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Neutrons as a Study Probe in the Research of Novel Functional Materials

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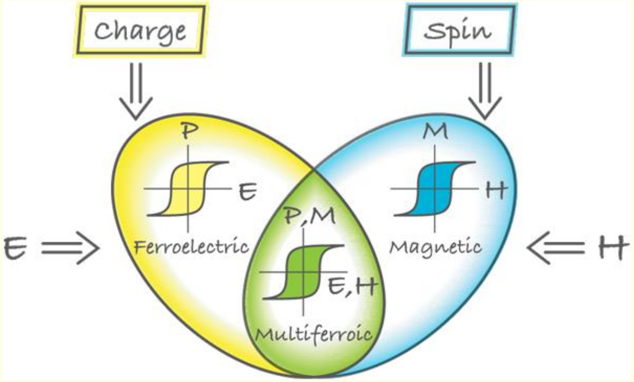
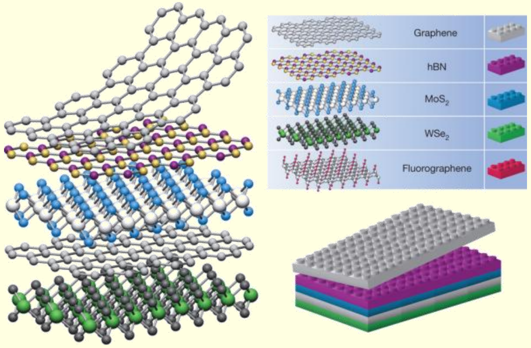
Outline

- Where we are (functional materials studied with neutrons)
- Ceramic-elastomer composites
    - Introduction
    - Experimental procedure D7 (ILL)
    - Results
- Magnetorheological elastomers
    - Introduction
    - Experimental procedure D11 (ILL)
    - Preliminary results
- Conclusions

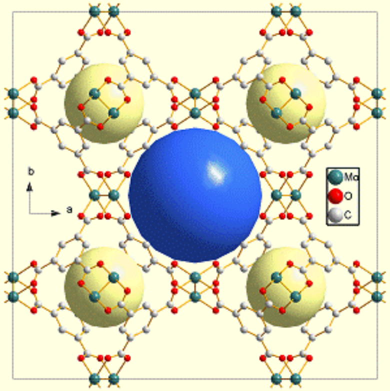
Functional materials studied with neutrons
(arbitrary, incomplete selection)



Multiferroics



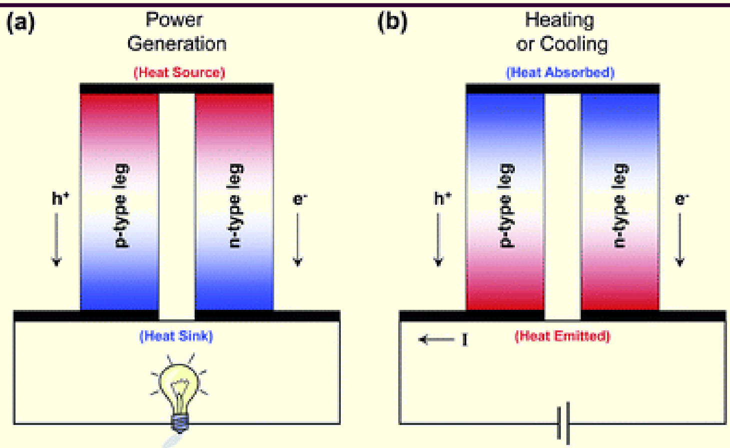
Heterostructures (also materials with competing order parameters)



Metal-organic frameworks

Photovoltaic materials

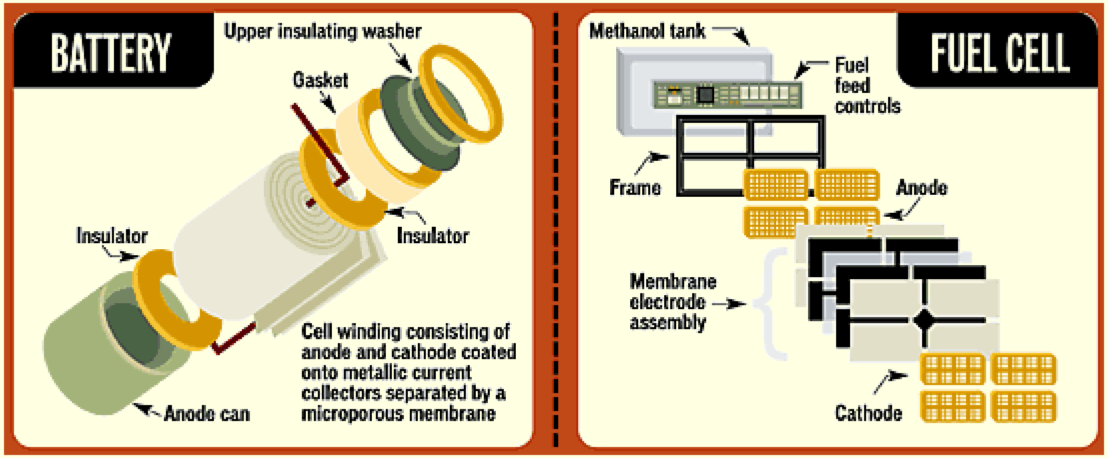
Functional materials studied with neutrons
(arbitrary, incomplete selection)



Thermoelectric materials

„Hard" stuff under the spotlight:

structure, dynamics,
coupling mechanisms, etc.



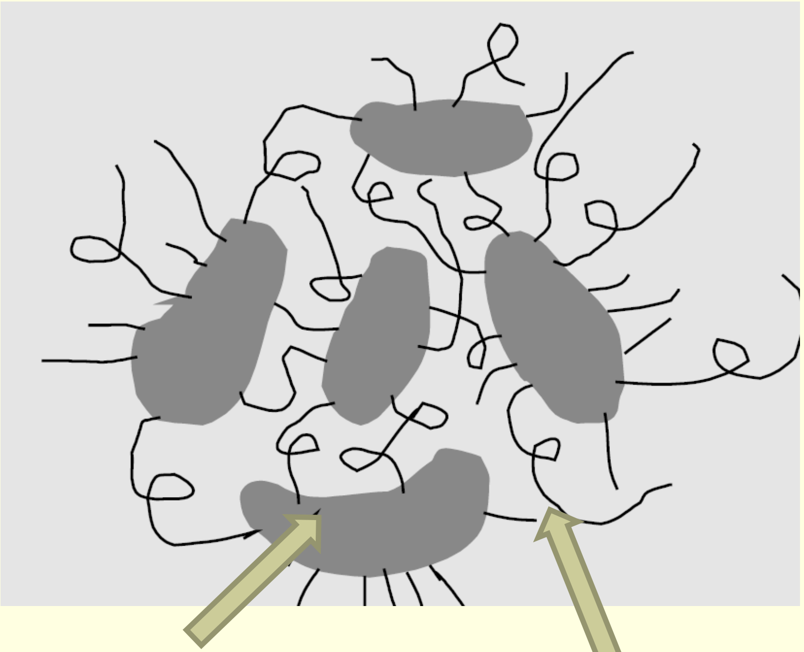
Batteries and fuel cells

Soft and elastic functional («intelligent») materials

now receiving more and more attention.

Domain structure of PU elastomers

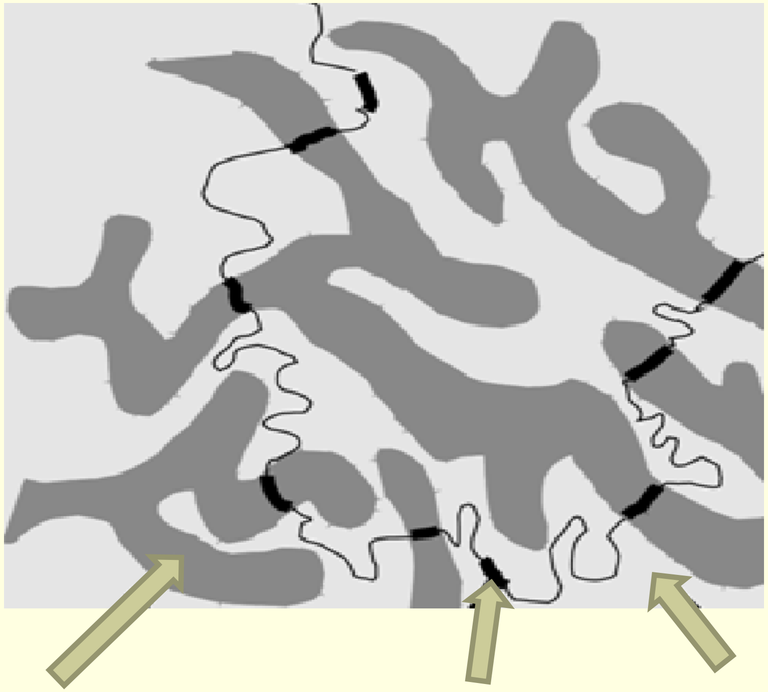
Low HS content



HS domain SS domain

Isolated domain structure

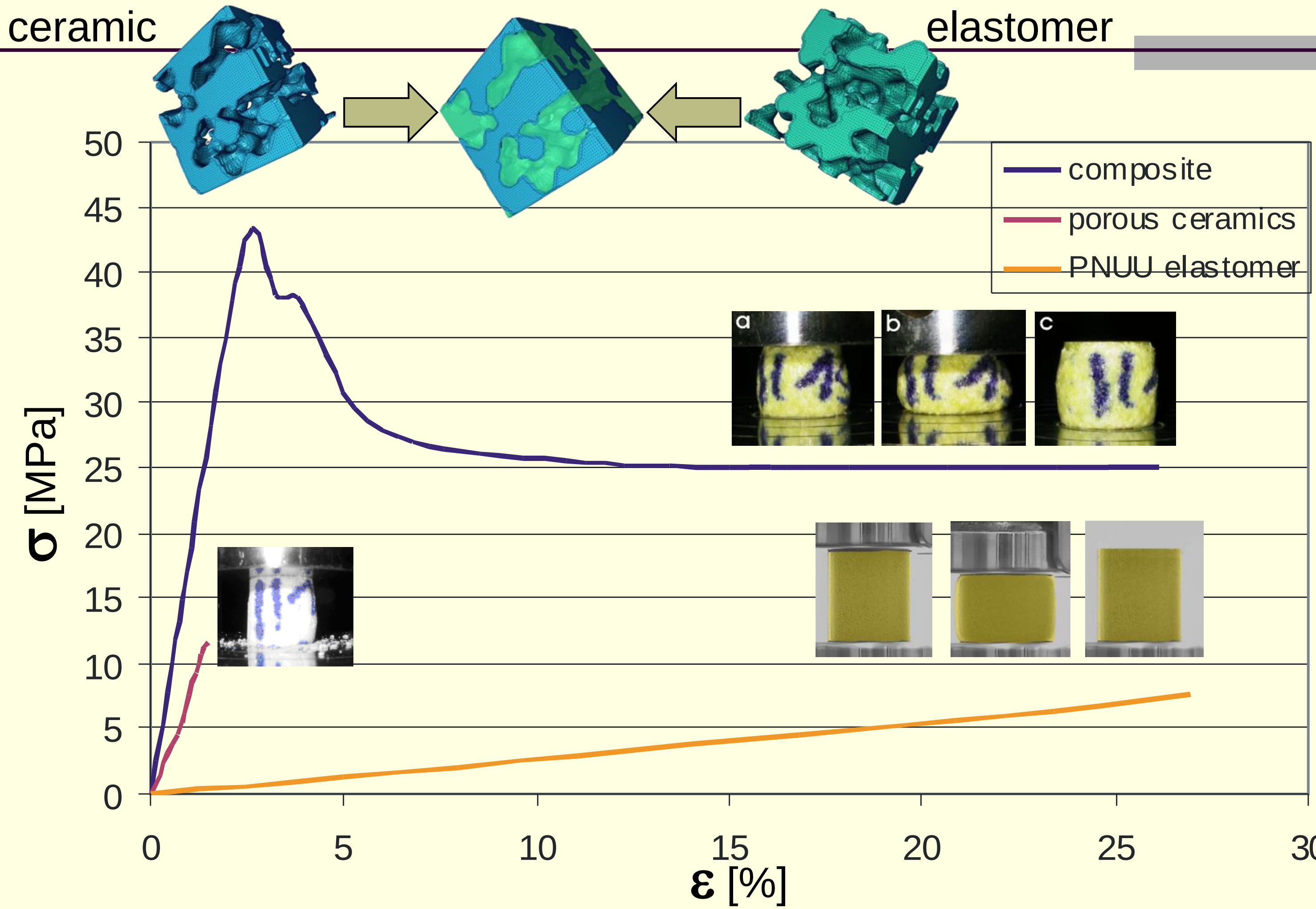
High HS content



HS domain isolated HS SS domain

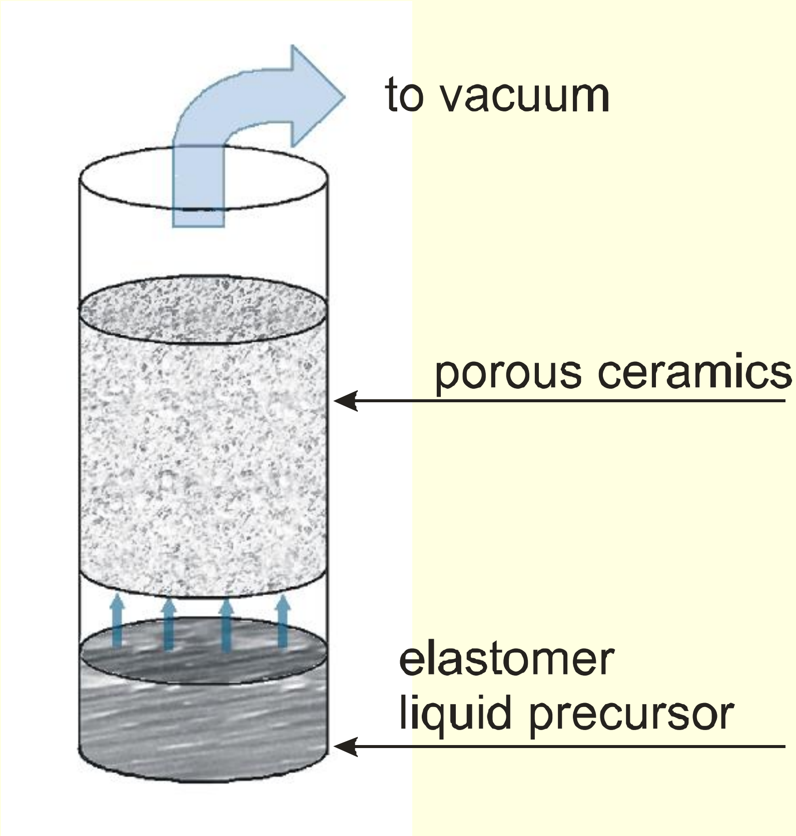
Continuous domain structure

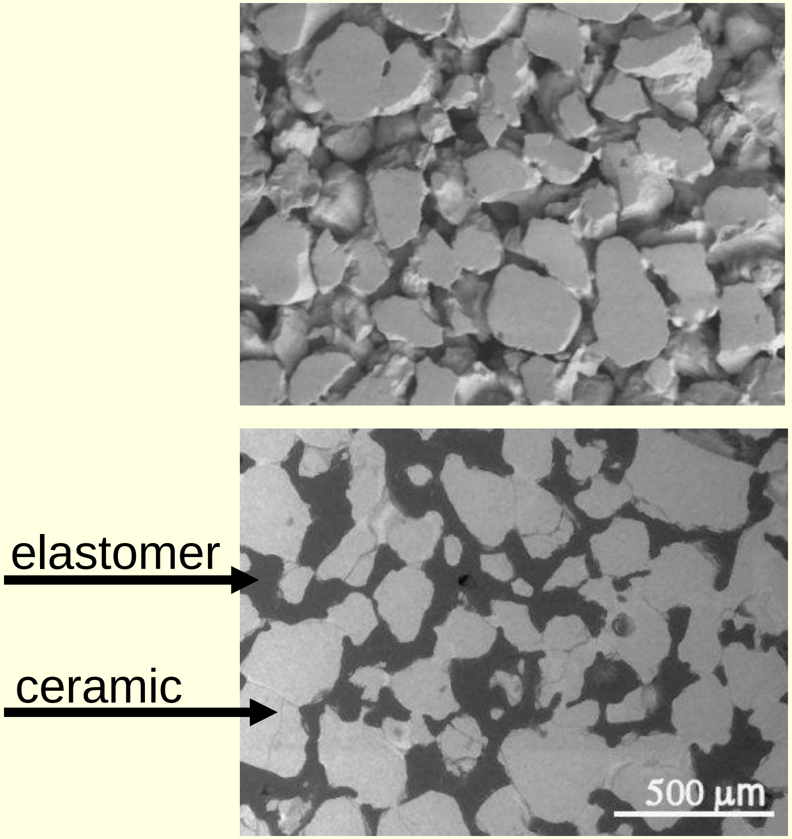
Ceramic–elastomer composites with 3D connectivity of phases - introduction



Combination of ceramics stiffness and high elasticity of elastomers.
Compressive stress–strain curves. Energy dissipation capabilities.

Fabrication process of ceramic-elastomer composites





Curing of elastomer is carried out inside ceramic pores at temperature elevated up to 120°C

Residual stresses formation

Aim of studies

- **To measure residual stresses in PU cured in ceramic pores**

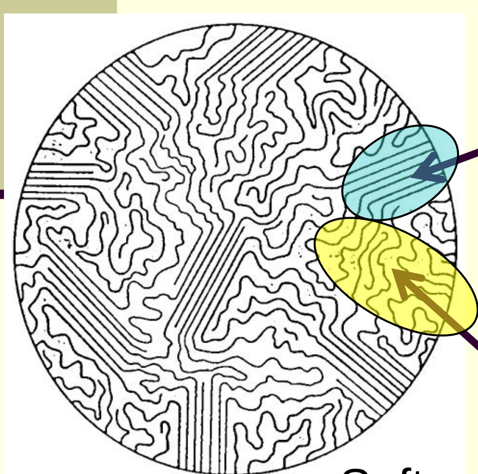
Experiment Title : Residual stresses in ceramic-elastomer composites (proposal no. 9-12-107)

Experiment place: D7 - ILL Grenoble (May 2007)

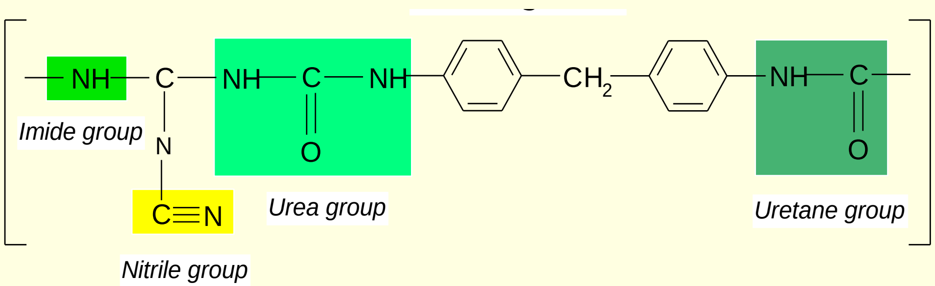
W. Zając, A. Boczkowska , K. Babski, K.J. Kurzydłowski, *Measurements of Residual Strains in Ceramic-Elastomer Composites with Diffuse Scattering of Polarized Neutrons*, Acta Materialia 56 (2008) 5964–5971

Characteristic of urea-urethane elastomers used in this work

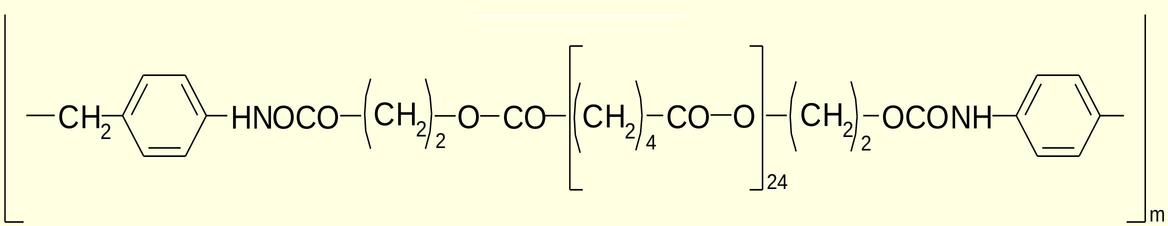
Sample code	MDI/ (PAE+DCDA) [mol/mol]	H/S [mol/mol]	H content [wt.%]	Schematic macromolecule structure
PU125	1.25	0.25	2.3	$[(S)_4(H)]_n$
PU25	2.50	1.50	12.5	$\{[(S)(H)_2]_3[(S)(H)]_2\}_n$



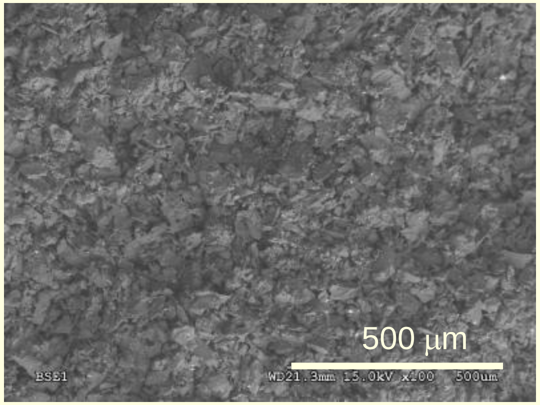
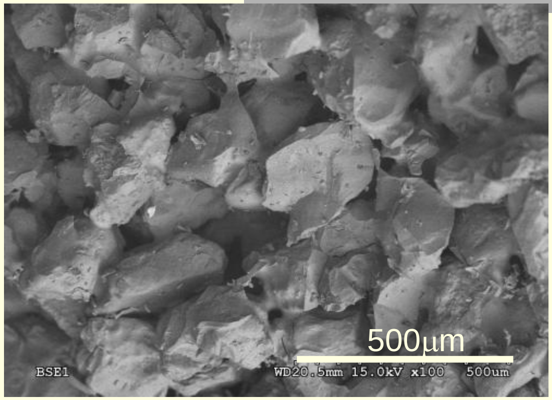
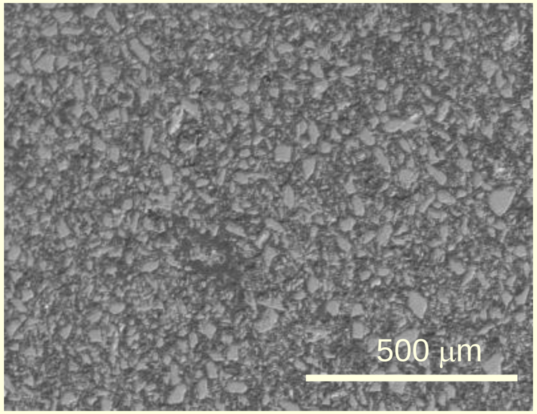
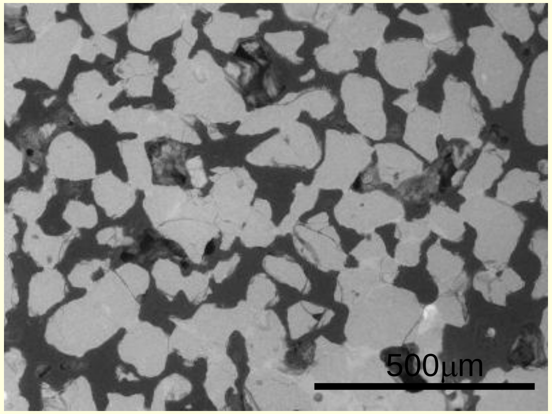
Hard segments (H)



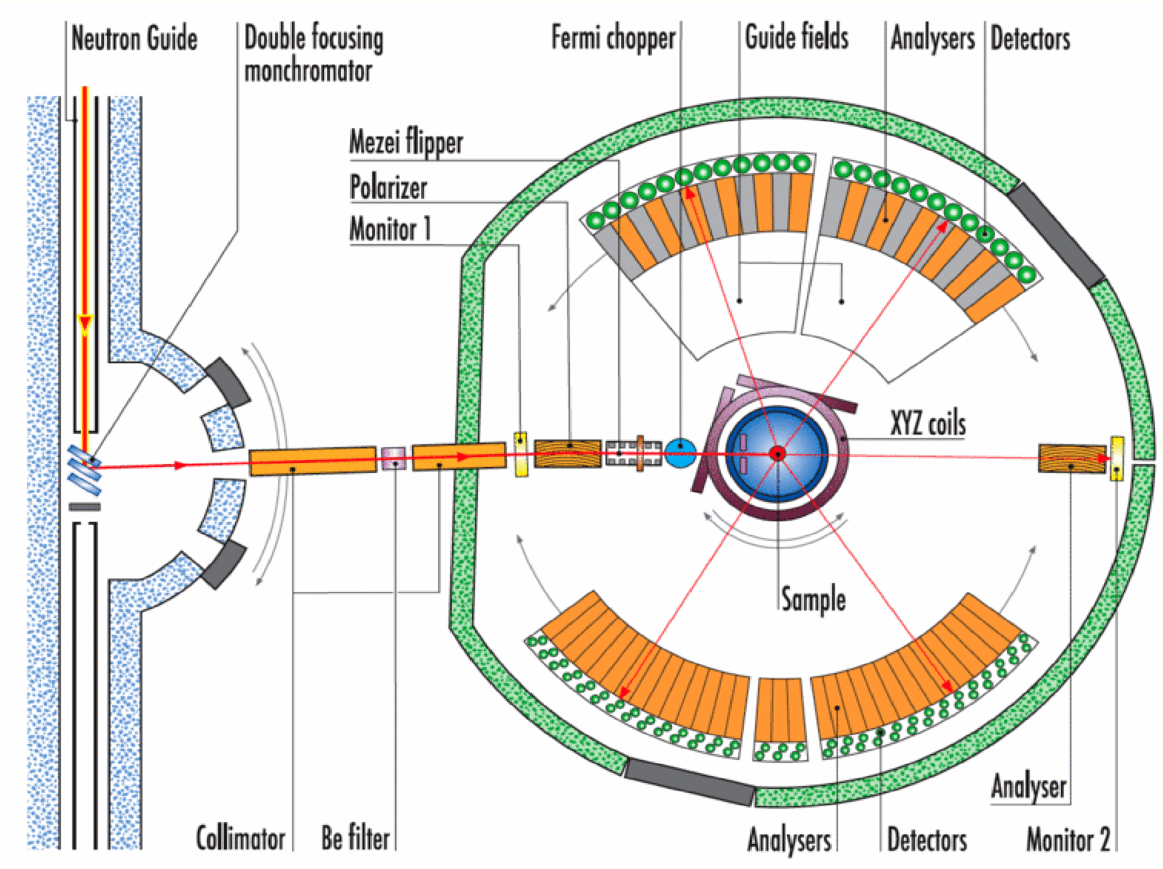
Soft segments (S)

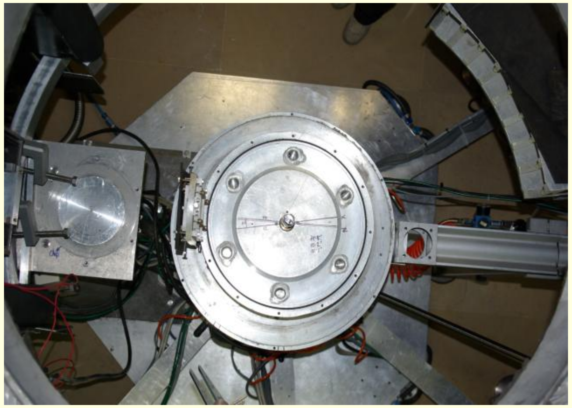


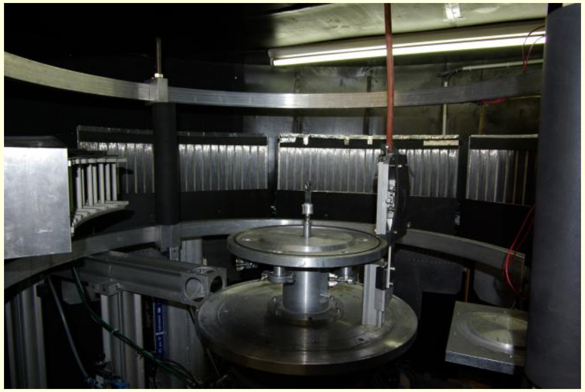
Porous ceramic and composites microstructure and characteristics

	Type A		Type B
Porous ceramic fracture surface		**Open porosity ~ 40%**	
Powder diameter:	**< 63µm**		**200-300µm**
Mean pores size:	**~20µm**		**~70µm**
Composite sections			
Specific surface of the interface:	**64.5 ± 3.8 [1/mm]**		**0.37 ± 0.01 [1/mm]**

D7 Diffuse Scattering instrument at ILL -
WANS Study with Polarized Neutrons

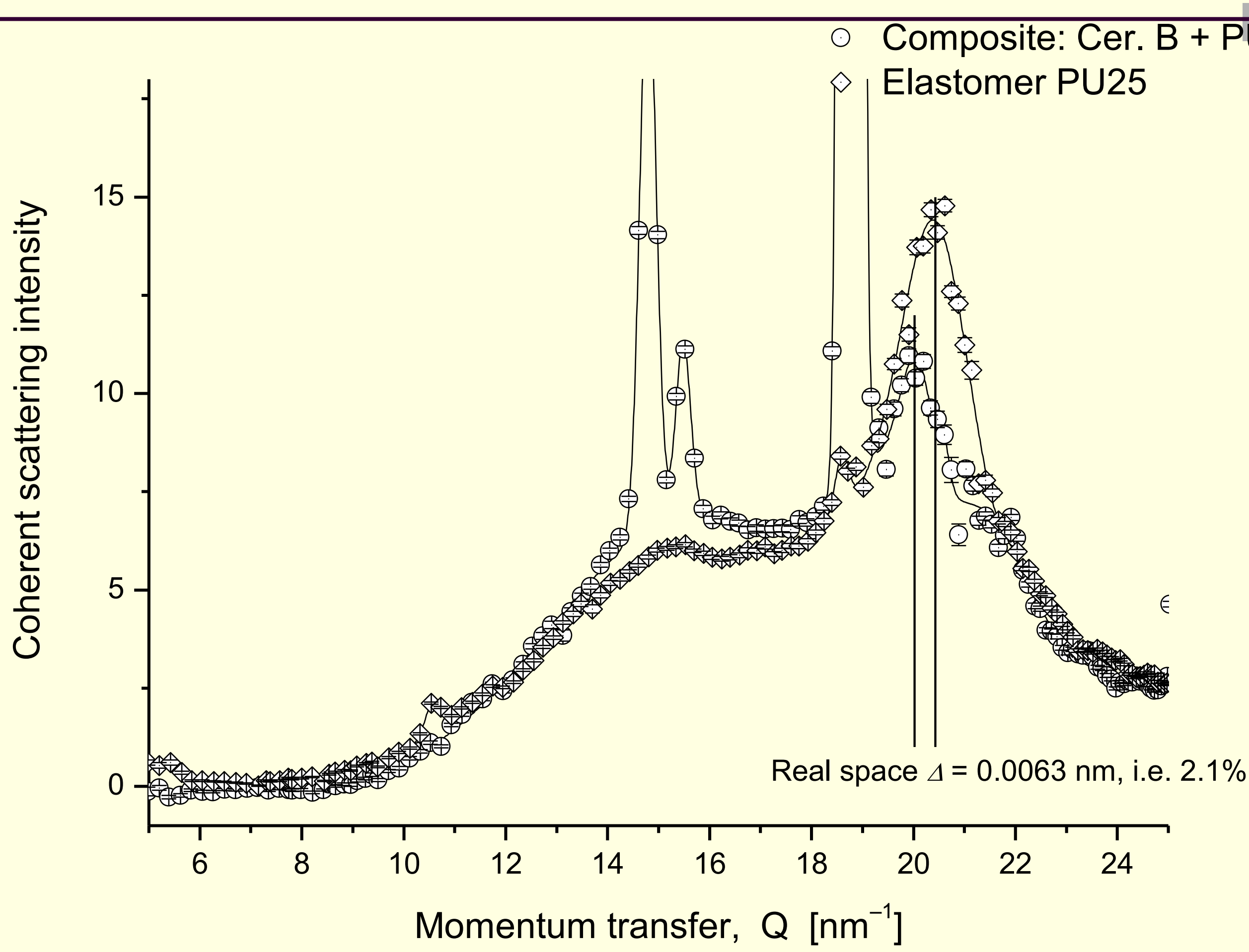






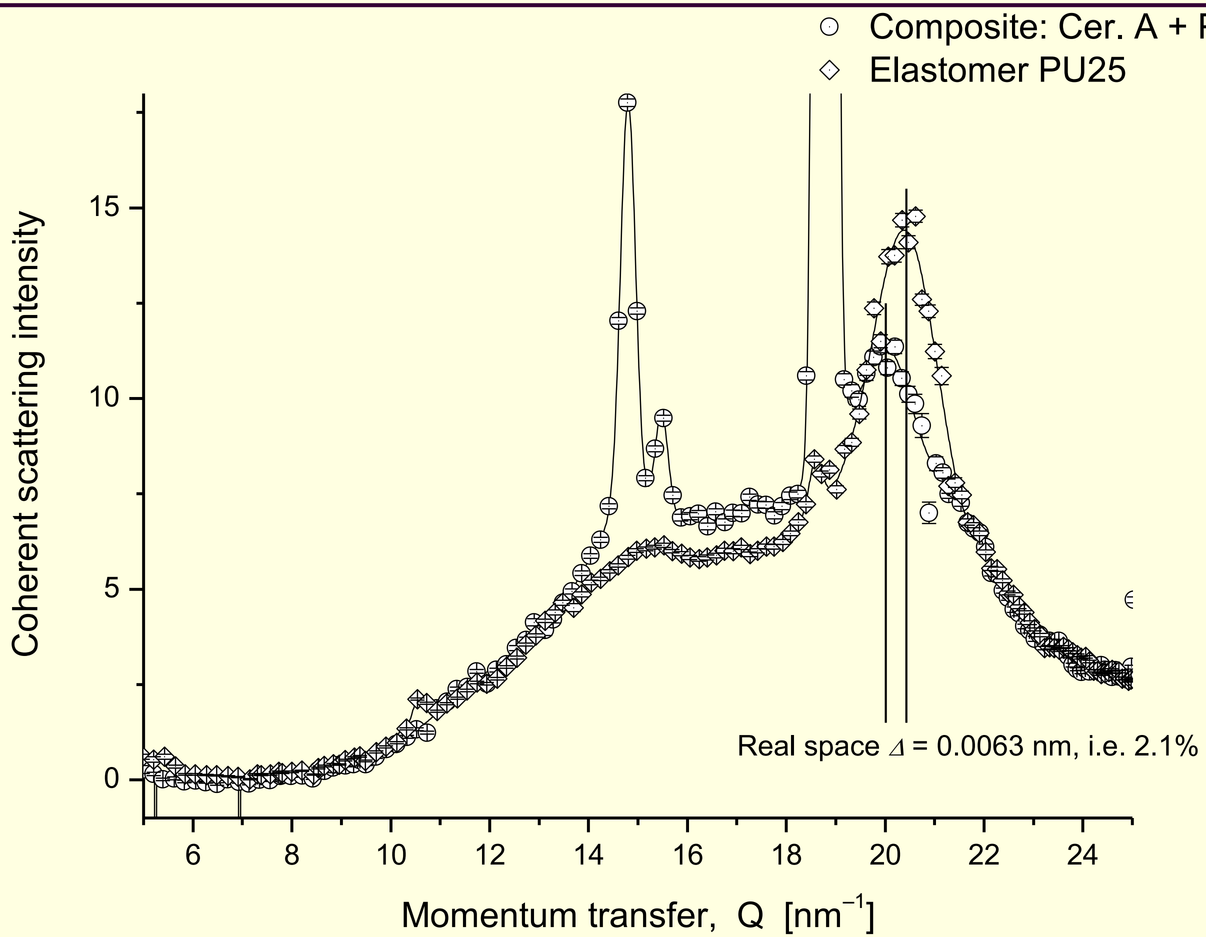
Polarized neutrons offer a unique opportunity of separating, **at the machine level, coherent from** incoherent scattering.

Results - coherent neutron scattering spectra of a composite B and elastomer PU25



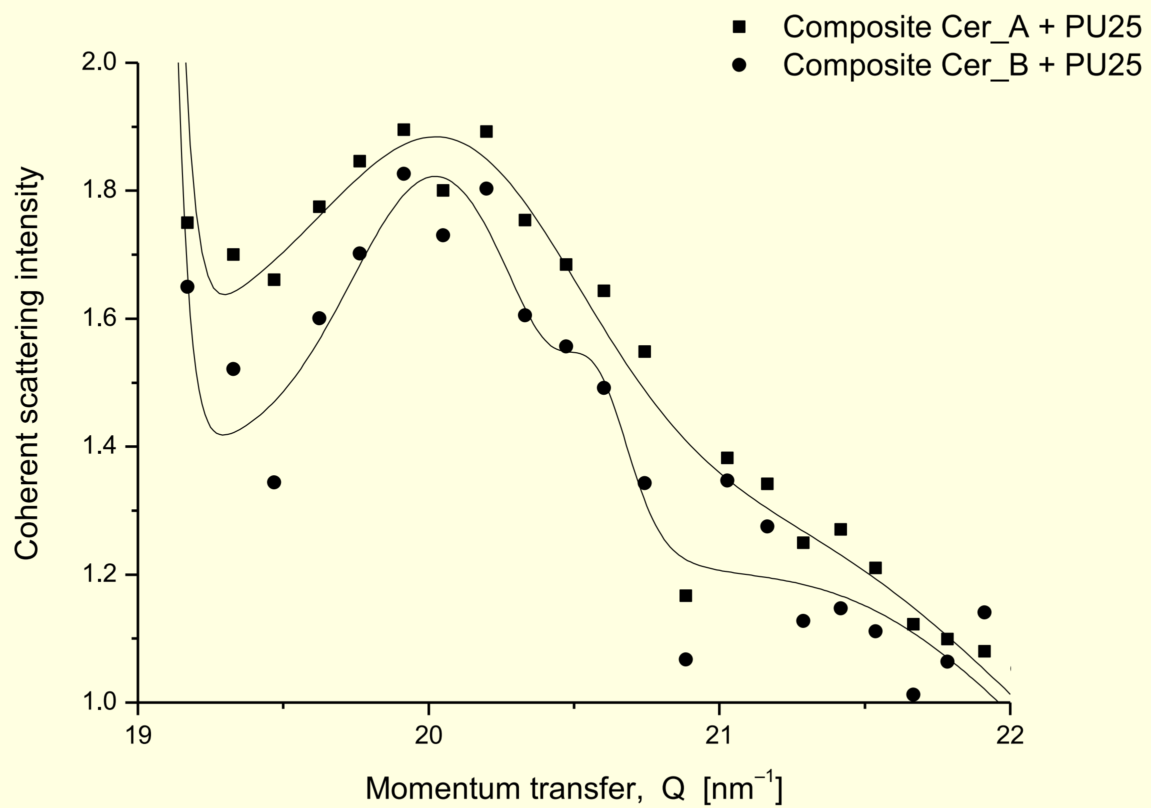
Scaled and 'zoomed' coherent neutron scattering spectra of type B composite and pure bulk elastomer PU25. Error bars are smaller than the point size.

Results - coherent neutron scattering spectra of a composite A and elastomer PU25



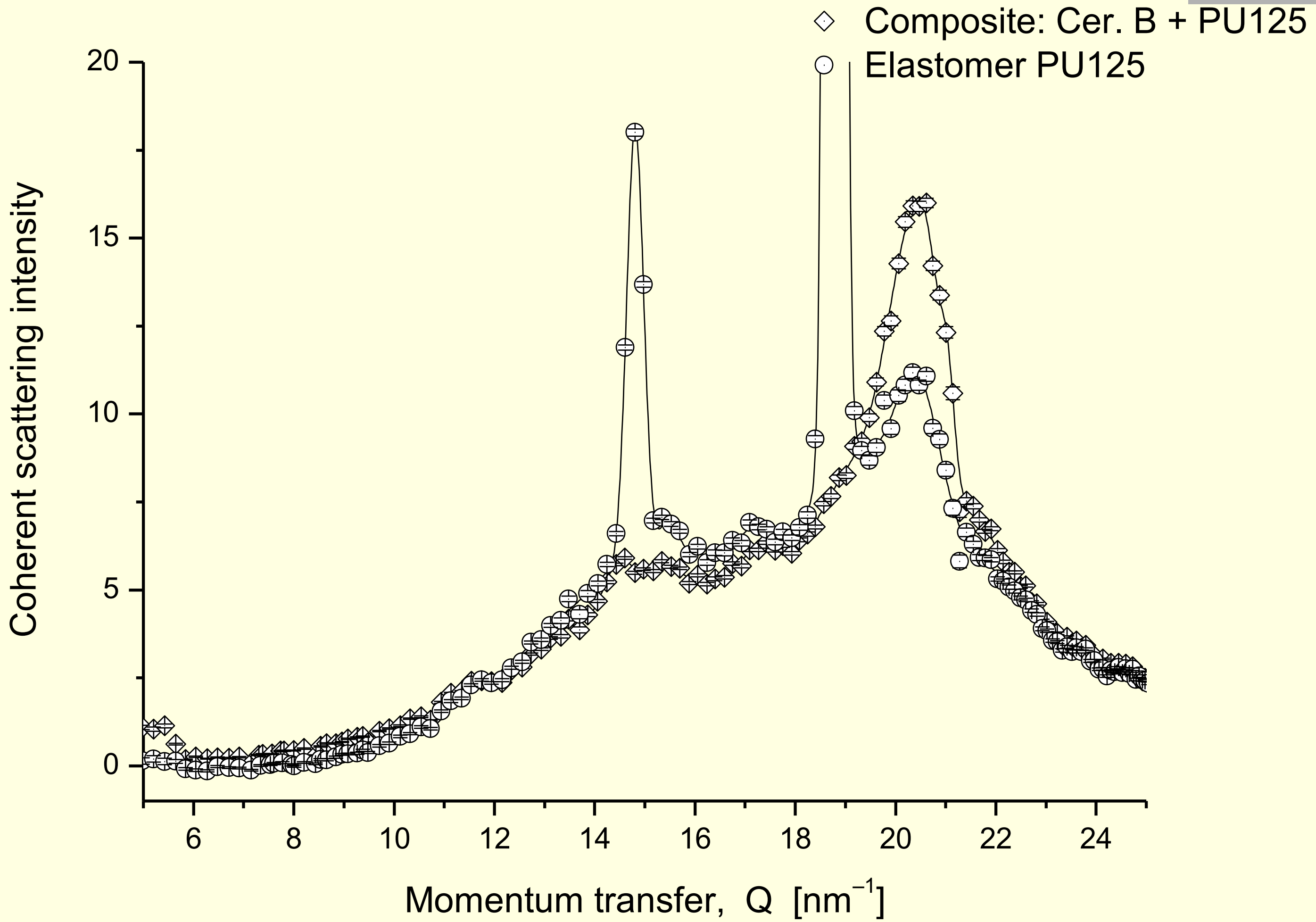
Scaled and 'zoomed' coherent neutron scattering spectra of type A composite and pure bulk elastomer PU25. Error bars are smaller than the point size.

Results - coherent neutron scattering spectra of a composite A & B and elastomer PU25



- 'Soft-segment' peak in both composites of type A and type B ceramics with the PU25 elastomer.
- Peak width corresponds to the correlation length.
- Broader peak means smaller correlation length inside smaller pores.

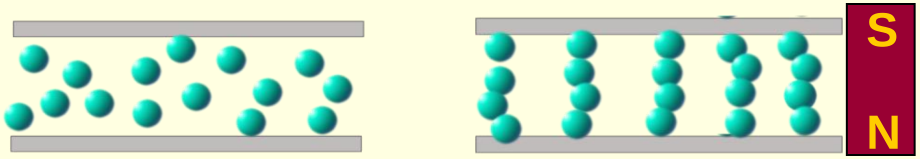
Results - coherent neutron scattering spectra of a composite B and elastomer PU125



No deformation in PU125 is visible. Large concentration of structured soft domains.

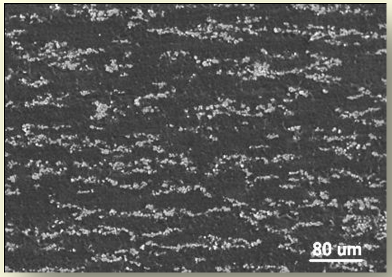
Magnetorheological elastomers (MRE) - indroduction

Composites of magnetically permeable particles in non-magnetic, viscoelastic polymers.

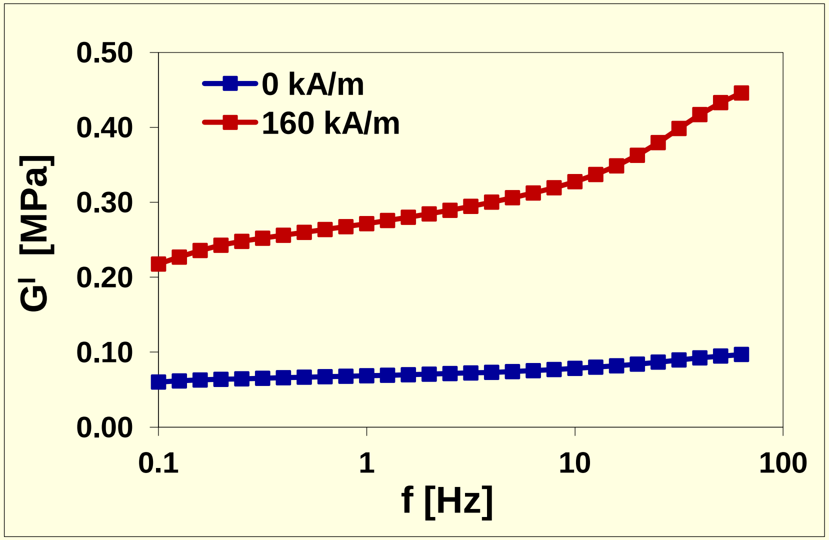


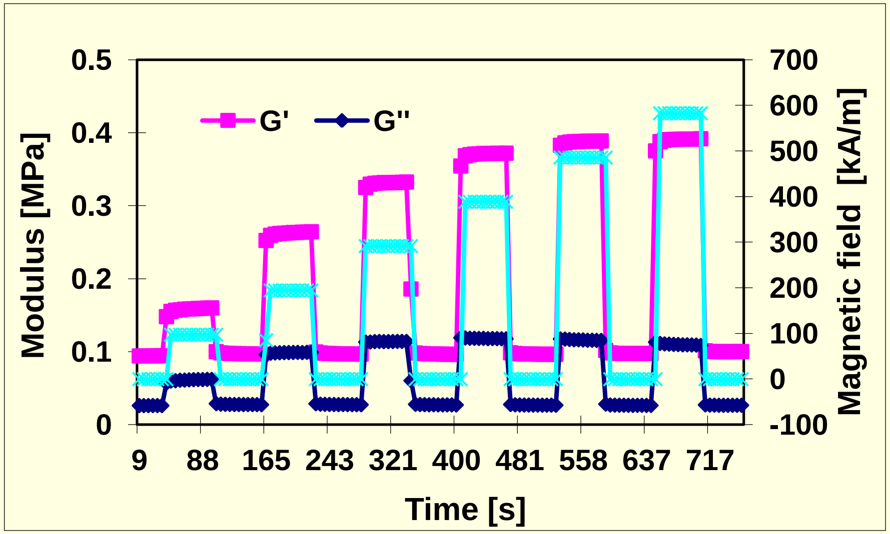
Before crosslinking After crosslinking

Magnetic field applied



They change their properties, shape and size continuously, rapidly and reversibly under the influence of an applied magnetic field.





Aim of the studies

- **To study the influence of various factors (composition, magnetic field strength, sample history) upon domain anisotropy in magnetorheological elastomers**.

- Experiment Title : **Reversible and irreversible effects of magnetic field upon hard-segmentdomains in magnetorheological elastomers** (proposal no. 1-04-78)

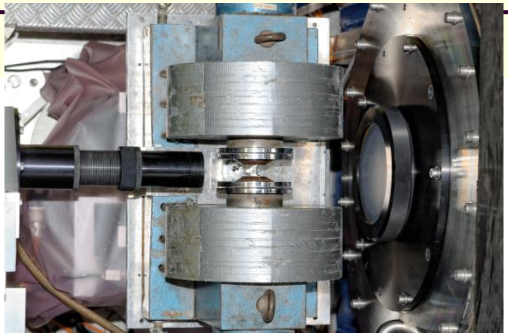
- Experiment place: D11 - ILL Grenoble (May 2013)

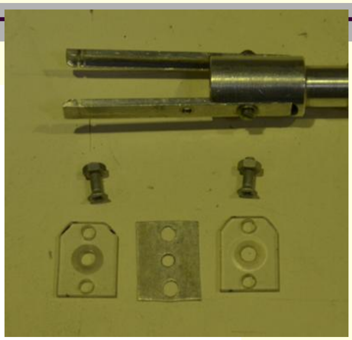
Materials used in this work

- Polyurethane (PU) - polyether polyols VORALUX® 14922 and HF 505 used in a blend with and isocyanate compound HB 6013 (weight ratio: 70:30:23 – **PU70/30** or 30:70:23 – **PU30/70**), supplied by Dow Chemical.
- Carbonyl-iron powder (CI) with the particle size 6-9 μm, supplied by Fluka.

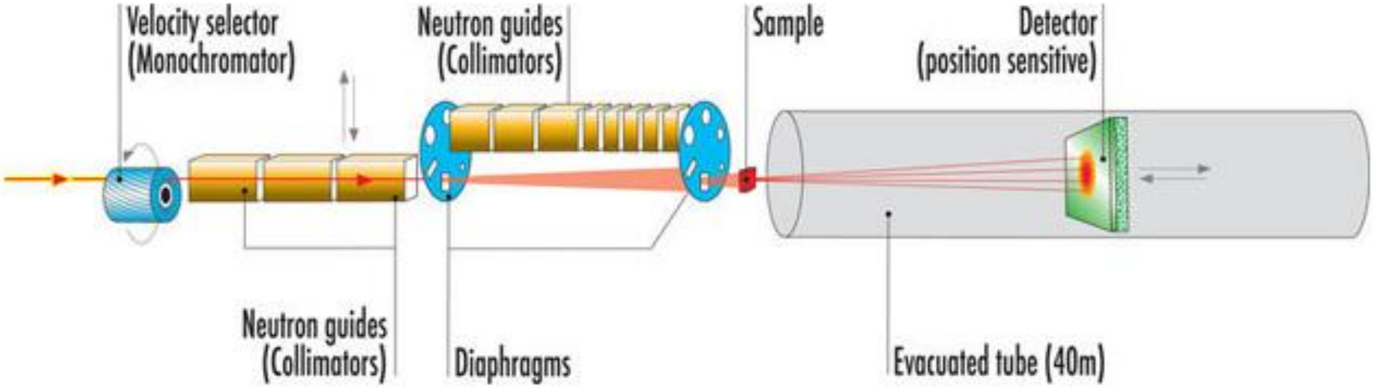
Matrix code	CI content [vol.%]	MF during curing [kA/m]	MF during test [kA/m]	No. of cycles under MF 240 kA/m
PU70/30	11.5	240	0/240	0
PU70/30	33	240	0/240	0
PU70/30	11.5	0	0/240	0
PU70/30	11.5	240	0/80/240/400	50
PU70/30	11.5	240	0/240	1000
PU30/70	11.5	240	0/240	0
PU30/70	33	240	0/240	0
PU30/70	11.5	240	0/80/240/400	50

D11 - small angle neutron scattering (SANS)





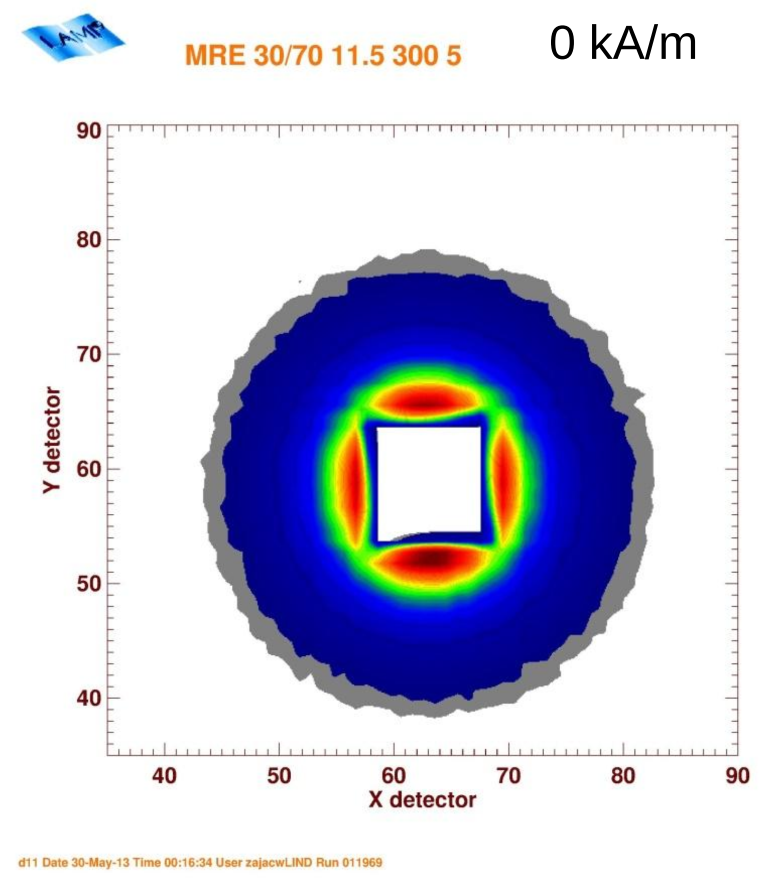
PMMA frame

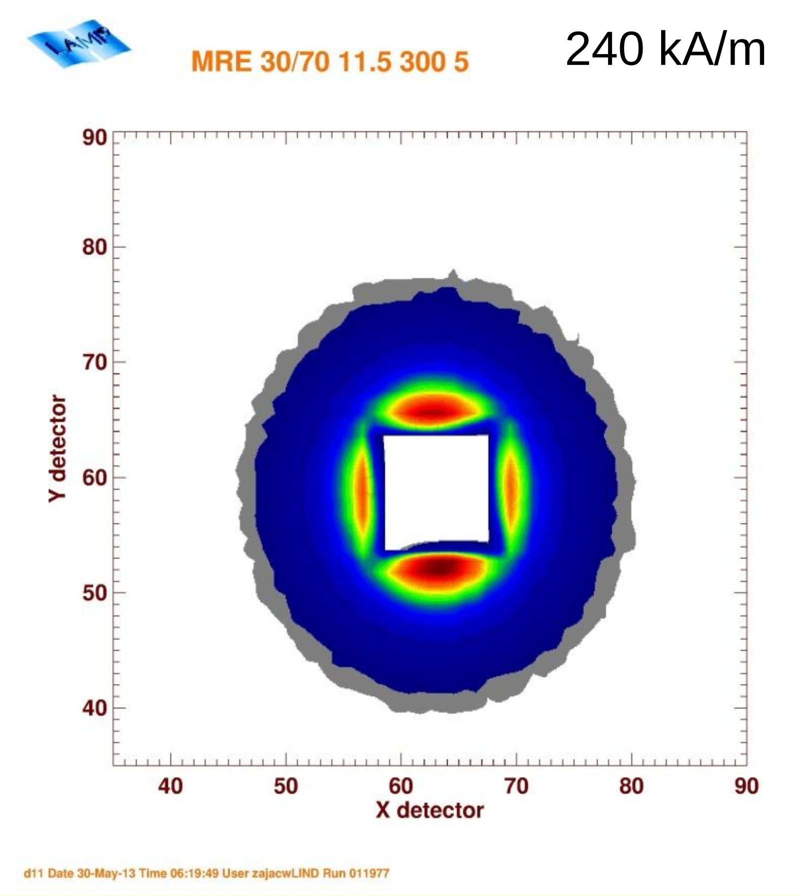


Lowest momentum transfer & lowest background small-angle neutron scattering instrument

Results – field dependence of domain anisotropy

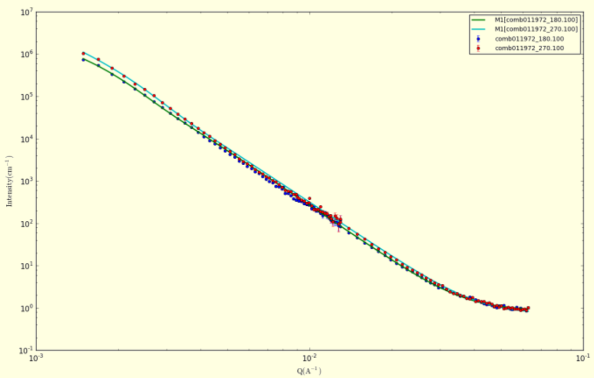
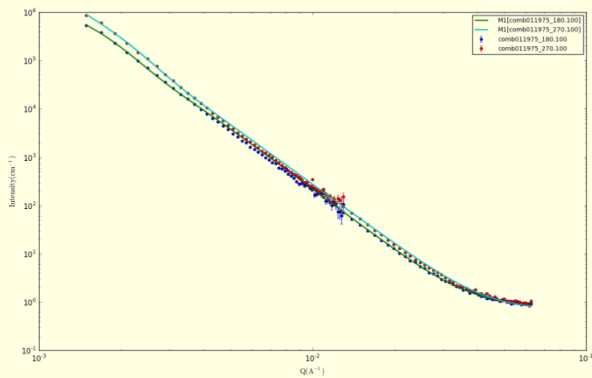
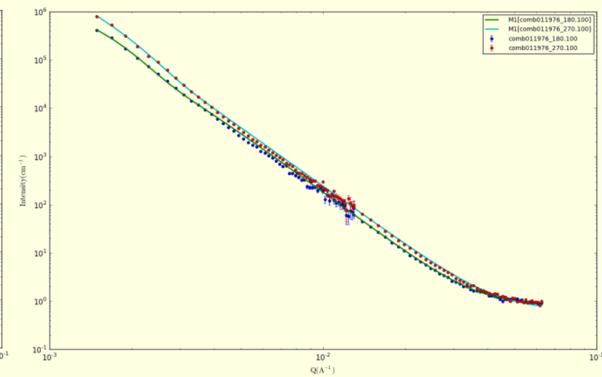
Field-induced (240 kA/m) anisotropic response of elastomer domain structure





Deformation of SANS image in MF – enhanced contrast

Results – field dependence of domain anisotropy

		
80 kA/m	240 kA/m	400 kA/m

Sample: PU30/70, 11.5vol% Fe, cured in field

colour coding: along field direction
perpendicular to field direction

Model adopted:
two characteristic length scales (a_1, a_2) as a concentrated polymer-in-gel suspension

$$I(Q) = I(0)_L \frac{1}{\left(1+\frac{D+1}{3}\cdot Q^2 a_1^2\right)^{D/2}} + I(0)_G \exp\left(-Q^2 a_2^2\right) + B$$

Conclusions

- Wide Angle Neutron Scattering (WANS) experiment with polarized neutrons made it possible to detect residual stresses in SiO2–PU25 ceramic-elastomer composite by measuring uniform deformation of polymer network through displacement of a coherent scattering line originating from the soft domains.
- In magnetorheological elastomers, apart from expected field dependence of domain anisotropy, an interesting effect was observed of enhanced SANS contrast of a sample in magnetic field. No significant effect of material „training" (1000 field-on/field-off cycles prior to experiment), except a very slight effect in PU30/70, 11.5vol% Fe, cured in field.

Thank you for attention