Radiation induced structural changes of (U)HMW Polyethylene with regard to its application for radiation shielding

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Outline

- Introduction and motivation
- Influence of irradiation
- Applied methods
  - Thermoanalytical
  - Optical
  - Weighing
- Results
- Conclusion
- Outlook

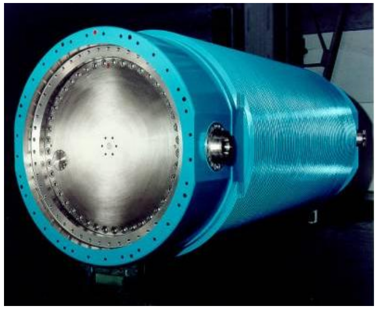
High-performance materials: (U)HMW-PE

Broad application range:

- Medical technology (artificial replacement, implant …)
- Mechanical engeneering (spur gear, chain guide …)
- Leisure equipment (sliding surface of skis, snowboards …)
- Chemical industry (Filtering of liquids …)
- n_0^1 - Moderator in CASTOR® casks

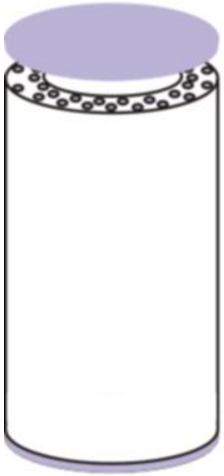
Characteristics:

- High impact toughness
- Very low abrasion / wear debris
- Very high chemical resistance
- Temperature resistance from -200 up to +90 °C (common applications)
- Very high hydrogen content



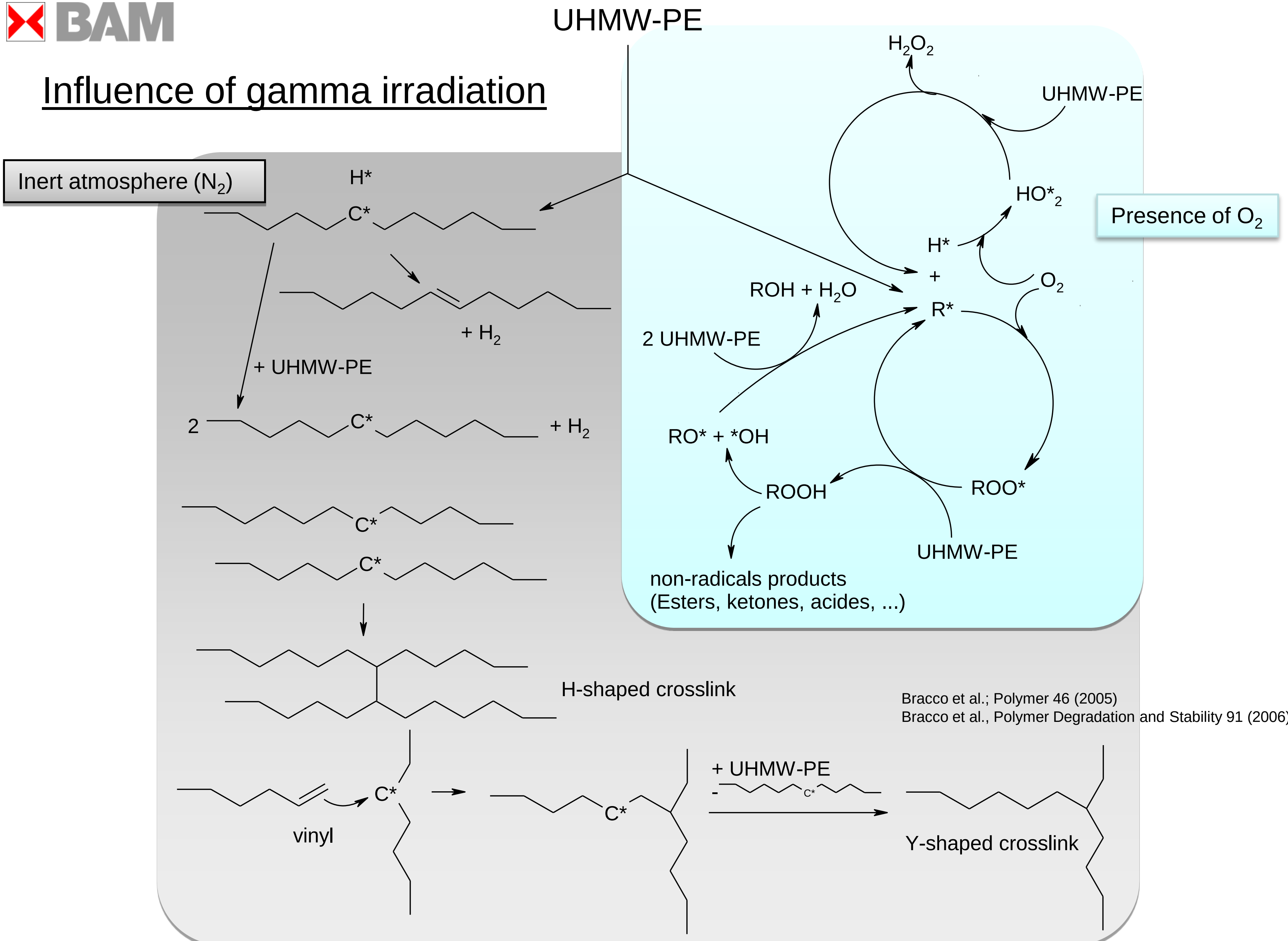
Motivation: (U)HMW-PE as neutron shielding material

- Shielding material in casks for storage and transport of radioactive material
- Installation of shielding material in wall (two concentrically aranged circles), top, and bottom of cask
- Role of material: shielding of neutron radiation



- Long term radiation shielding over a period of 40 years and more without any degradation affecting safety relevant aspects
- Open questions:
  - Impact of continuous but decreasing radiation (causing embrittlement, avoiding neutron windows)
  - Behaviour during operation under normal and incident (fire) conditions (time and temperature)

Influence of gamma irradiation



Bracco et al.; Polymer 46 (2005)
Bracco et al., Polymer Degradation and Stability 91 (2006)

Materials and Methods

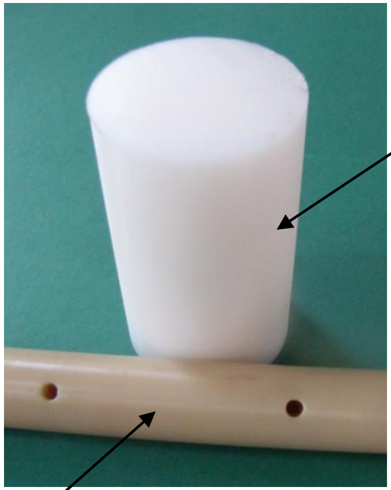
Analysed materials

- ***H**igh **m**olecular **w**eight **p**oly**e**thylene; LUPOLEN 5261Z*
- ***U**ltra-**h**igh **m**olecular **w**eight **p**oly**e**thylene; GUR 4120*

- Gamma irradiation: dose of ~600 kGy at RT under inert conditions

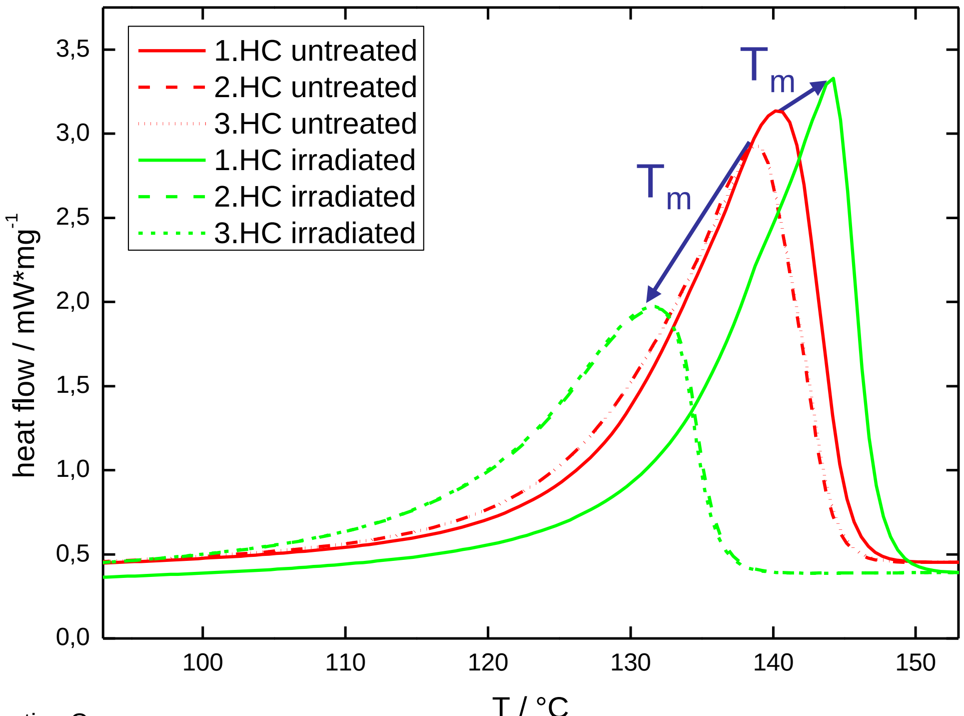
Applied methods

- Thermoanalytical methods
  - ***D**ifferential **S**canning **C**alorimetry*
  - ***T**hermo **M**echanical **A**nalysis*
  - ***T**hermo**g**ravimetry*
  - ***D**ynamic **M**echanical **A**nalysis*
- Optical methods
  - FTIR-Spectroscopy
- Weighing methods
  - ***D**ensity **g**radient **c**olumn*
  - Degree of crosslinking



Differential Scanning Calorimetry

HMW-PE: irradiated vs. untreated



HC: Heating Curve

Measurement conditions:
Heating rate: 10 K/min

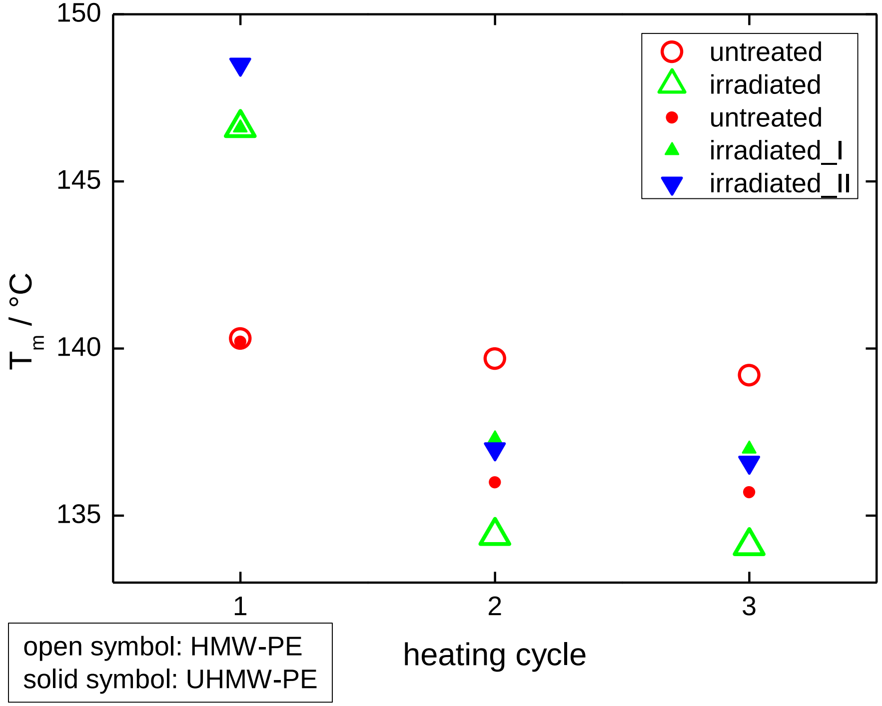
sample ~ 10 mg

Irradiation impact on melting peak:

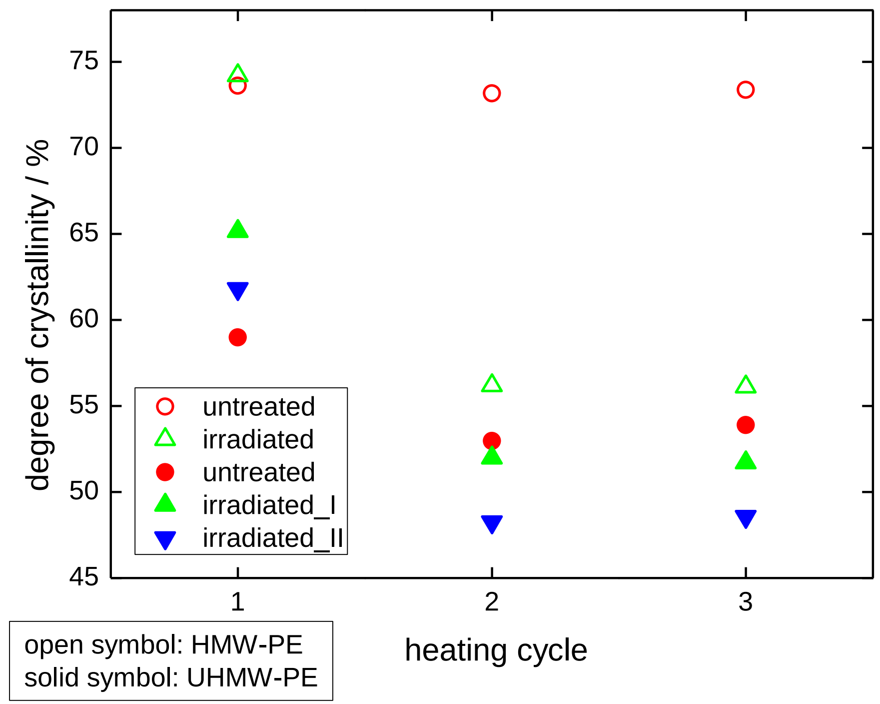
- 1st heating curve: Shift of T_m to higher temperatures (increase of peak area)
- 2nd and 3rd heating curve: Shift of T_m to lower temperatures (decrease of peak area)

Differential Scanning Calorimetry

Melting temperatures



Degree of crystallinity



Impact on T_m:

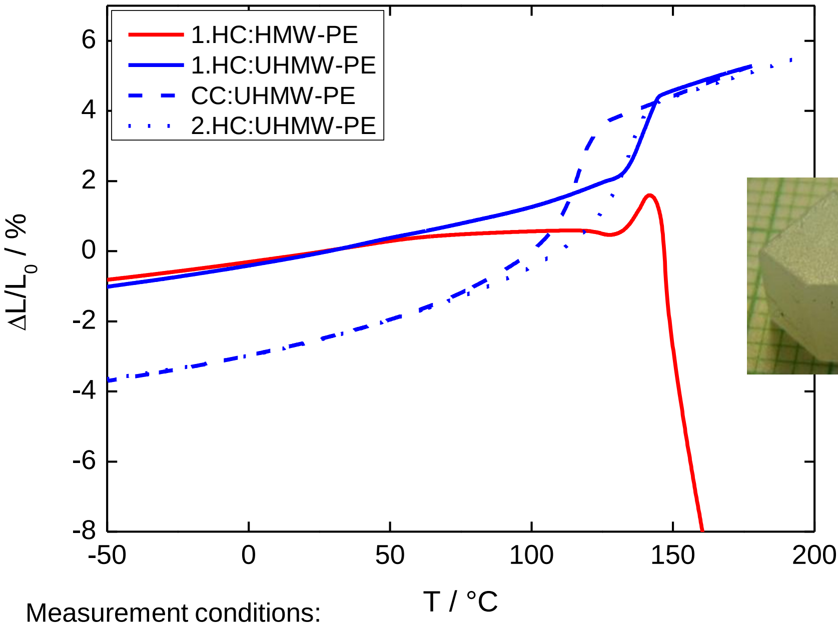
- Irradiation: ↑
- Subsequent thermal treatment: ↓
- Untreated HMW-PE shows no significant difference in melting temperatures

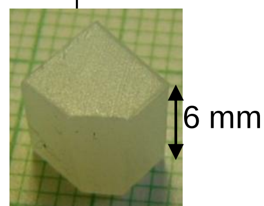
Impact on degree of crystallinity:

- Irradiation: ↑
- Subsequent thermal treatment: ↓
- Similar values for degree of crystallinity of HMW-PE independent of thermal treatment

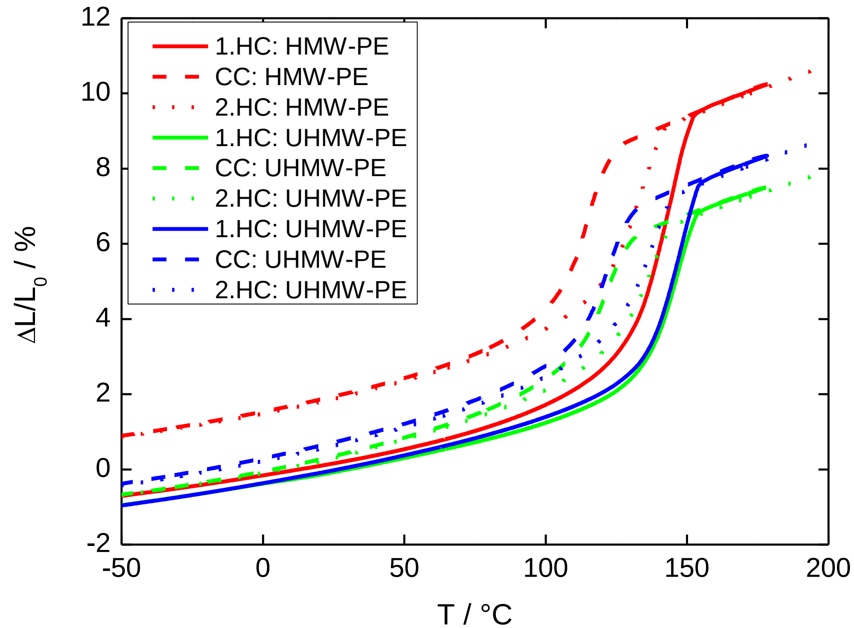
Thermomechanical Analysis

HMW-PE vs. UHMW-PE (untreated)





HMW-PE vs. UHMW-PE (irradiated)



Measurement conditions:
Heating rate: 10 K/min; load: 1 mN/m²

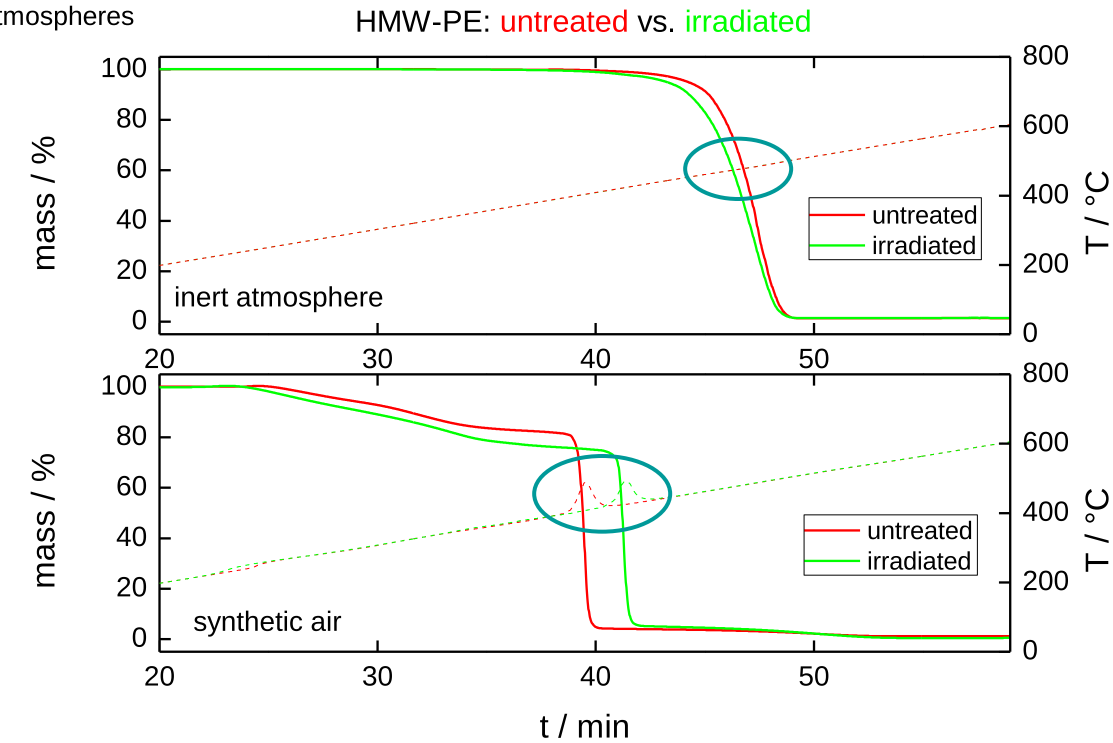
Sample	Treatment	α (T<60°C) [$K^{-1}*10^{-4}$]	α (T>160°C) [$K^{-1}*10^{-4}$]
HMW-PE	**untreated**	**0,643 (1.HC)**	**-**
HMW-PE	**irradiated**	**1,43**	**2,85**
UHMW-PE	**untreated**	**2,47**	**3,12**
UHMW-PE	**irradiated**	**1,42**	**2,62**
UHMW-PE	**irradiated**	**1,46**	**2,94**

Findings:

- Values of thermal expansion coefficients are similar for irradiated materials
- Untreated UHMW-PE clearly shows larger coefficient values
- Untreated HMW-PE shows a quite different behaviour: it starts to flow at temperature higher than 145 °C

Thermogravimetry

Measurement conditions:
Heating rate: 10 K/min; two atmospheres
(inert and synthetic air)



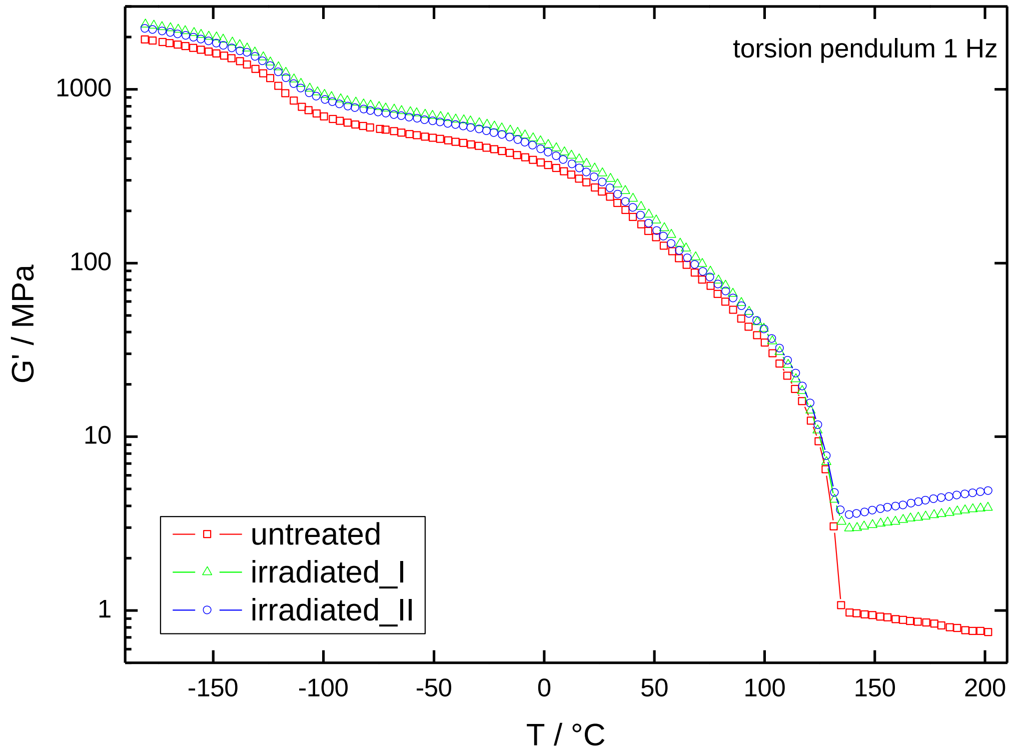
Findings:

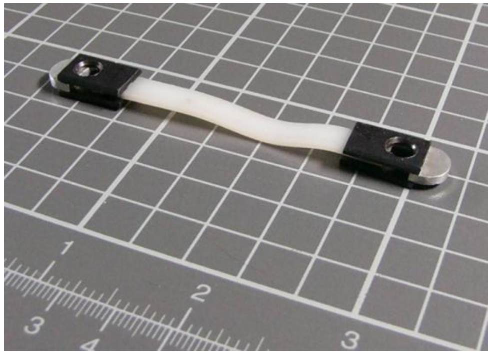
- One-step process (inert atmosphere); two-step process (synthetic air)
- Degradation starts earlier for irradiated material
- Synthetic air: *Insertion of oxygen* at a temperature range of 240 °C to 250 °C
- Peak temperatures of maximum weight loss are similar for both materials under the same atmosphere

Dynamic Mechanical Analysis

Shear modulus

UHMW-PE - untreated vs. irradiated material



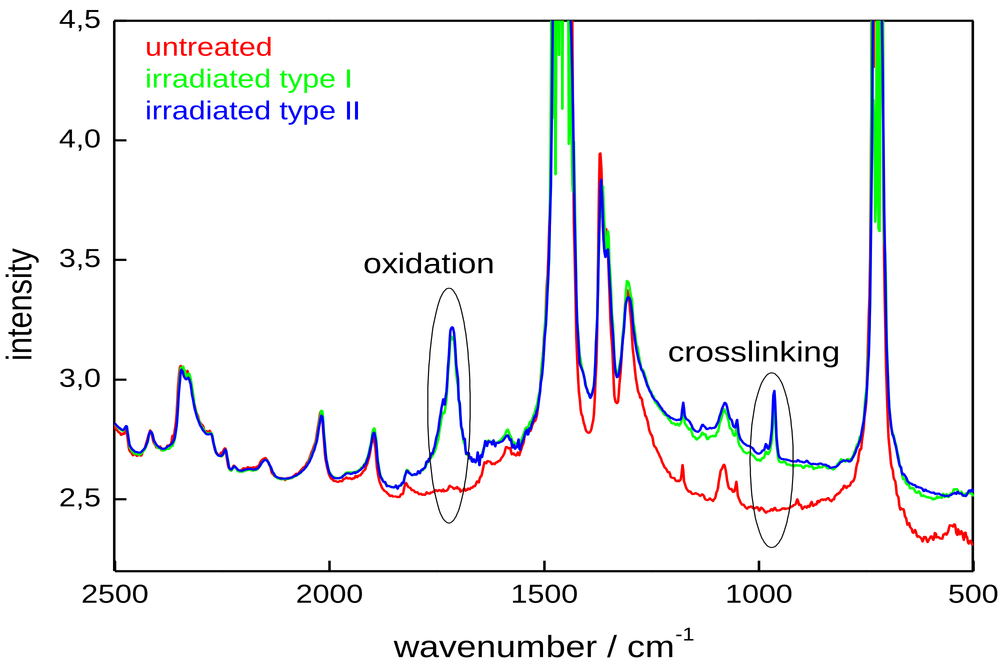


Findings:

- Large similarity of shear modulus independent of gamma irradiation
- Plateau values of shear modulus: indication for degree of crosslinking
  - Untreated UHMW-PE: physical crosslinking of long polymer chains
  - Irradiated UHMW-PE: higher plateau values → higher degree of crosslinking

FTIR Spectroscopy

IR-Spectra (Transmission): UHMW-PE untreated vs. irradiated



Conditions:

- Spectra measured in transmission
- Interesting absorption bands:
  - 965 cm^{-1} (trans-vinylene group)
  - 1700 cm^{-1} (C=O group in aldehydes, ketones, carboxyls)
- Reference band at 2022 cm^{-1} (methyl group stretching)

Spiegelberg et al., CPG

Findings:

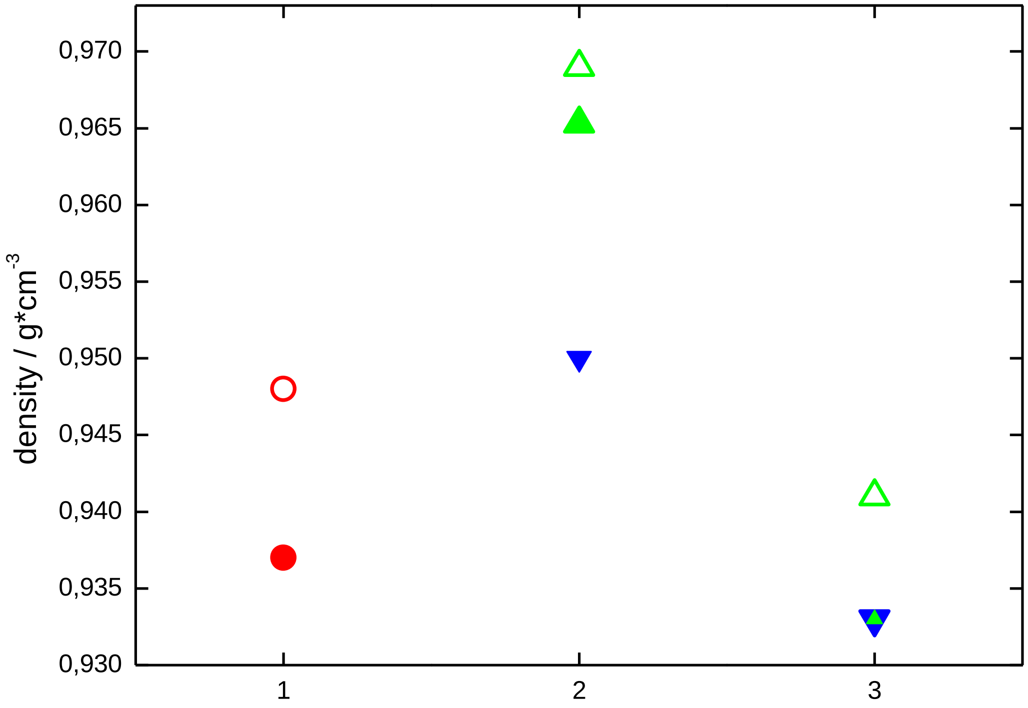
➢ Spectra of irradiated material: two new absorption bands

- 965 cm^{-1}: related to crosslinking
- 1700 cm^{-1}: related to insertion of oxygen

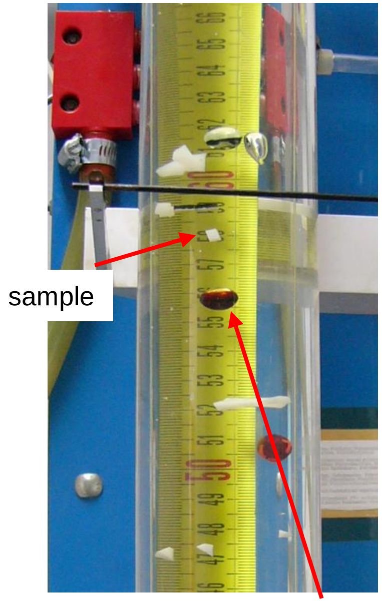
Density Gradient Column

gradient: 0,86 – 1,00 ± 0,0001 g/cm³

mixture of diethylenglycol and isopropanol



open symbol: HMW-PE
solid symbol: UHMW-PE



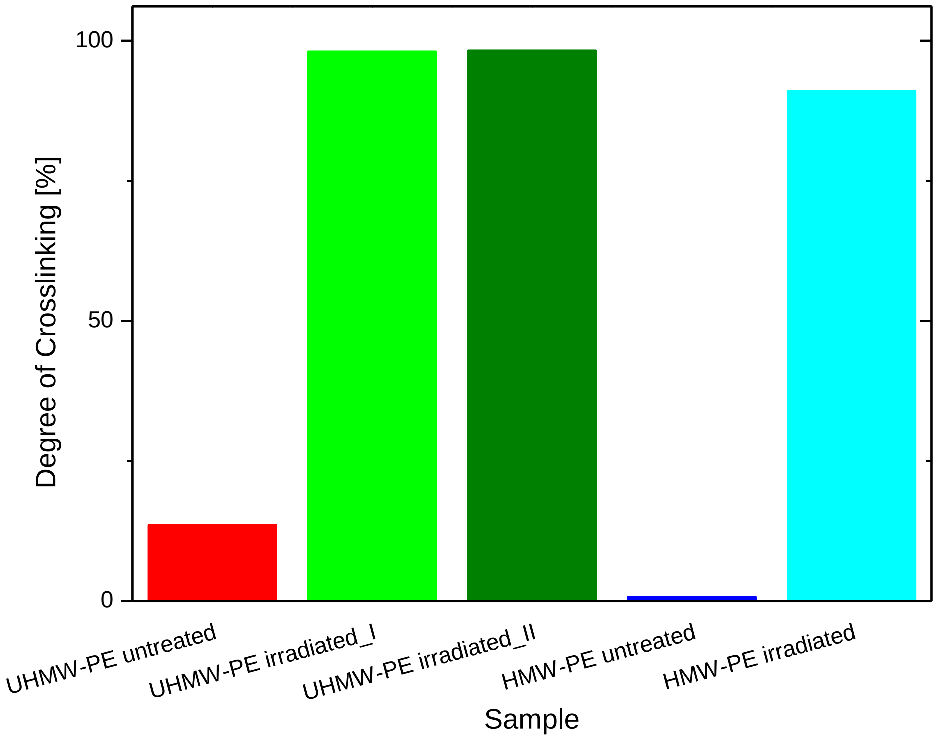
Object with defined weight

Findings:

- γ-irradiation: increase of density / degree of crystallinity
- Irradiation and thermal treatment (subsequent melting and recrystallization): decrease of density / degree of crystallinity

- After irradiation and thermal treatment density values are lower compared to those of the untreated material

”Degree of crosslinking” (DIN 16892)



Procedure:

- Determination of initial weight
- 8h in xylene (boiling under reflux), 130 °C
- Drying for 3h at 140 °C
- Determination of weight

➢ Obvious increase of insoluble, crosslinked fraction after γ irradiation

Conclusion / Outlook

- Comparison between untreated and high dose irradiated material
- Determination of changes of (U)HMW-PE induced by γ-irradiation possible with the applied conventional techniques
- Qualitative irradiation impact on material properties was shown
- For quantification of the obtained results reference samples are needed

- *Detected changes of the irradiated material are not safety relevant for the application of polyethylene as moderator material*
  - *moreover, some properties actually improve via irradiation*

- Analysis of a series of samples irradiated with different doses and different rates

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Thank you for your attention!