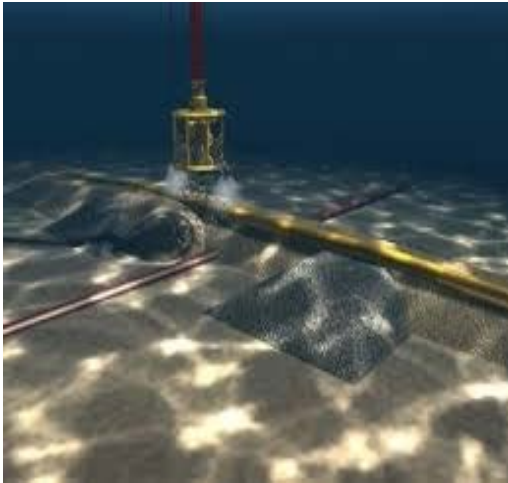


NMR as a Versatile Tool in the Study of Polymer Aging



Alina Adams
ITMC, RWTH Aachen University

Problems around Marine Aging of Polymers

- Marine aging is due to the effect of pressure, saline water ingress, UV action, temperature
- In order to establish water profiles in marine components modelling is necessary, but the validity and limits of these models need to be addressed.
- Need of more realistic experimental test facilities and improved models of the mechanical response.
- Proper lifetime prediction requires the knowledge of the changes at the molecular level leading to failure.
- Depth-dependent measurements of the water ingress to validate and improve the existing models.
- Application of non-destructive analytical tools for in-situ condition monitoring.

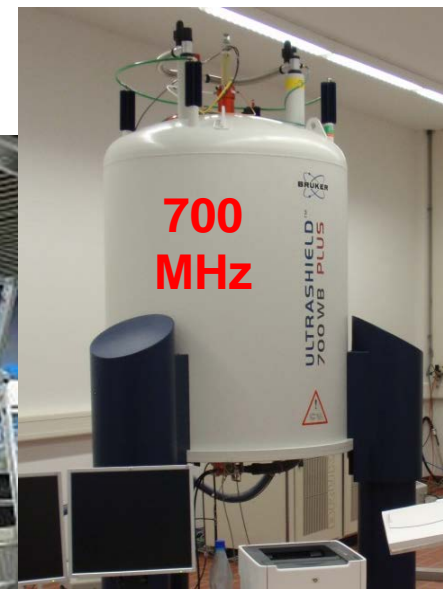
NMR of Polymers @ ITMC RWTH Aachen

Spectroscopy

Relaxation

Diffusion

Imaging



Composite materials

Structure and morphology of polymers in solid state

NMR methodology

Morphology of nanocomposites

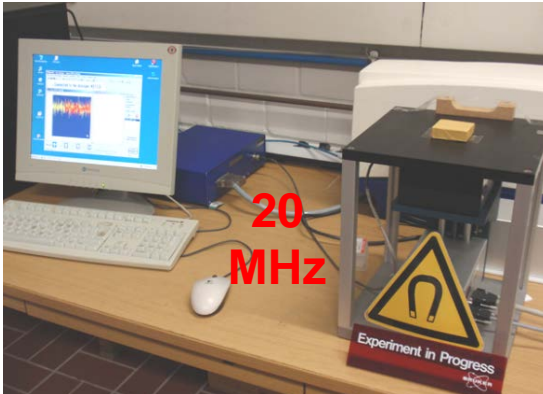
Interaction of polymers with liquids

Condition monitoring and aging of polymers

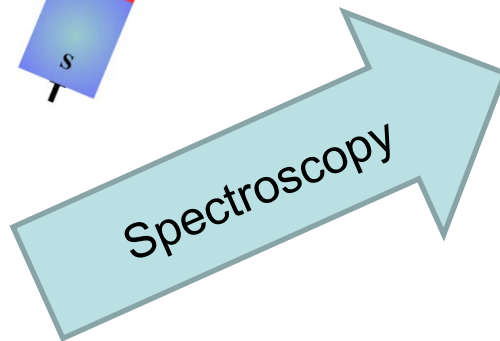
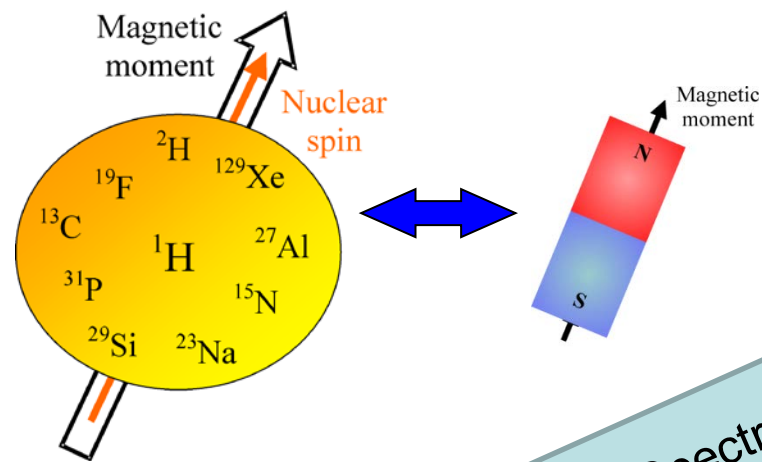
Non-destructive quality control by compact NMR

20 MHz

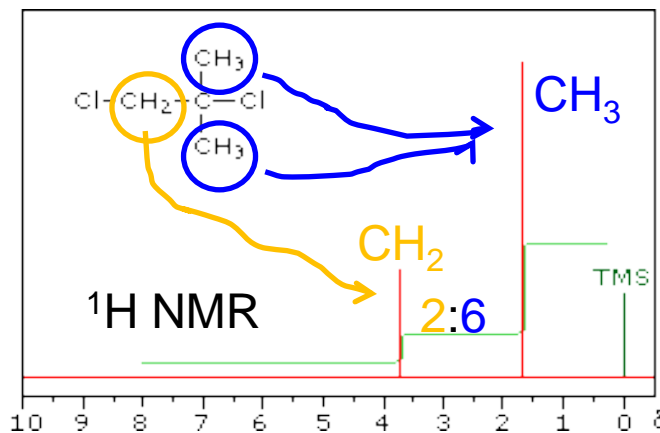
Experiment in Progress



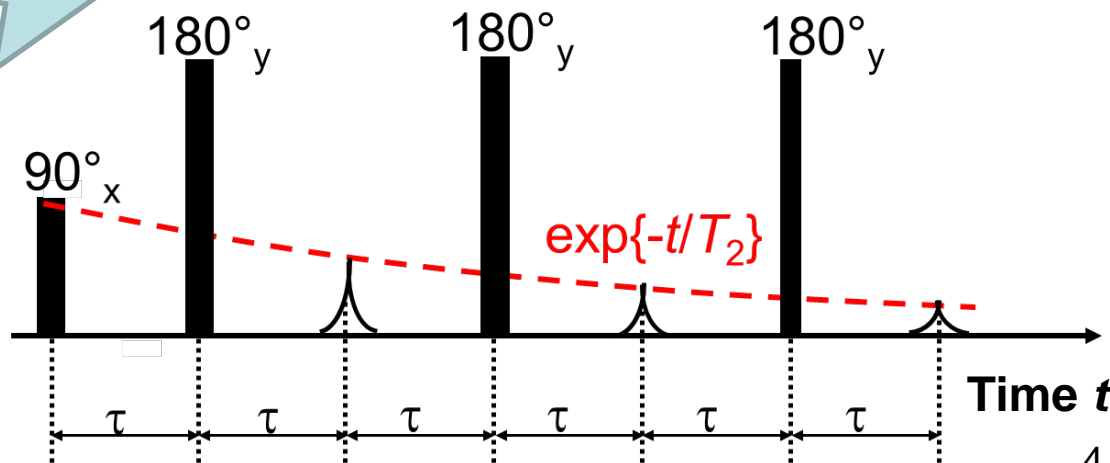
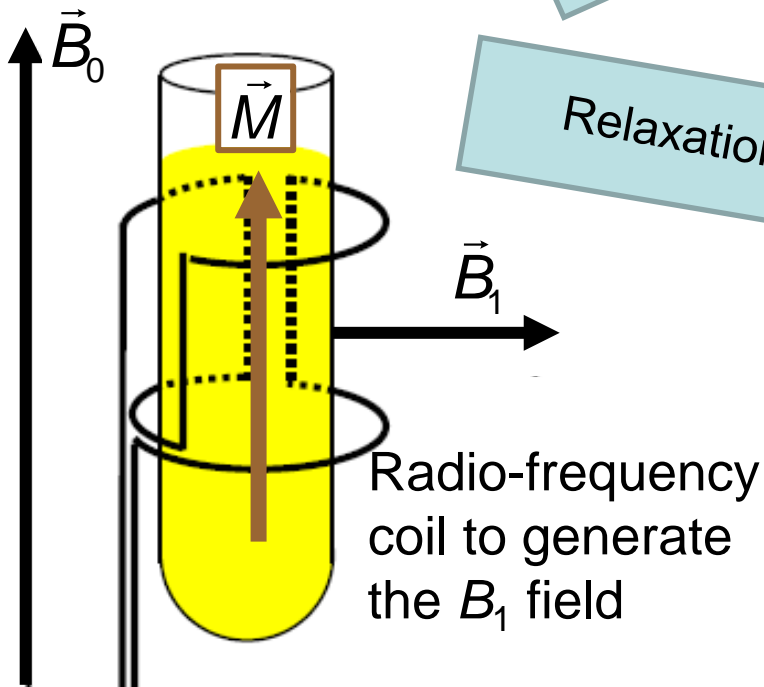
NMR: Communication in Magnetic Fields



NMR spectrum determined by the chemical structure

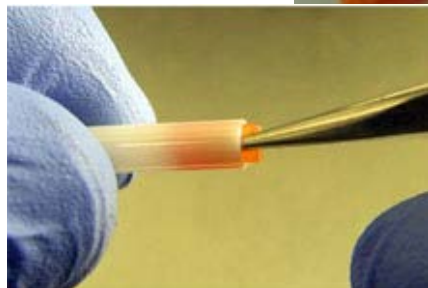
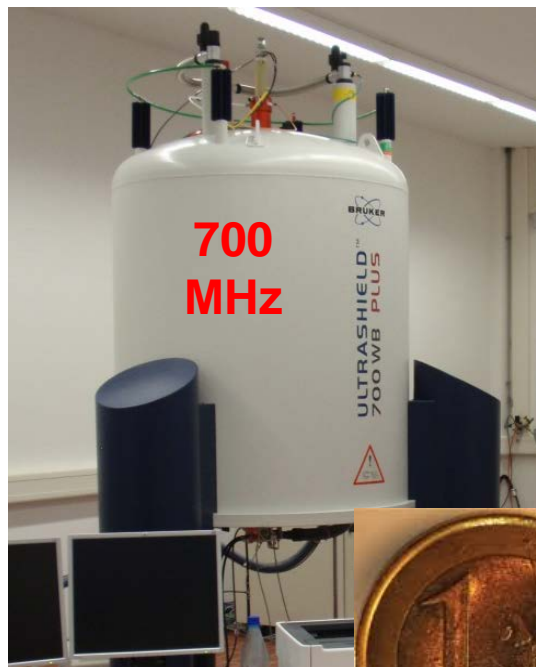


Relaxation decay determined by the molecular mobility / morphology



NMR of Solid Polymers

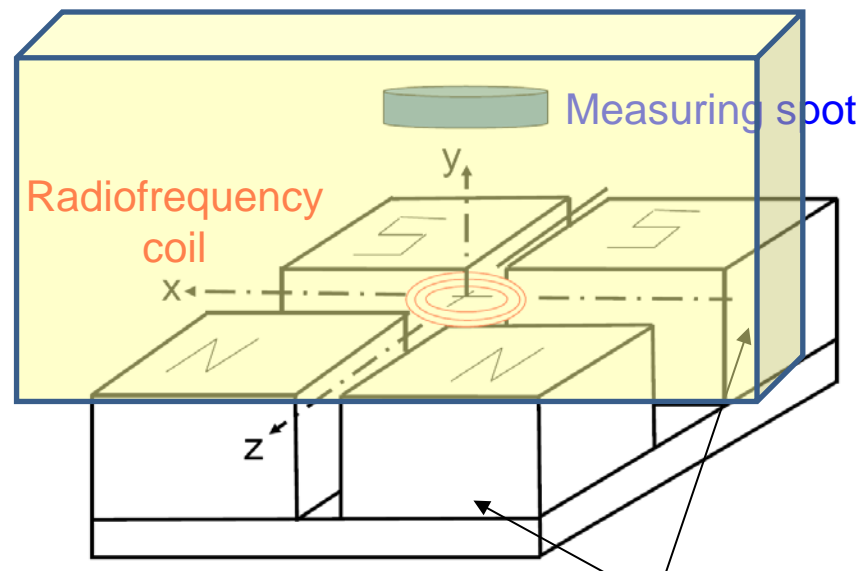
Bulk Relaxometry, Diffusometry, and Spectroscopy by High-Field NMR



Non-Destructive Depth-Dependent Relaxometry and Diffusometry by Compact Single-Sided NMR



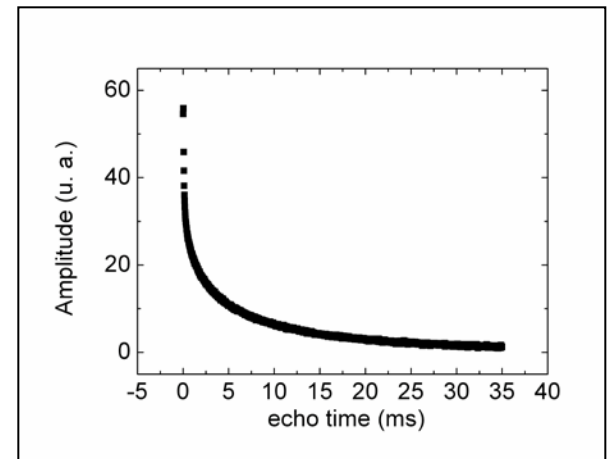
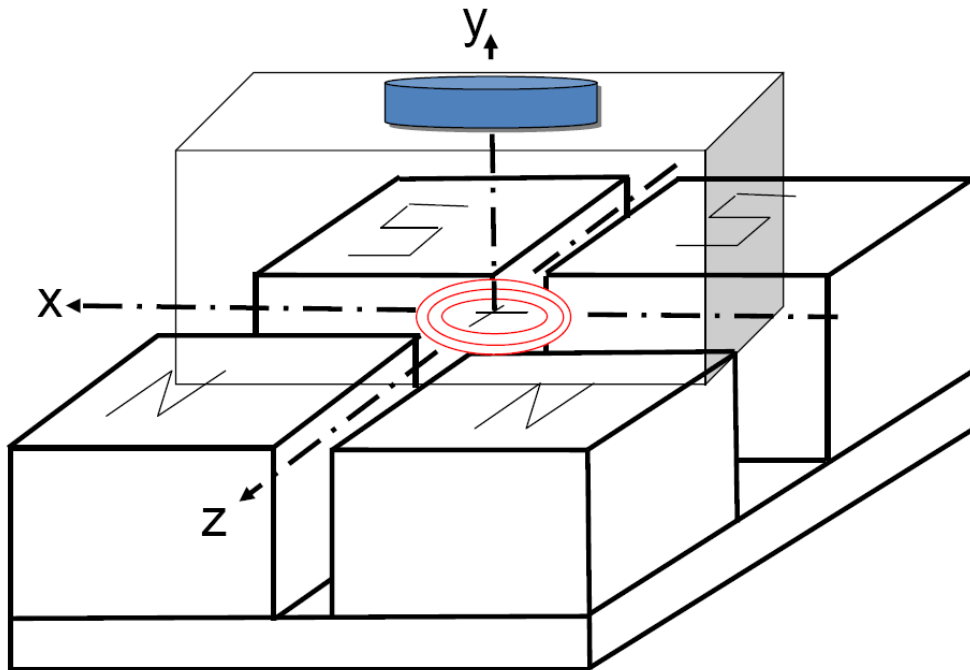
Sample



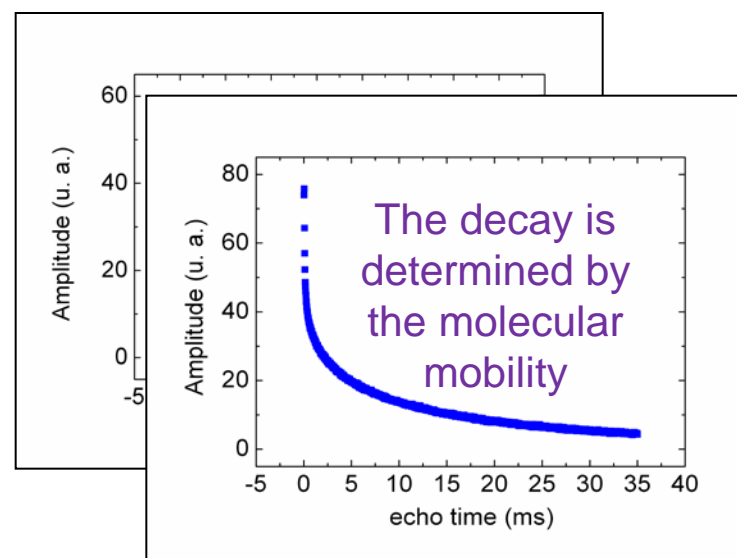
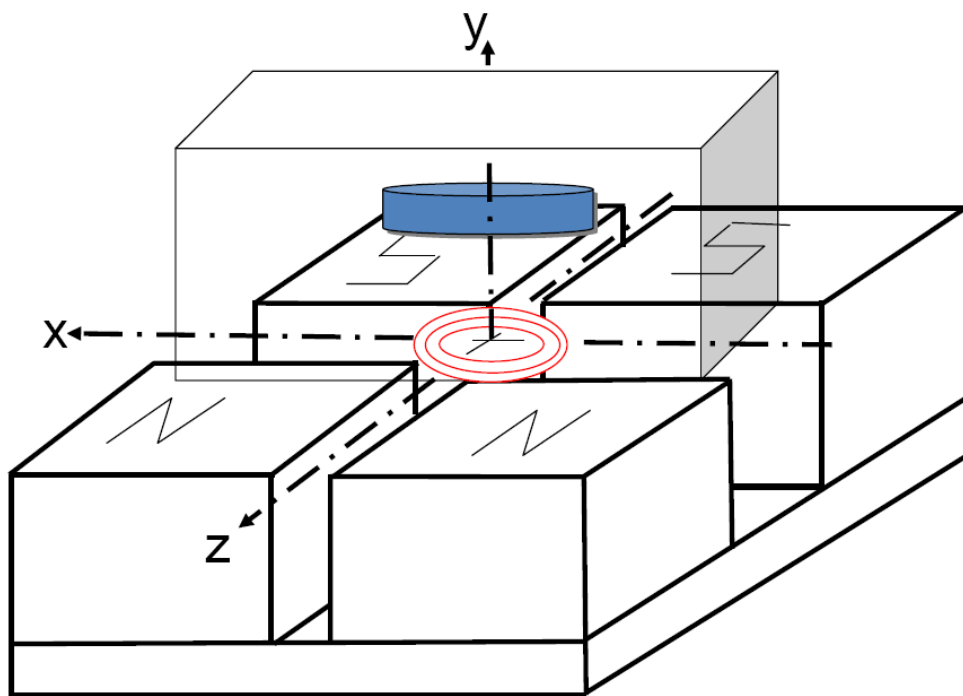
A. Adams, Trends Anal. Chem., 83, 107-119 (2016)
A. Adams, Magn. Reson. Imaging 56, 119-125 (2019)

Permanent magnets

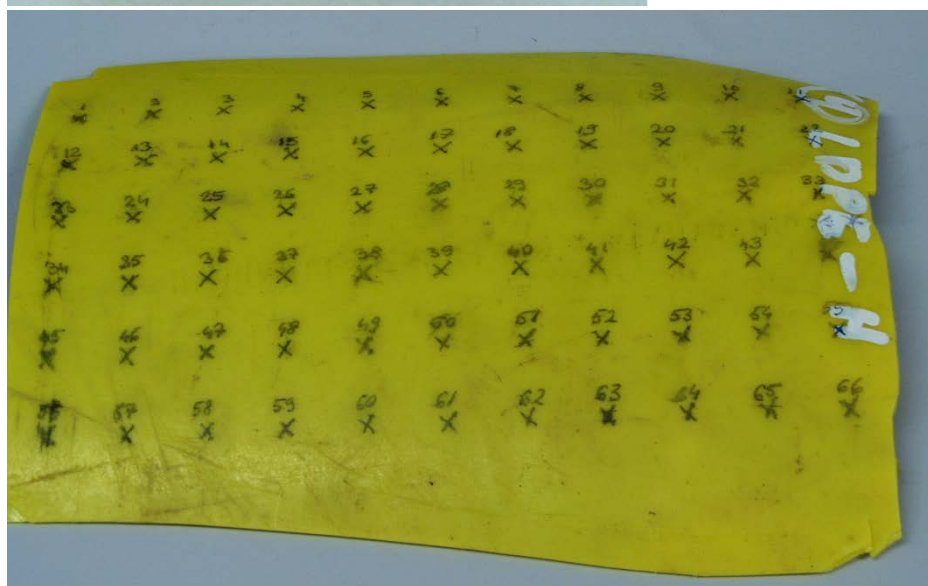
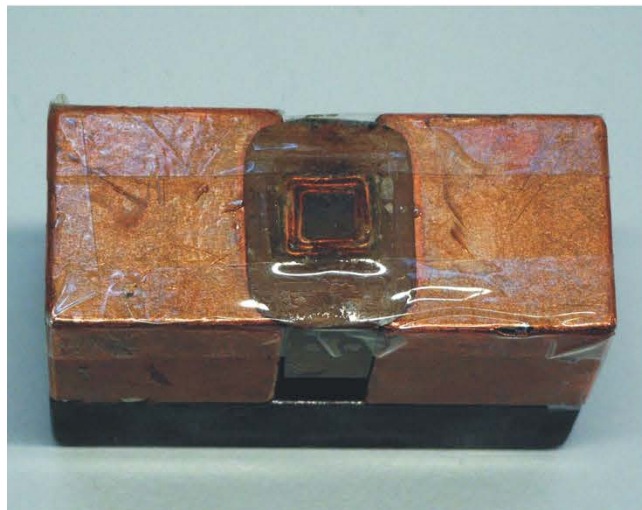
Principle of the Measurement



Principle of the Measurement



Non-Destructive Morphological Studies of Large Objects With the NMR-MOUSE

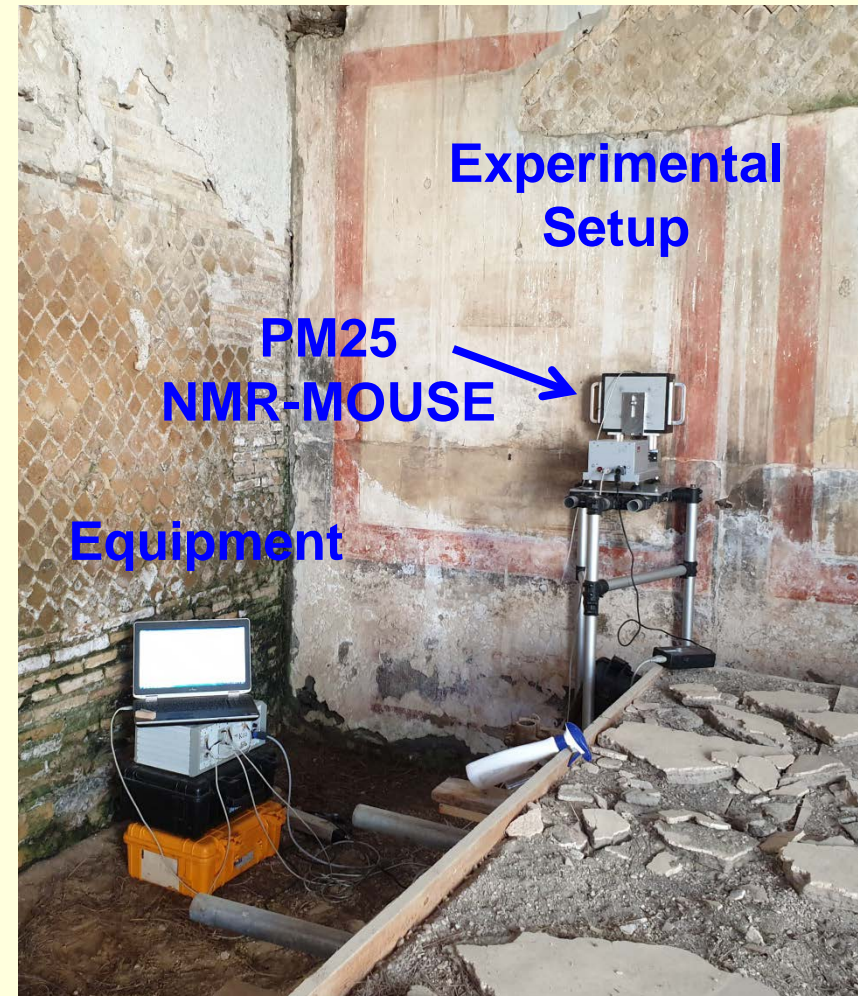


Dedicated and Portable Low-Field NMR Equipment

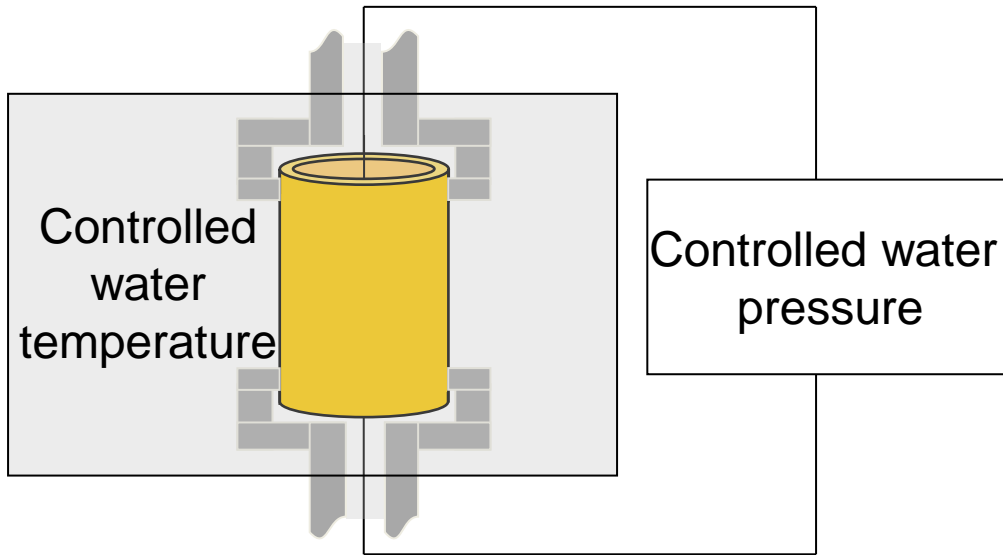
Measurement of Biofilms
in Yellowstone National Park



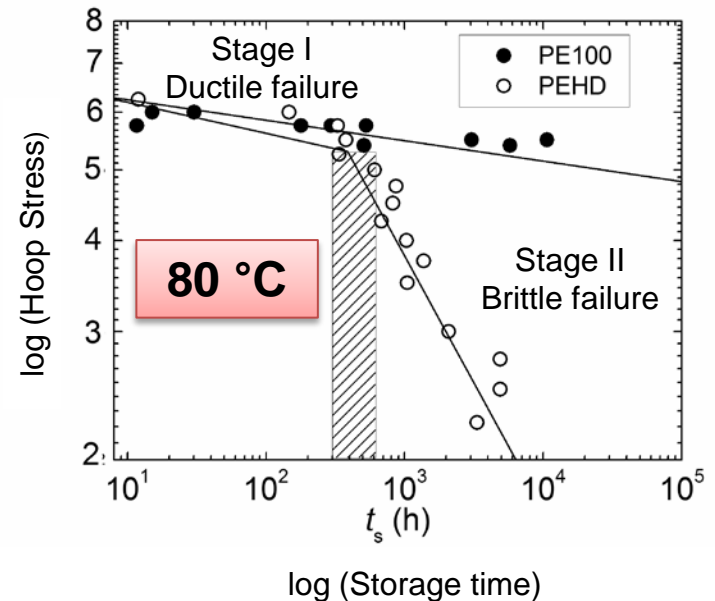
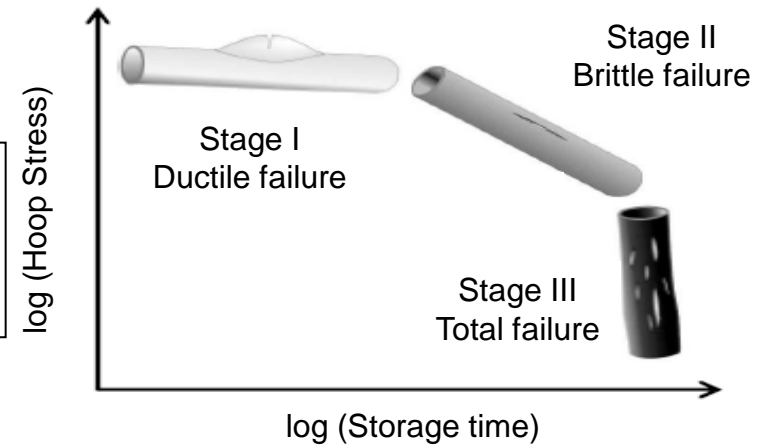
Measurement of Frescos
in Ostia, Italy



Aging of Polyethylene Pipes under Hydrostatic Pressure and at Elevated Temperatures



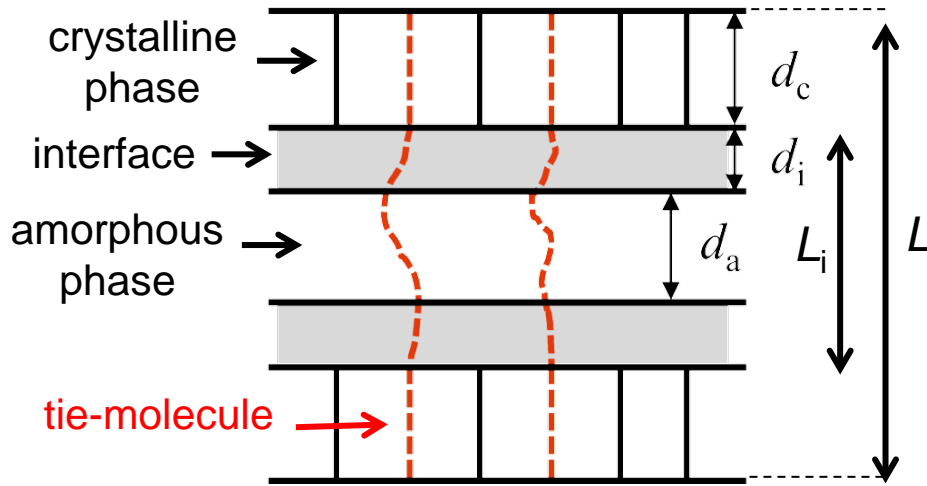
- Hydrostatic pressure tests are the most frequently used laboratory tests to predict the life time of a polymer pipe → 50-100 years
 - often questioned about their relevance to field aging
 - very long testing times
 - the changes of the molecular network during the various aging stages are largely unknown



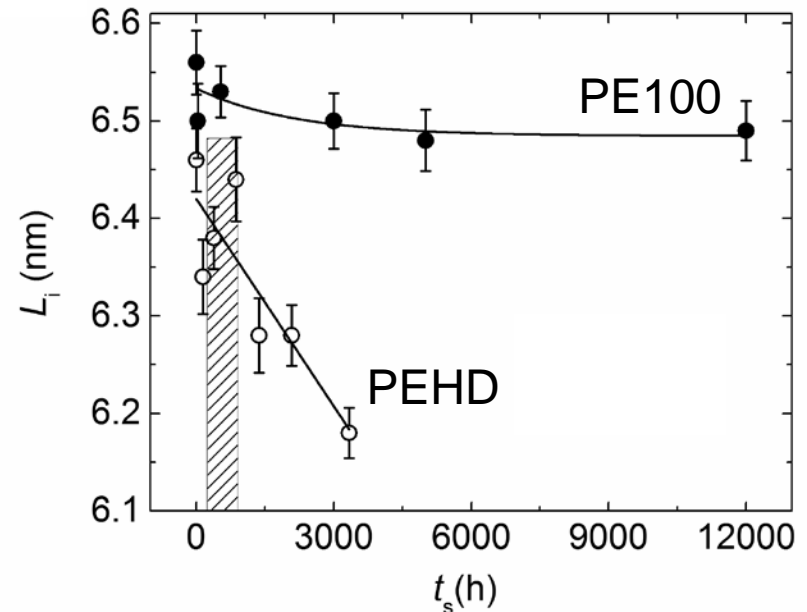
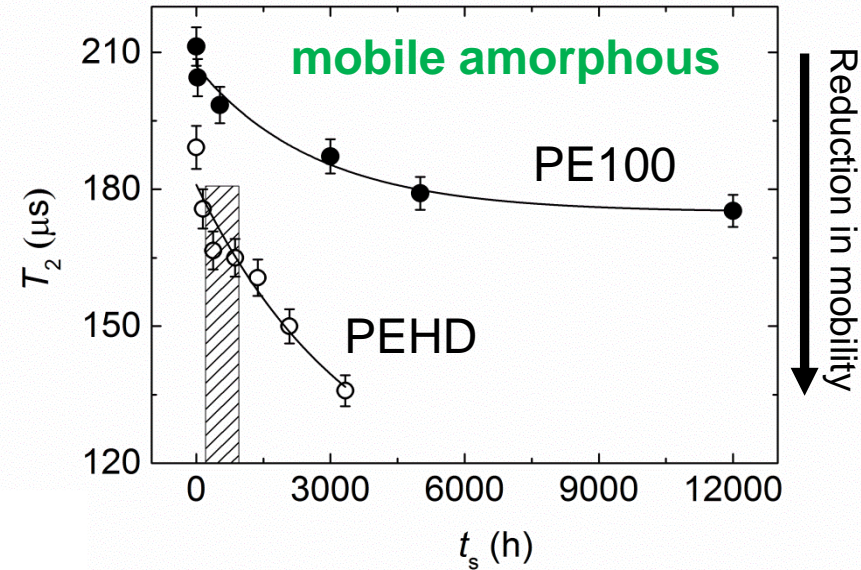
Morphological Changes with the Storage Time

According to the literature:

- The morphological changes are due to **annealing** and **hydrostatic pressure**.
Minor
Major
- The density of tie-molecules is the main factor for controlling the long term behavior of PE-pipes.

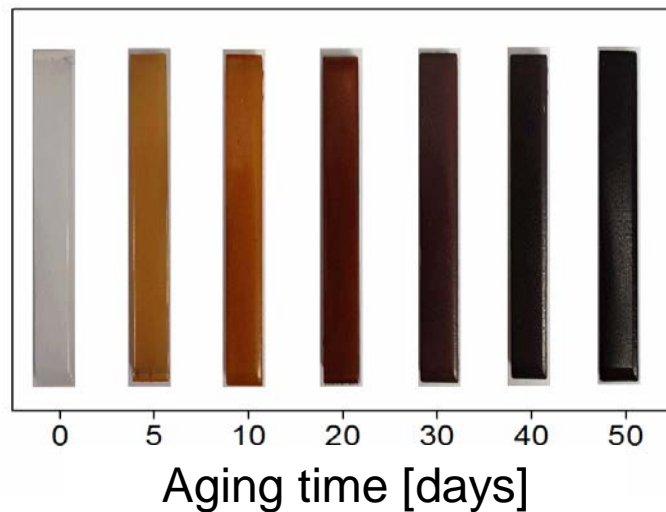


The theoretical density of tie-molecules fails to describe the behavior of PE100 and PEHD.

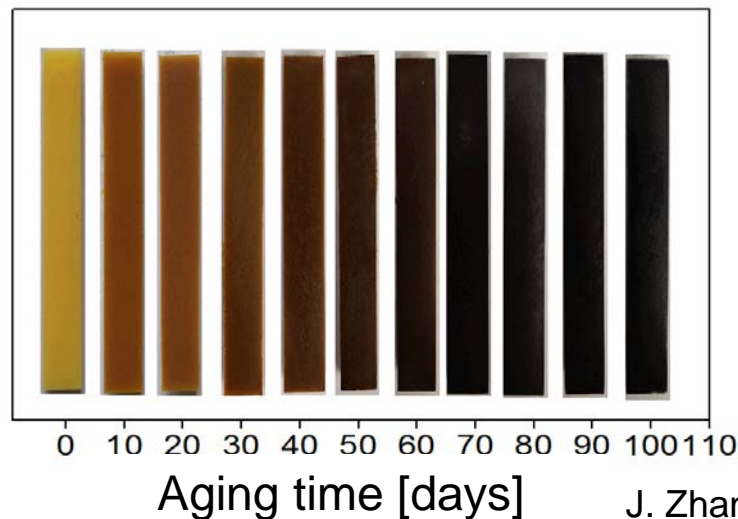


Effect of Stabilization on the Thermal Aging of PA12 at 140 °C

Non-stabilized PA12



Stabilized PA12



Methods



High-Field NMR Relaxometry

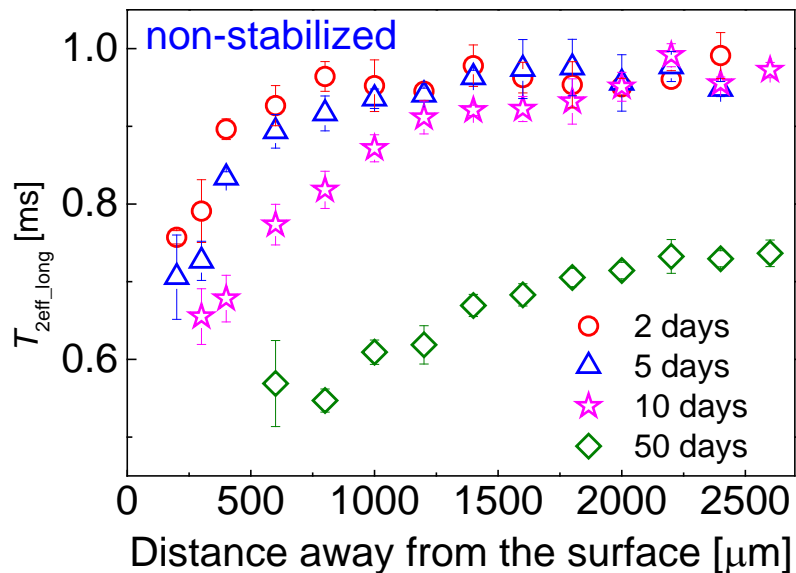
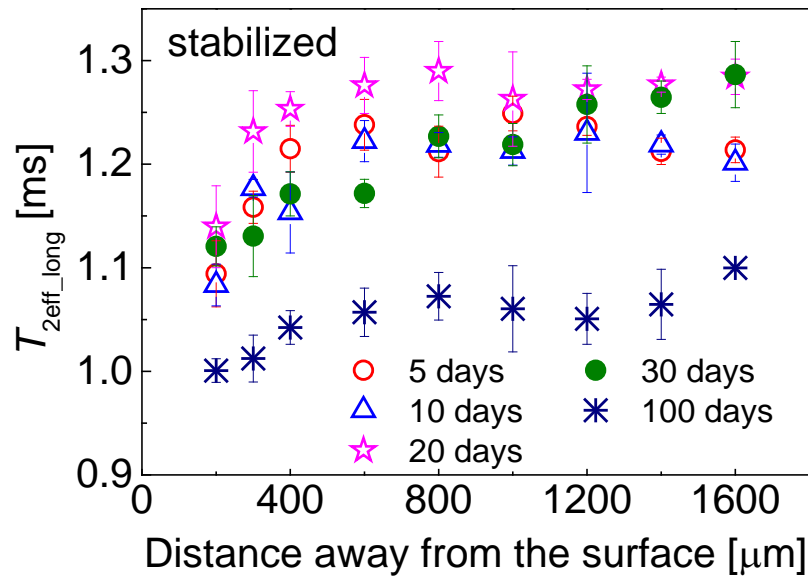
FT-IR

DSC

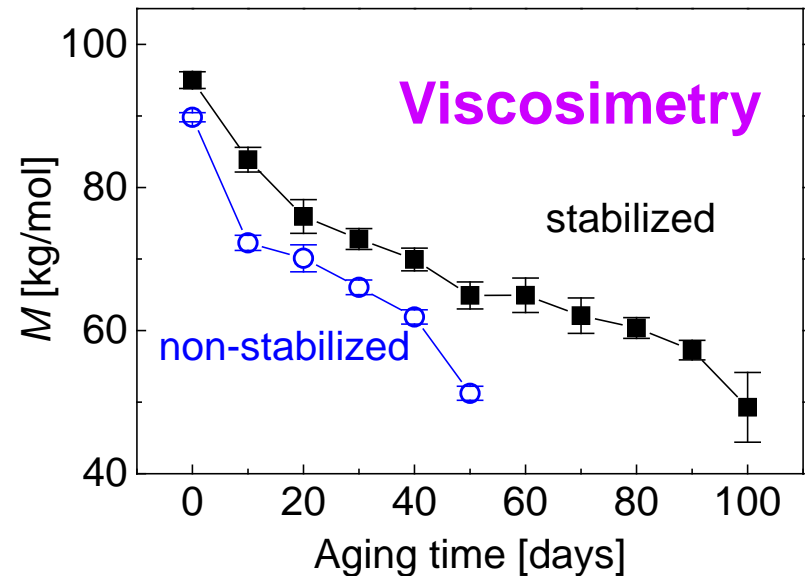
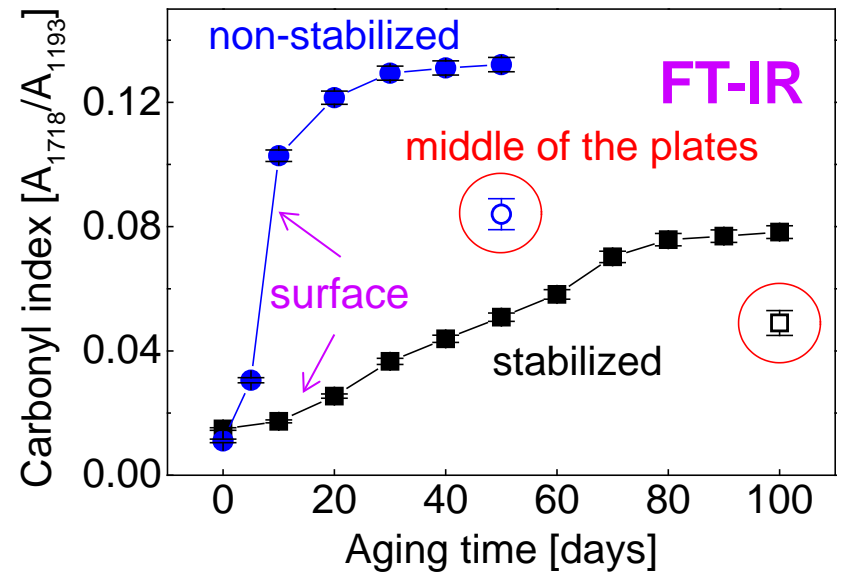
Viscosimetry

NMR-MOUSE Relaxometry

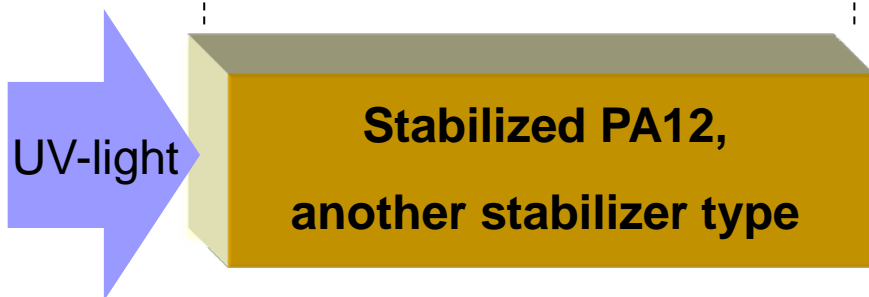
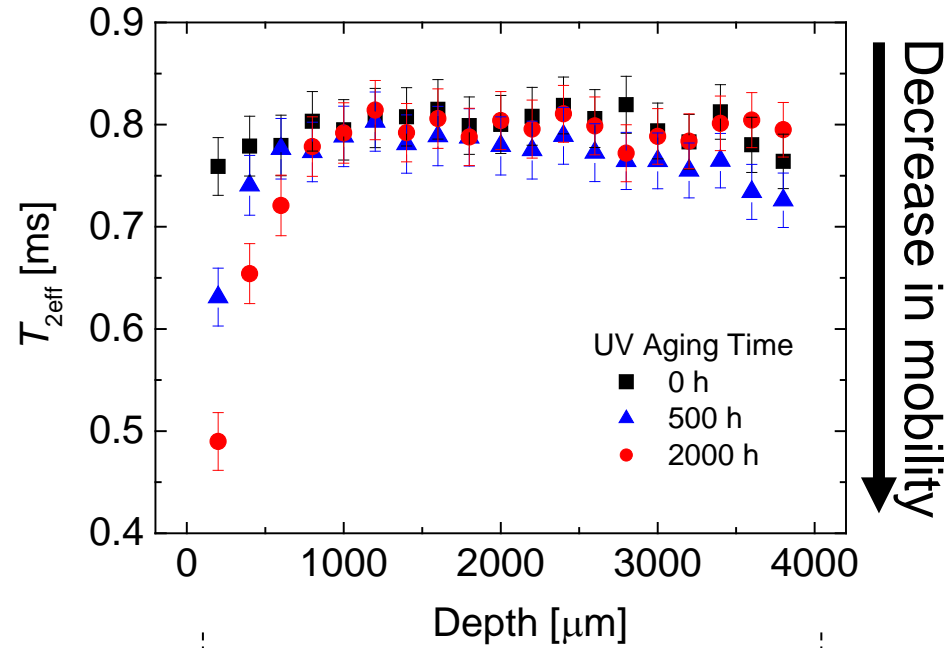
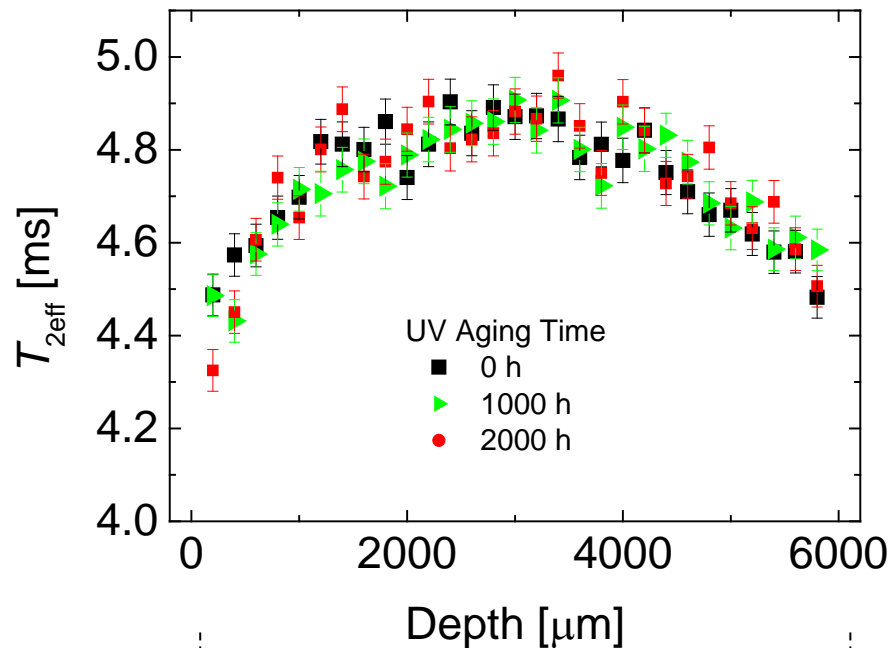
Depth-Dependent NMR Morphology



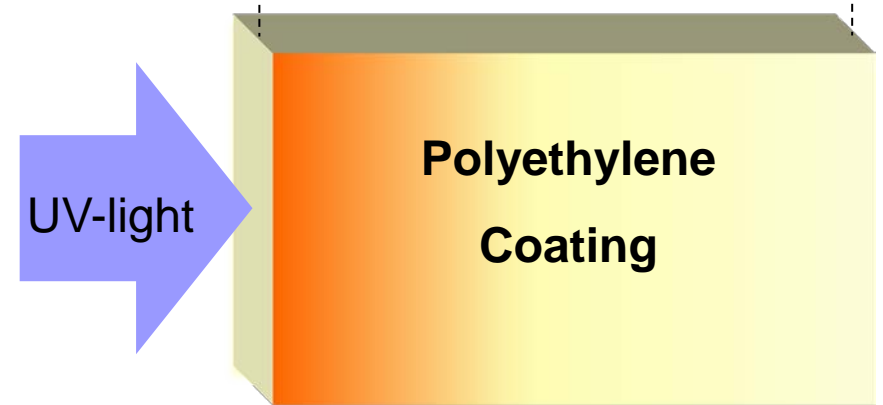
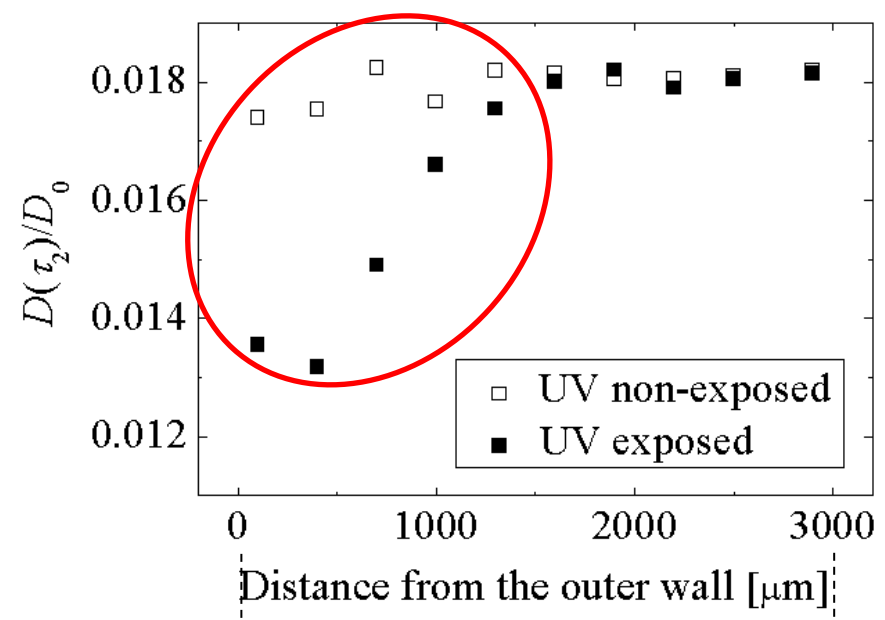
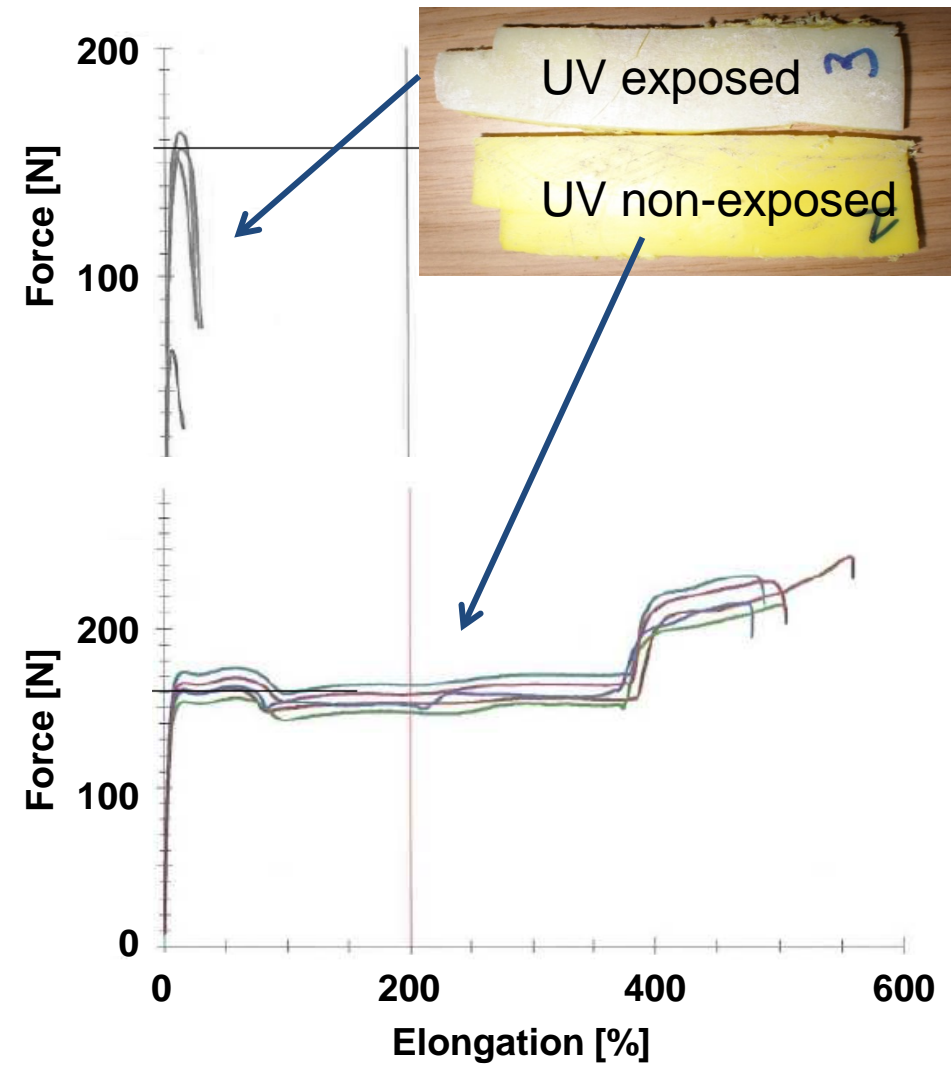
Supporting the NMR Results



Monitoring the UV-Aging of PA12



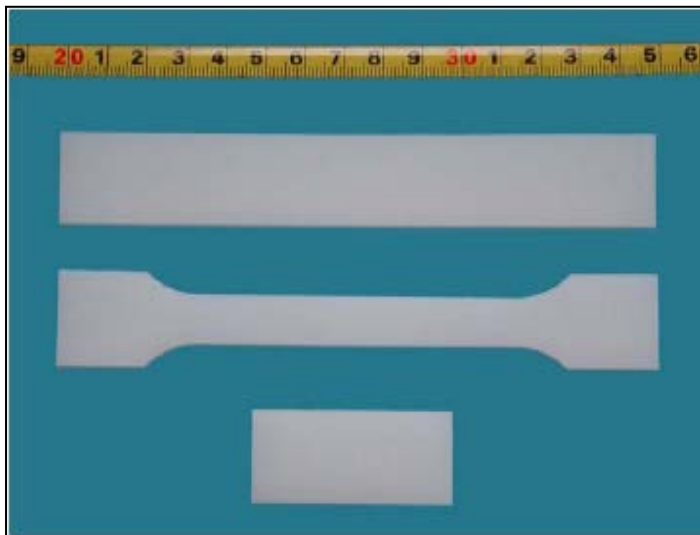
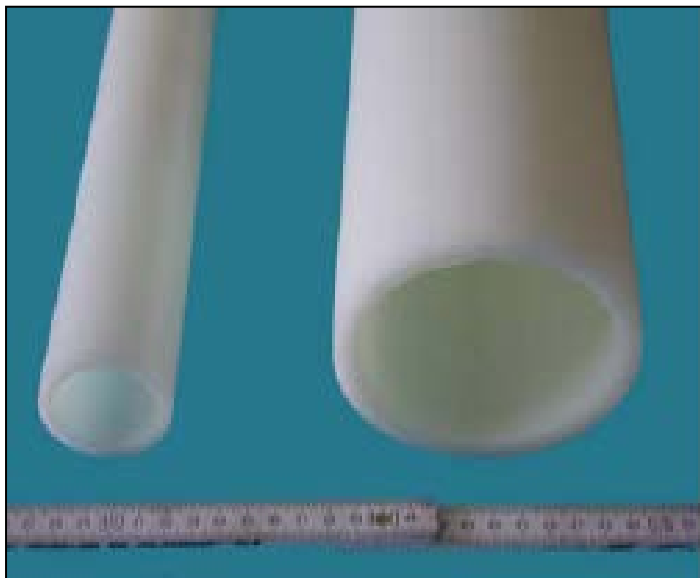
UV-Aging of Polyethylene Coatings by ^1H Self-Diffusion Coefficients



H.-J. Kocks et al *3R Int.* 2011 , 8/9 , 618.

Chemical Aging of Crosslinked Polyethylene

Exposure to 6 various aging media
at 60 °C up to 6 months



Methods



Changes in the Weight

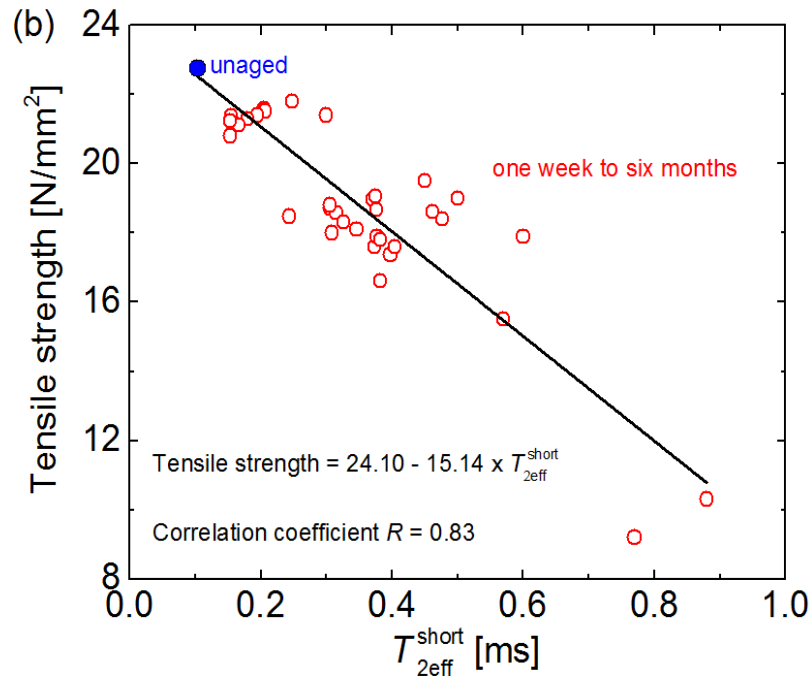
Crosslink Density Measurements

Mechanical Measurements


Differential Scanning Calorimetry
(DSC)

NMR-MOUSE

Correlation NMR/Mechanical Measurements



The changes in the relaxation time of the amorphous phase correlate with the changes of the tensile strength.

 With the help of a calibration curve, the mechanical state of a pipe at a certain time can be predicted by simple nondestructive NMR measurements.

Conclusions

- NMR methods working at high and low magnetic field were successfully applied to characterize:
 - Morphological changes of PE pipe grades during a hydrostatic pressure test
 - Morphological changes during thermal and UV-aging of stabilized and non-stabilized PA12 samples
 - Ingress of solvents in various polymers
 - Chemical aging of crosslinked PE
- The mobility of the amorphous phase is the most sensitive microscopic parameter towards aging.
- Correlations of the single-sided NMR data with the mechanical measurements could enable in-situ mechanical condition monitoring.

Thank you to my Collaborators:

Dr. N. Sun, former RWTH Aachen

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Dr. R. Kwamen, former RWTH Aachen

Prof. Dr. G. Schmitt, FH Iserlohn

J. Zhang, former RWTH Aachen

Dr. J. Berger, Evonik Marl

M. Adams, RWTH Aachen

**Thank You
very much for your attention!**



Questions?

Then, please contact me at:

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