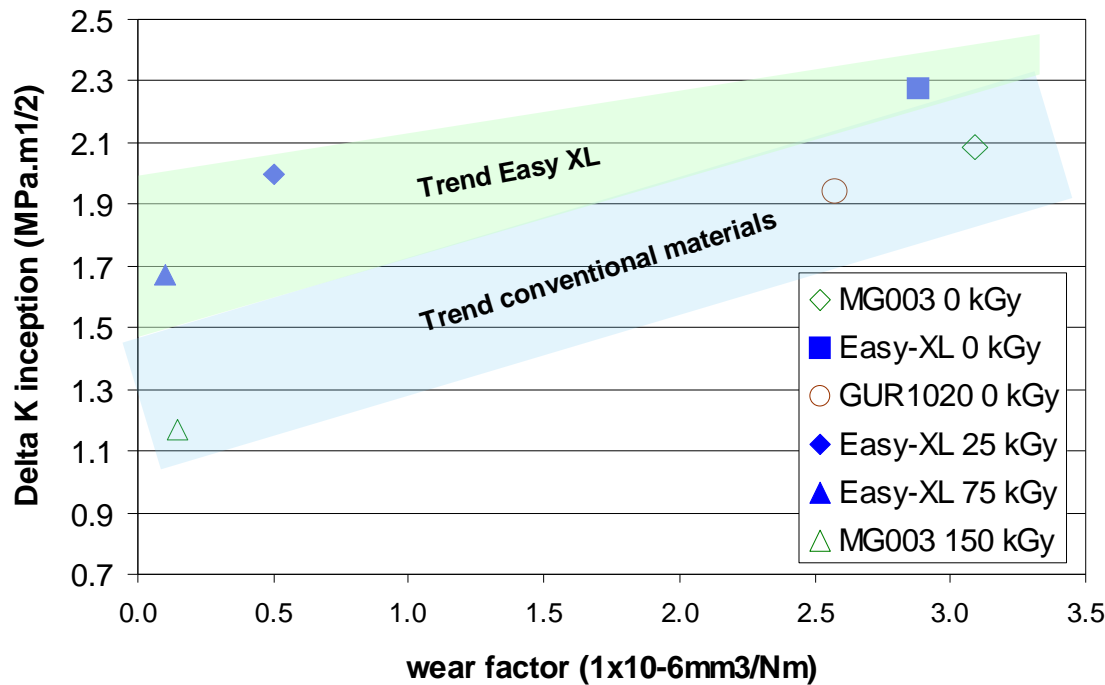
- There is a unique relation between swell ratio and wear factor only for UHMwPE materials with roughly similar Mw and similar crystallinity

## Discussion:

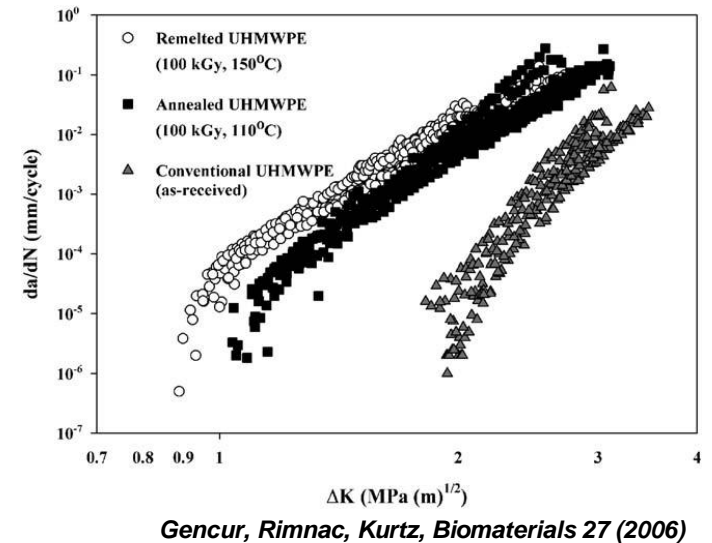
- Most cross-links will be formed in the amorphous phase; which will swell much less than the crystalline phase: The high crystalline Easy-XL™ material will have more swelling.
- The crystalline lamella do contribute to the network fixation and prevents strain accumulation on the wear surface, which is the precursor for wear particle formation.



# Higher FCP $\Delta K_{\text{Inception}}$ at low wear factors



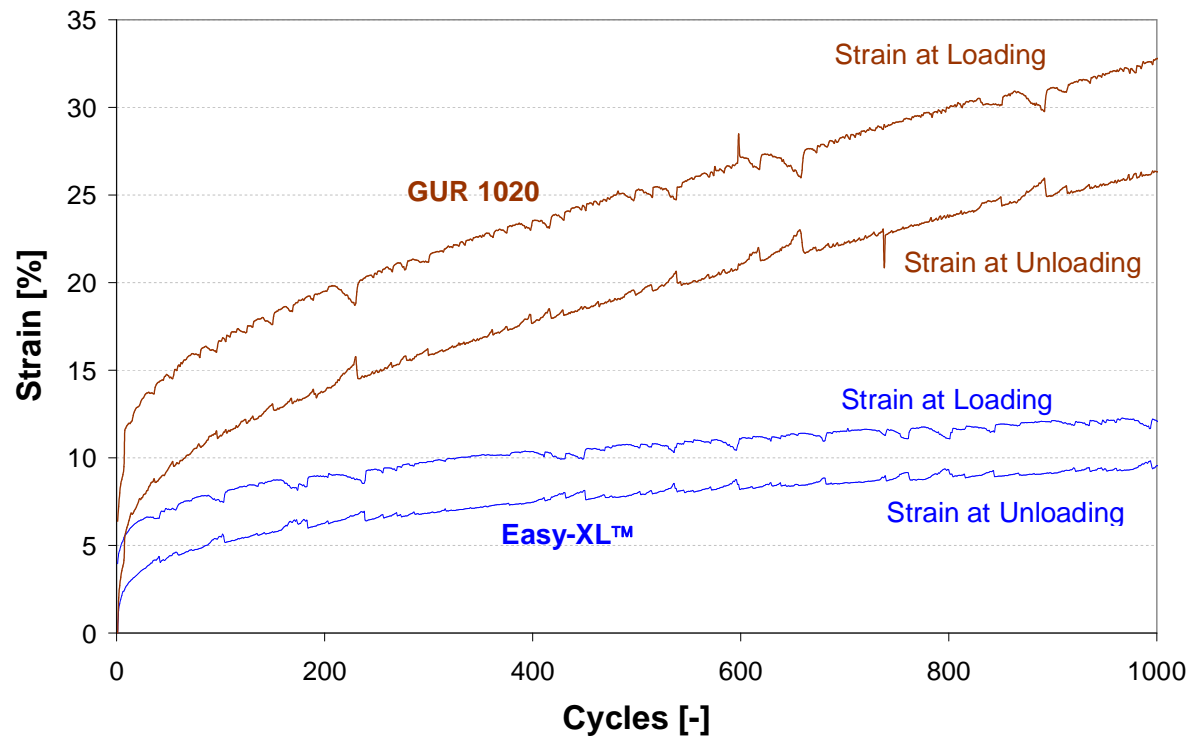
“Besides wear, the second most important property change induced by irradiation is its fatigues resistance.” (Pruitt, Biomaterials, 2005)



- The  $\Delta K_{\text{inception}}$  of 2 MPa.m<sup>1/2</sup> is comparable with non crosslinked UHMWPE, which however has a factor 5 lower wear resistance

# Hysteresis tensile fatigue

- Easy-XL™ material is less sensitive to deformation and creep, which potentially reduces the change on fatigue damage



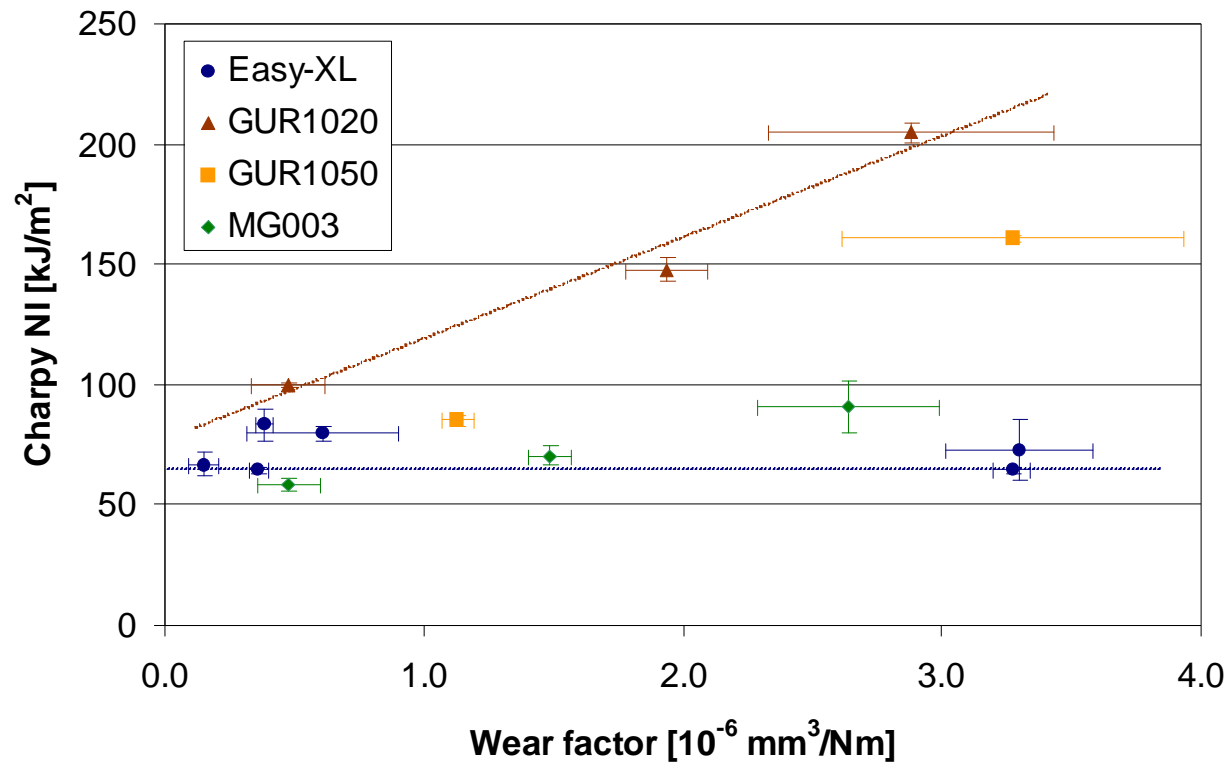
$S_{max}$  20MPa

$F_{min}$  0.5N

frequency 0.5 Hz

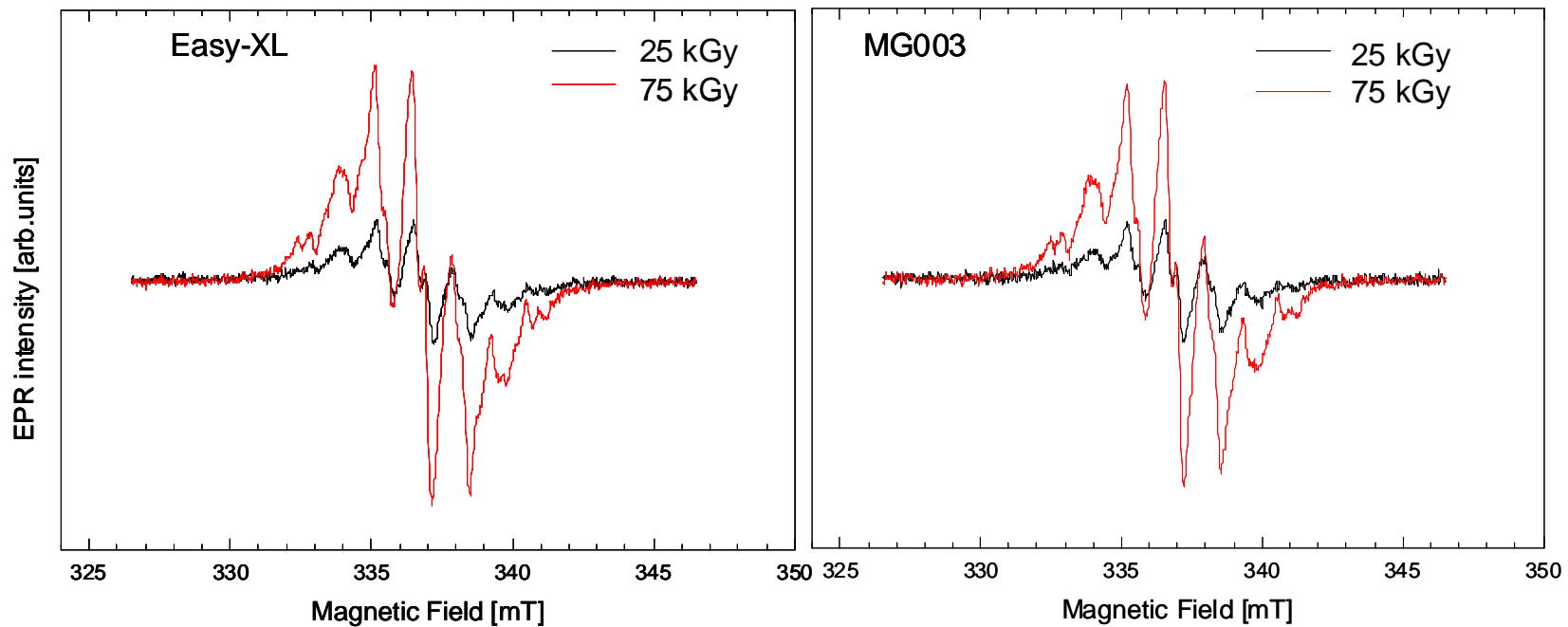
room temperature

# Impact versus wear resistance



- Impact strengths at high wear resistance levels are converging towards the same order of magnitude.
- Initial differences in non crosslinked polymers disappear

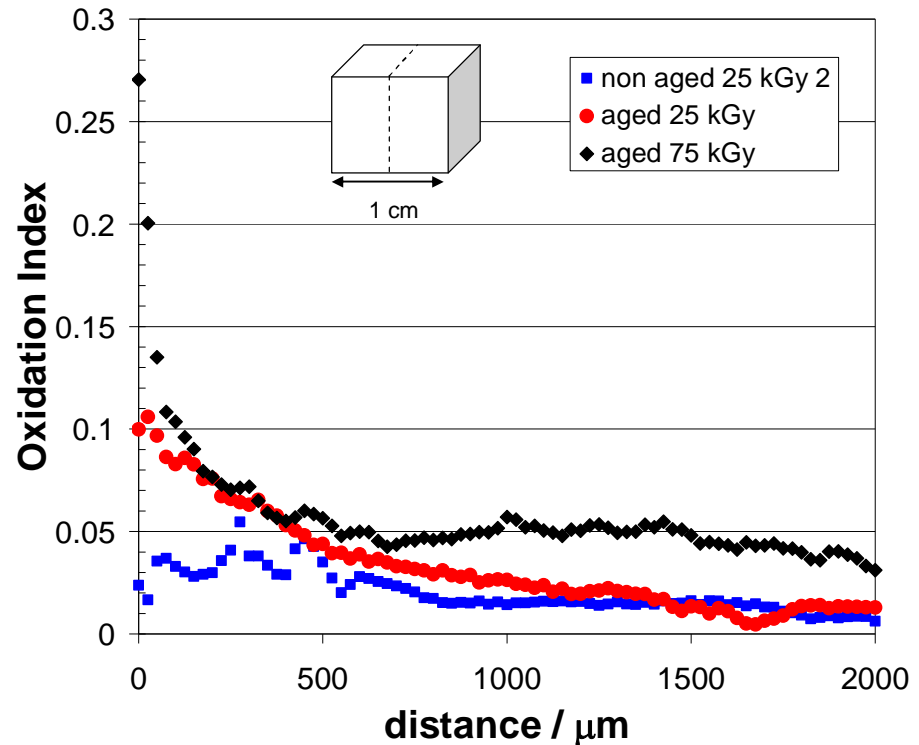
# ESR - Free radical content



- Nr of free radicals scales with irradiation dose, regardless of type of polymer
  - Both Easy-XL™ polymer and reference UHMWPE material MG003 show that 75 kGy radiation leaves behind 2-3 times higher radical content than 25 kGy

# Aging - Oxidation profile

- 3x lower level of irradiation needed; reducing OI levels
- Thermal treatment + stabilizers further improve oxidation resistance
  - like with conventional UHMWPE's



- *Oxidation Index (OI) according to ASTM F2102 of aged Easy-XL™ polymer cubes of 1 cm. No thermal treatment; no stabilizer. Aging: 6 wks at 70°C in an air oven*

# Conclusions

- The introduction of extra vinyl double bonds via diene copolymerization did increase the crosslink efficiency significantly.
  - a 3x lower irradiation dosage (25 kGy) was required to achieve a high wear resistance material
- It enables the production of a lower Mw material with improved mechanical properties
  - Higher fatigue resistance, yield strength and elongation
- The melt processability of the Easy-XL™ polymer enables new processing and product technologies like composite materials and stabilizer blending
  - New material for innovations



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