Effect of irradiation on functional properties of polymers for superconducting accelerator magnets

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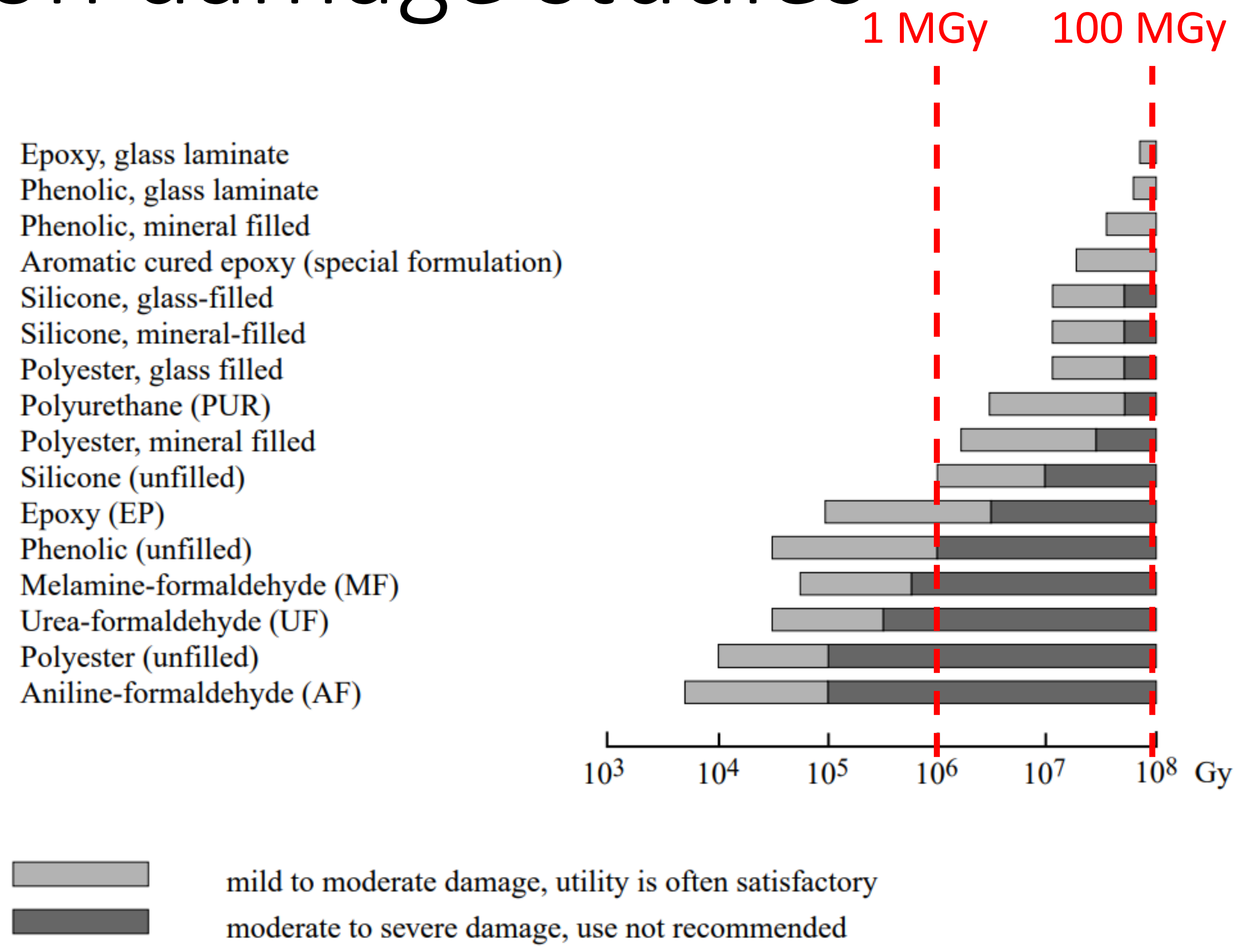
Outline

- Introduction
- Experimental
  - Irradiation sources
  - Sample characterisation
- Irradiation damage case studies
  I. Epoxy resins for coil impregnation
  II. POLAB Mix epoxy resin with improved fracture toughness at cryogenic temperature
  III. 3D printable resins
  IV. MCBC/MCBY magnet constituent materials
- Outlook

Previous polymer radiation damage studies

- Extensive radiation damage programs on magnet coil insulation and on cable insulation materials have been carried out at CERN for decades [1].
- The comprehensive compilations of polymer radiation damage data can serve for pre-selection of materials.

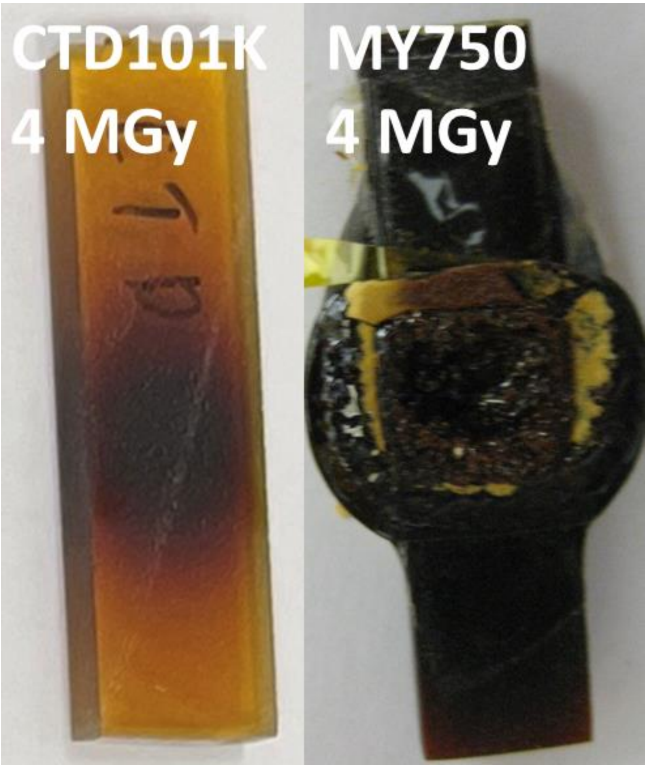


General classification of thermoset resins and composites with respect to their radiation resistance, from M. Tavlet, "Compilation of radiation damage Part 2, 2nd edition, Thermoset and thermoplastic resins, composites

[1] See for instance H. Schönbacher and M. Tavlet, Compilation of radiation damage test results, CERN 79–04, 79–08, 82– 10, 89–12 and 98–1, CERN, Geneva, 1979–1998.

Why a new study on polymer radiation damage?

- When proposing a new polymer for use in radiation environment its aging behaviour under relevant radiation conditions (e.g. cryogenic temperature, absence of oxygen) needs to be known.
- It is not sufficient to assume a typical aging behaviour of a class of materials.
- Even if the same epoxy resin is used, its additives and processing details can strongly influence aging rates.
- The effect of radiation on functional materials properties is rarely known.
  - Mechanical properties of composites under the relevant loading conditions
  - Dielectric properties
  - Thermal properties



Visual aspect of two epoxy resin systems after an absorbed dose of 4 MGy in air.

The polymerlab irradiation study

- We study the effect of ionising radiation on functional properties of polymers under irradiation conditions relevant for superconducting and resistive magnets.
  - Dose rates in the order of kGy/h
  - The predicted peak dose in HL-LHC inner triplet coils is 30 MGy, and magnets for future accelerator projects polymers will be exposed to doses up to 100 MGy.
  - Irradiation temperatures from liquid helium temperature to ambient.
- This study does not include the aging of cable insulation outside the magnets.
  - peak doses typically <1 MGy
  - comparatively low dose rates
  - different irradiation environments and aging stresses
  - different polymer types
  - different methods to assess radiation damage

Two stages of the polymerlab irradiation study for HFM

- 1st stage: Effect of different irradiation sources, irradiation atmosphere and irradiation temperature on polymers for accelerator magnet applications [2]
  - Irradiation sources: Gamma rays, protons, neutrons
  - Irradiation atmospheres: Air and inert gas
  - Irradiation temperatures: ambient and 4.2 K
- 2nd stage: Predict the changes of functional properties and the life-time of magnet coil insulation systems under relevant irradiation conditions

[2] "Characterization program (1st stage) of radiation resistance of impregnation resins as a function of environmental conditions", CERN Polymerlab report, EDMS No. 2563597, May 2022

Materials and components studied

The polymer irradiation program serves different projects:

- HFM study (candidate materials for coil impregnation and electrical insulation) [3]
- LHC Triplet Task Force (inner triplet magnet wedges and spacers, corrector magnet constituents, superconducting wire insulation, impregnated coil segments, fibre reinforced epoxy ground insulation) [4], [5], [6]
- HL-LHC (impregnation resin, instrumentation wire insulation, quench heater insulation)
- PS Booster (candidate impregnation resins)
- Other structural polymers including 3D printed materials
- Polyurethanes, e.g. candidate materials in jacks for magnet alignment

[3] D.M. Parragh et al, "Irradiation induced aging of epoxy resins for impregnation of superconducting magnet coils", IEEE Trans. Appl. Supercond., accepted, https://ieeexplore.ieee.org/document/10319395
[4] G. Arduini et al, LHC Triplet Task Force Report, CERN, November 2023, https://cds.cern.ch/record/2882512
[5] C. Scheuerlein, "Irradiation study of MCBC and MCBY LHC corrector magnet polymer constituents", EDMS No. 2861509, March 2023 (https://edms.cern.ch/document/2861509/1)
[6] D.M. Parragh, "Effect of gamma irradiation on the thermomechanical properties of MCBY corrector magnet constituent material ISOPREG 2704," CERN, Polymerlab report EDMS No. 2816963, February 2023. (https://edms.cern.ch/document/2816963/1)

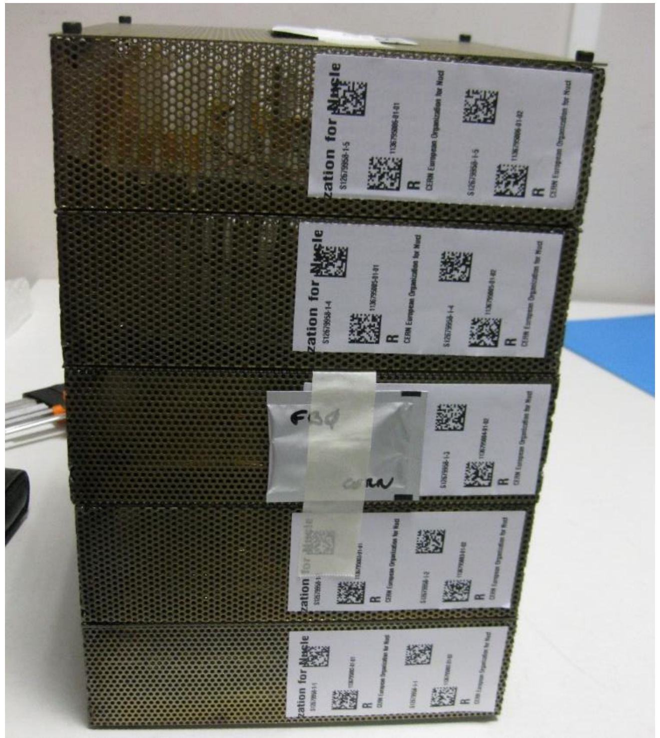
Irradiation sources

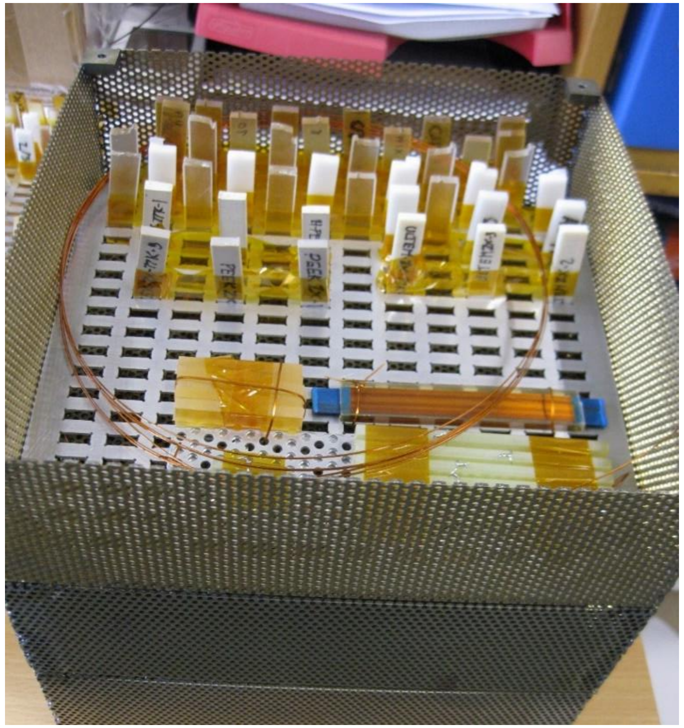
Irradiation sources and environments

- Proton irradiation at CERN IRRAD
  - at 20 °C in ambient air
  - at 20 °C in inert gas
  - at -20 °C in dry air
  - in liquid helium
- Gamma irradiation at Steris Marcoule
  - in ambient air
- Neutron irradiation at Triga Mark II reactor of ATI Vienna
  - in ambient air
  - in vacuum at ambient temperature
- Neutron irradiation at nTOF NEAR
  - in ambient air

Gamma irradiation in ambient air

- Gamma rays (^{60}Co source) at the Gammatec facility at the Marcoule site of the company STERIS.
- **Samples are not activated.**
- Dose rate 2 to 3 kGy/h.
- **Large sample volume** 200 × 200 × 300 mm^3.
- Smaller sample holders can be withdrawn at intermediate dose levels.
- **Precise dosimetry** with Perspex dosimeters at different positions outside and inside the sample holder.
- Sample holders rotate during irradiation for achieving best possible **dose homogeneity**.
- Irradiation in ambient air, temperature is controlled <25°C.

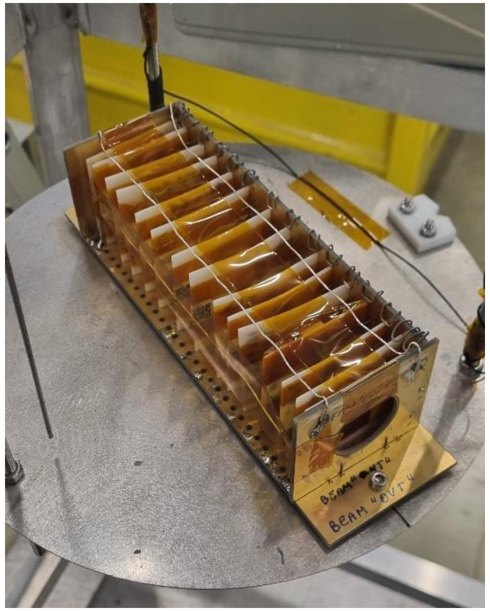




Five sample holders 200 mm x 200 mm x 60 mm, stacked onto each other. Four Perspex dosimeters are attached at different locations outside and inside the sample holders.

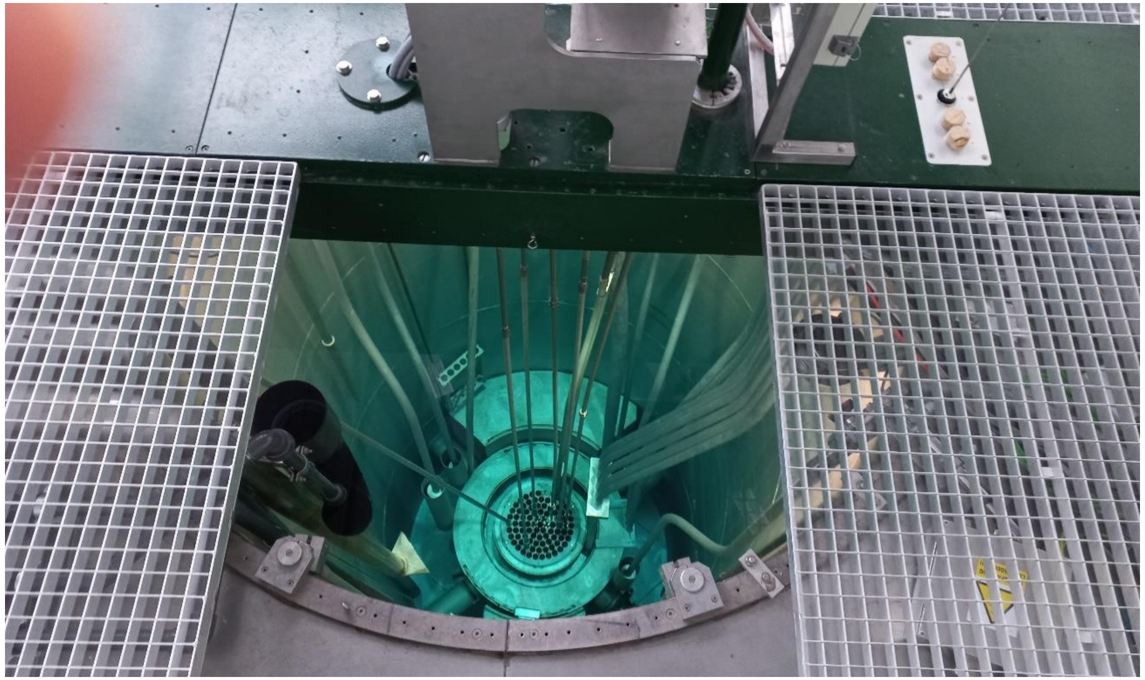
24 GeV proton irradiation in liquid helium

- Irradiations possible thanks to G. Pezzullo, F. Ravotti and IRRAD team, and T. Köttig and CERN cryolab team.
- Two sets of 13 identical samples are irradiated simultaneously
  - Inside the cryostat immersed in liquid helium
  - Outside the cryostat in ambient air
- A proton fluence of about 10^{16} p/cm^2 is accumulated over typically 2 weeks of irradiation, which corresponds with about 3 MGy.

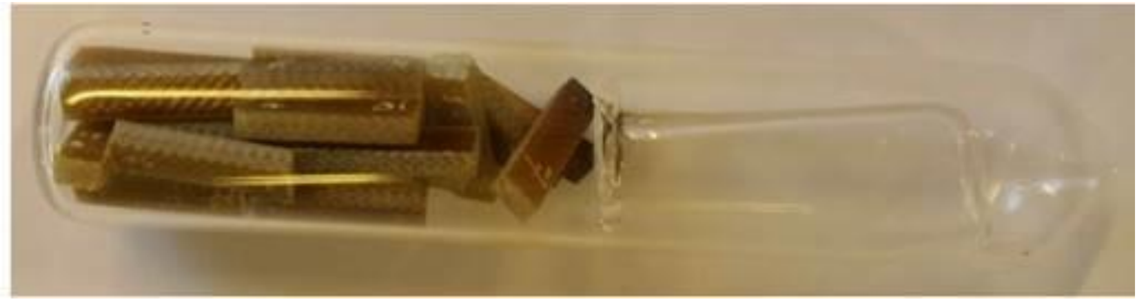


Neutron irradiation at the TRIGA Mark II nuclear reactor of TU Vienna

- Radiation dose results from mixed neutron and gamma radiation.
- Fast neutron fluence of 1×10^{21} m^{-2} (E>0.1MeV)
- In a first step, combined neutron and gamma dose levels of 1 MGy, 3 MGy and 10 MGy have been achieved.
- Before irradiation the samples are sealed in quartz glass capsules to prevent direct contact with the reactor water.
- Capsules are filled either with ambient air or with inert gas, and then sealed before irradiation starts.
- For **outgassing measurements** samples are irradiated under vacuum.
- **Very high dose rates can be achieved.**



TRIGA Mark II reactor core.

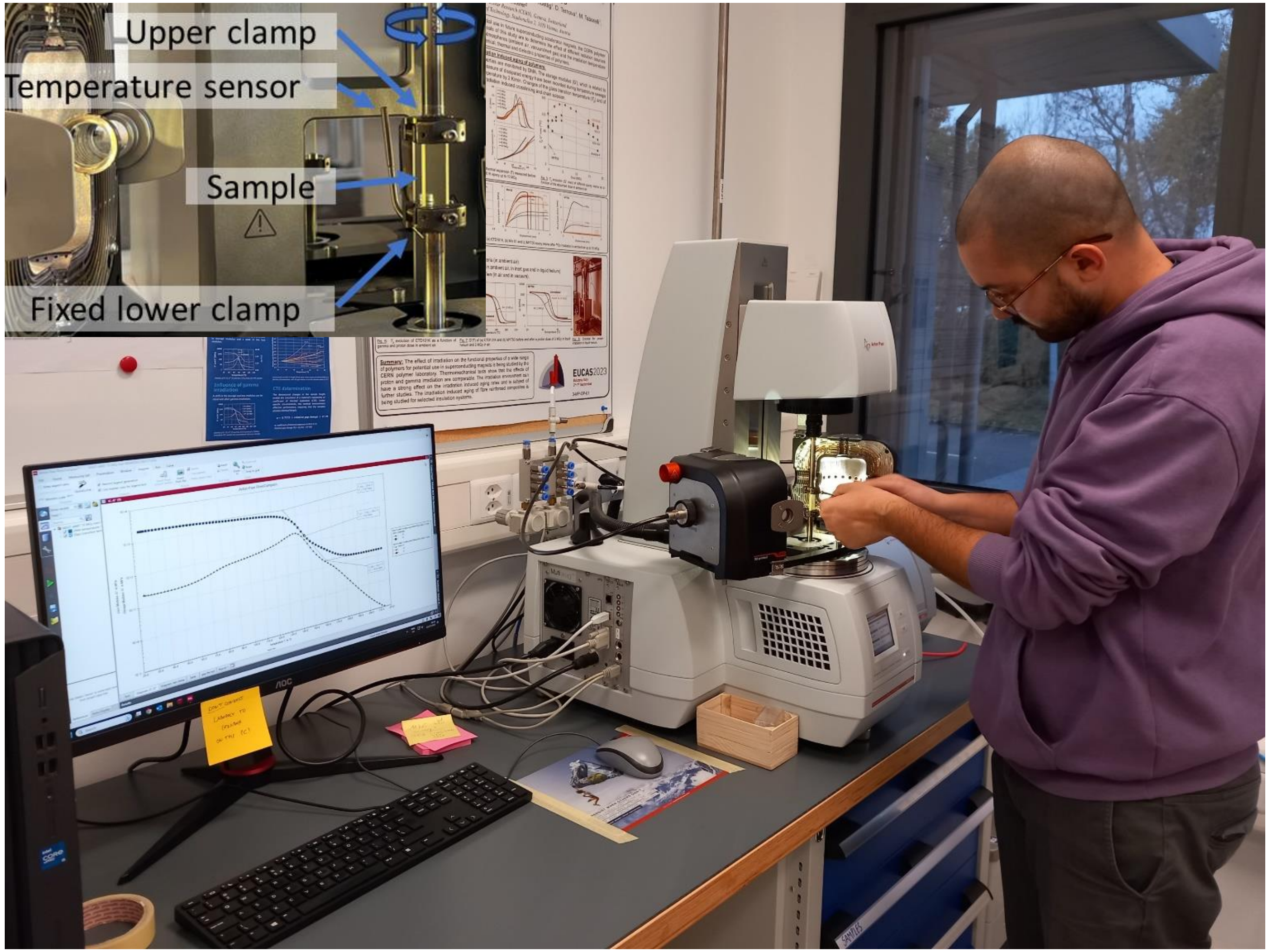


Sealed irradiation capsule with samples for mechanical tests.

Materials characterisation methods

Rheometer for Dynamic Mechanical Analysis (DMA)

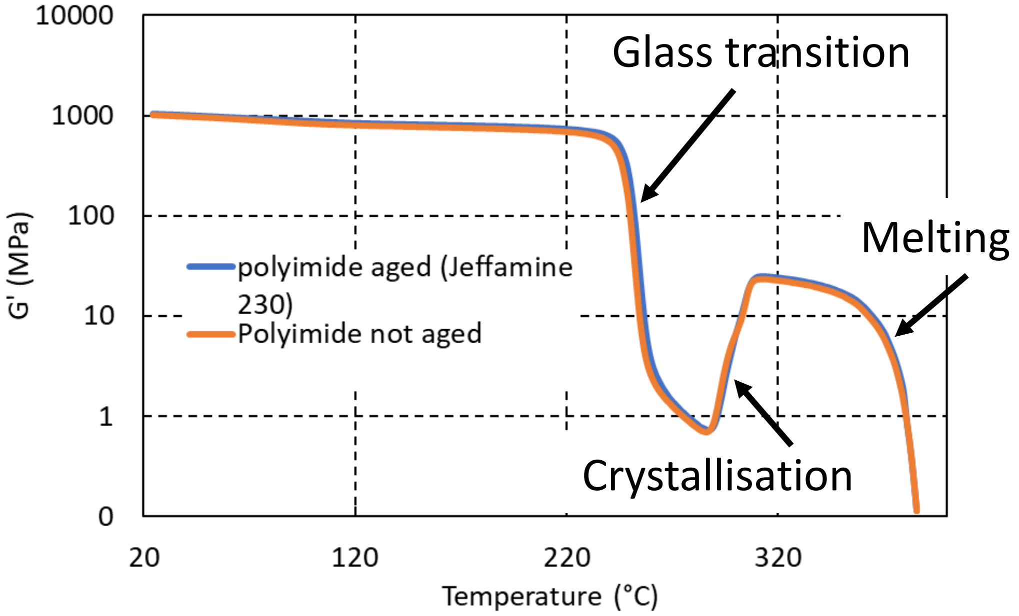
- DMA measures **viscoelastic materials properties** of the solid resin.
- In torsion mode, DMA measures the response to an applied torque, probing the sample shear properties.
- The storage modulus (G’) is related to sample stiffness, and the loss modulus (G’’) measures the dissipated energy (viscous portion).
- Temperature sweep: Measure G’ and G’’ as a function of temperature.
- Test parameters for irradiation study:
  - Frequency 1 Hz
  - Temperature ramp 2K/min
  - Sample dimensions 4×10×40 mm^3

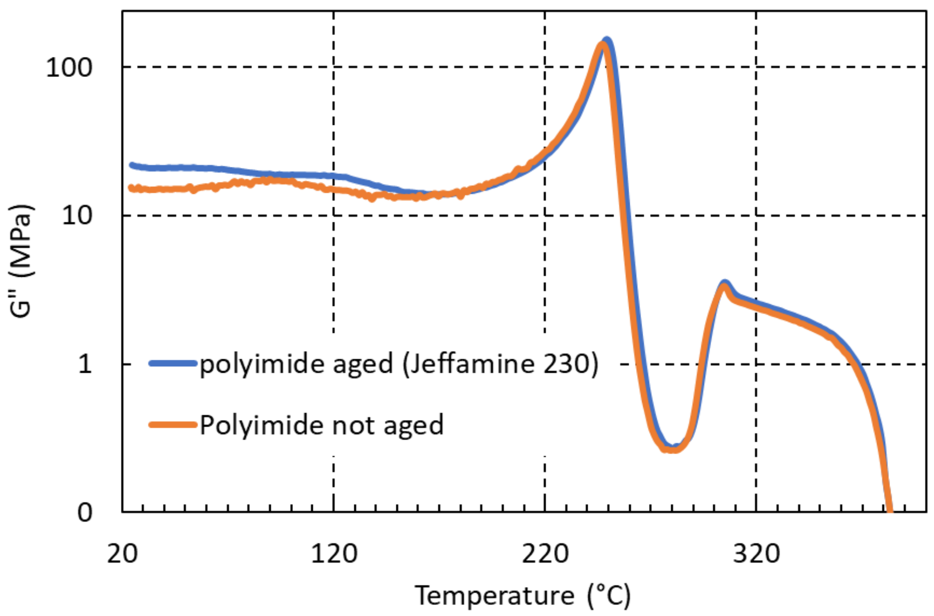


Anton Paar MCR702e rheomter set-up for DMA in torsion mode.

Sensitivity and repeatability of DMA tests

- DMA is highly sensitive to temperature and frequency changes.
- Exceeding the glass transition of polymers typically causes a G’ drop by about 3 orders of magnitude.
- G’ (T) and G’’(T) represent average sample properties and can have very good repeatability.

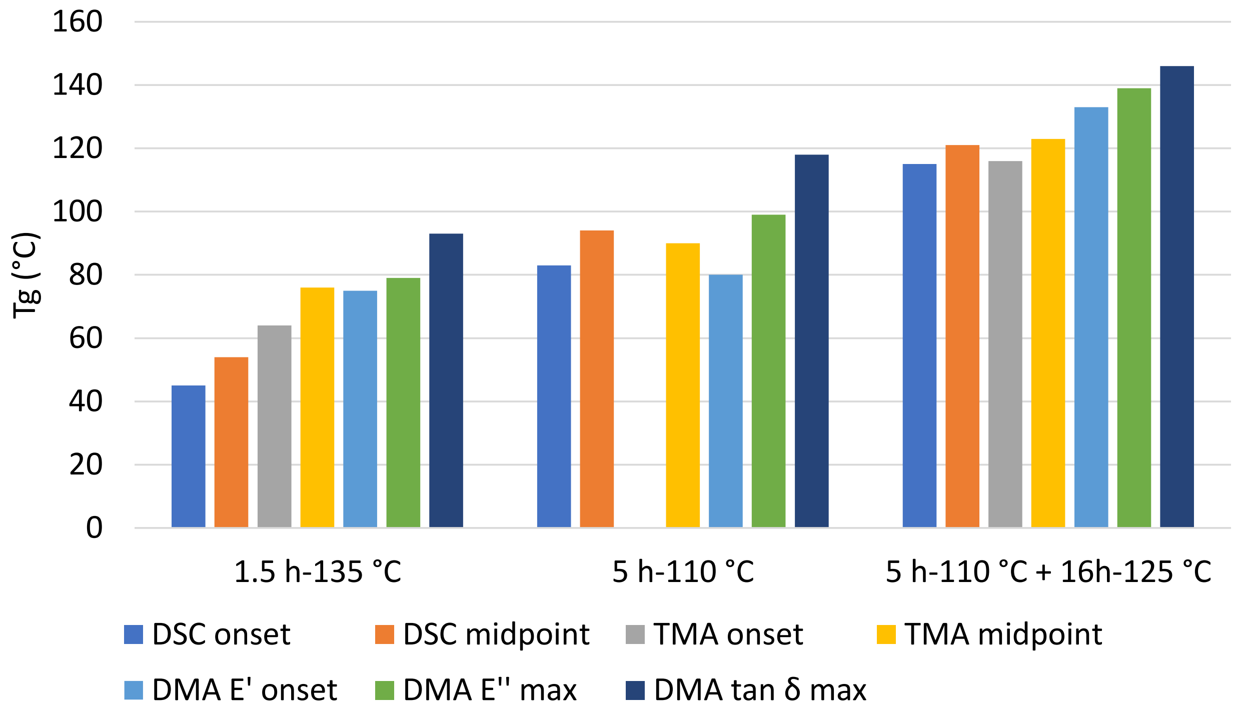




DMA temperature sweeps G’(T) and G’’(T) of two extruded polyimide samples.

Glass transition temperature derived by DMA, DSC and TMA

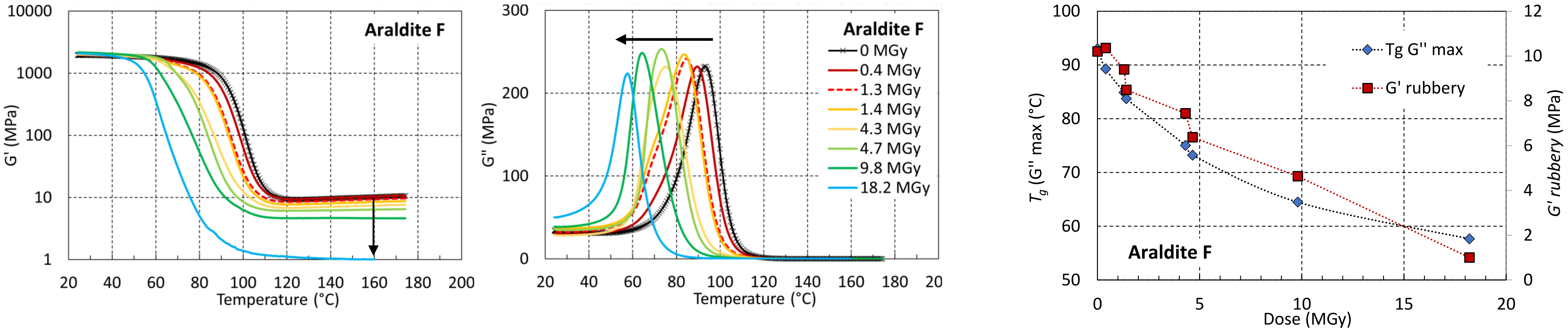
- The glass transition temperature (T_g) is the temperature at which an amorphous polymer changes from a glassy to a rubbery state.
- T_g can be determined by different methods:
  - DMA measures the reduction of storage modulus (G’) and the loss modulus (G”) peak.
  - DSC detects the change of heat capacity.
  - TMA detects the change of thermal expansion.
- The determined temperature value depends on the method used to measure T_g.
- The glass transition can be very broad (e.g. the Mix 61 epoxy system G’ onset is at -38 °C, and tan δ max is at 73 °C).



T_g values obtained by different methods for CTD101K after different curing heat cycles.

DMA for monitoring radiation effects

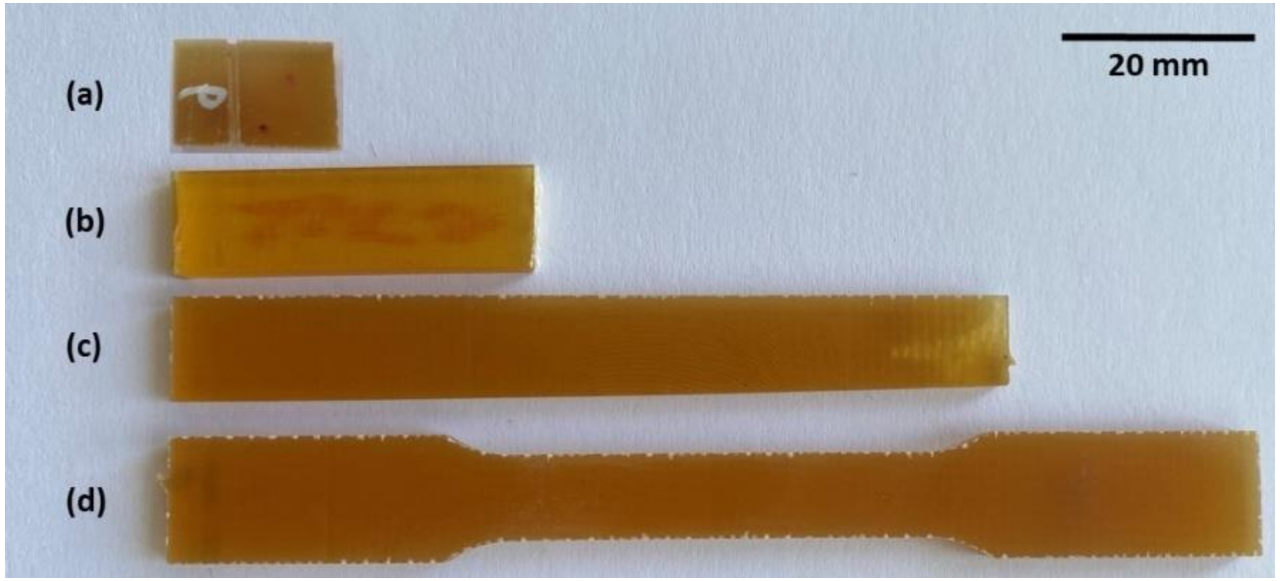
- Irradiation effects like formation of new cross links and chain scission influence the viscoelastic properties, and thus the storage and loss moduli.
- T_g vs dose evolutions allow to compare aging rates. Increasing T_g indicates that formation of new cross links prevails, decreasing T_g that chain scission rate dominates.
- The storage modulus in the rubbery state (above T_g) depends on the molecular weight between cross links.



Araldite F storage modulus G' (T) and loss modulus (G'' (T) evolutions after different proton doses absorbed in ambient air. Chain scission reduces T_g and the rubbery modulus.

Mechanical testing of irradiated samples

- Destructive testing in the polymerlab is only done with non-radioactive samples (after gamma irradiation).
- Irradiation volume is limited, therefore volume and number of samples is limited too.
- Static loading tests mainly in short beam configuration because of the smaller sample size.
- Impact tests in the Dnystat configuration because of the comparatively small sample size.



Sample used for (a) Dynstat notched impact tests, (b) short-beam bending tests, (c) three-point bending flexural tests and (d) uni-axial tensile tests.

Case study I

Radiation damage of epoxy resins for impregnation of superconducting magnet coils (HFM program 1st stage)

Driving question:

- Effect of different irradiation sources,
- effect of irradiation atmosphere,
- effect of irradiation temperature on polymers for accelerator magnet applications

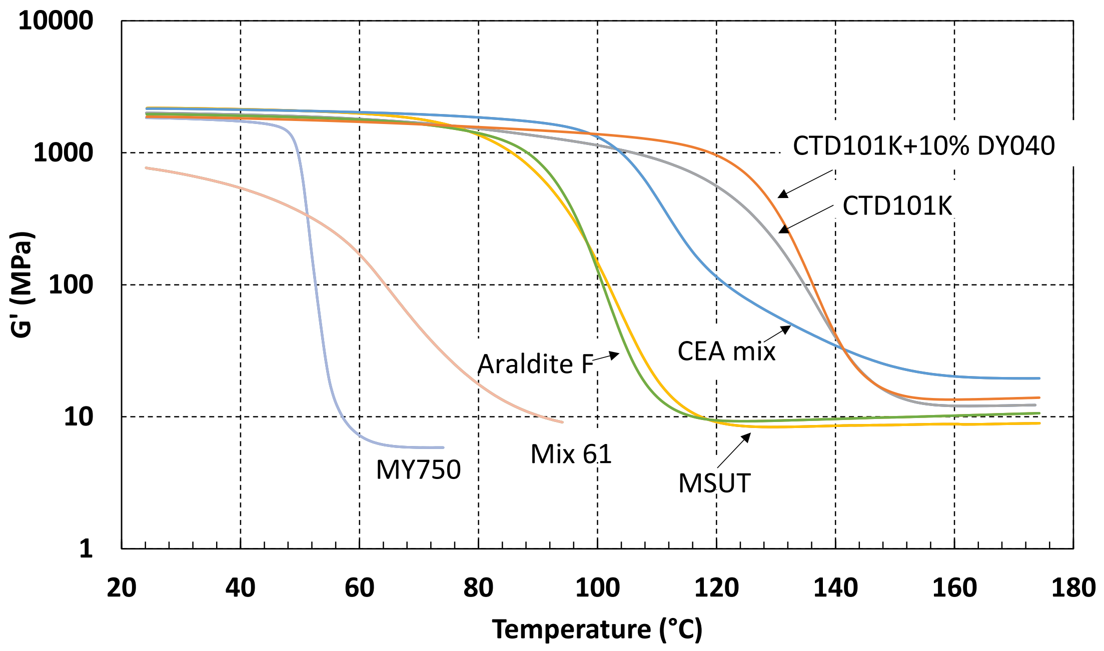
Epoxy resin systems studied

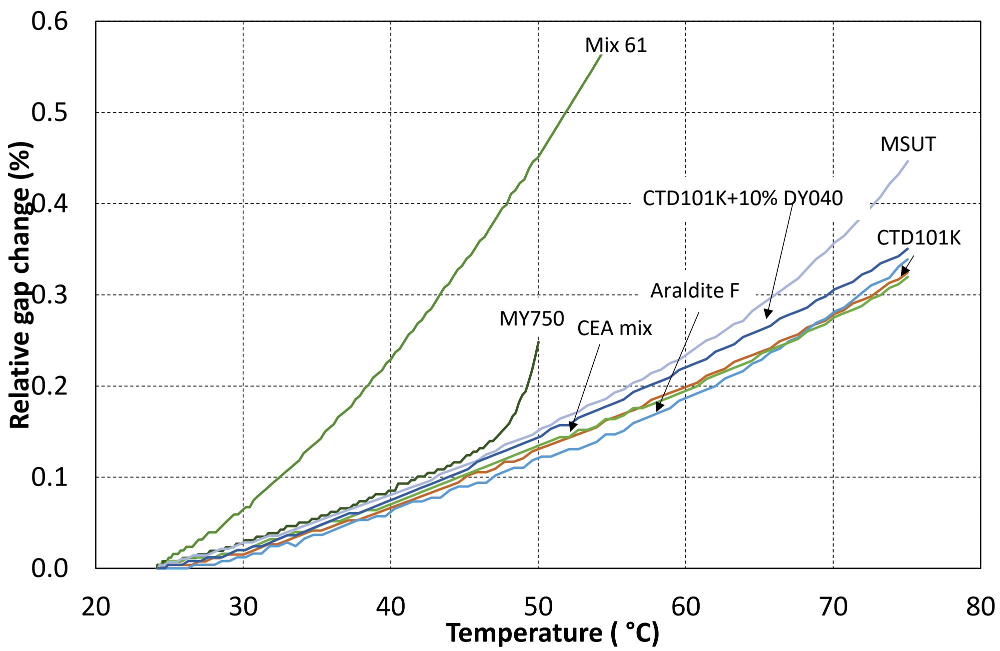
- Irradiation behaviour of epoxy resin systems can be affected by addition of constituents like hardeners, composition and the degree of conversion.
- We study commercially available and widely used epoxy resin systems with curing cycles optimised to achieve highest possible conversion, and epoxy resin systems that are used for superconducting magnet coil impregnation with the processing parameters used by the magnet builders.

1) **CTD101K:** baseline impregnation system for the HL-LHC superconducting magnets, consists of diglycidyl ether of bisphenol-A (DGEBA), a carboxylic anhydride hardener, and an accelerator, all of which are supplied by Composite Technology Development Inc. (U.S.A.). These components are mixed in the proportion CTD101K resin : hardener : accelerator = 100 parts by weight (pbw): 90 pbw : 1.5 pbw. The curing temperature cycle comprises two plateaus 5 h-110 °C and 16 h-125 °C post-curing.
2) **MSUT:** Consists of the Araldite MY740 bisphenol A / epichlorohydrin resin (type DGEBA, Mw < 700 g/mol), cured with the carboxylic anhydride hardener of mixed composition Aradur HY906, and the amine accelerator DY062 in the respective ratio 100 pbw: 90 pbw: 0.2 pbw. The curing temperature cycle comprises two plateaus 4 h-85 °C and 16 h-110 °C post-curing.
3) **MY750:** Composed of the Araldite MY750 bisphenol A / epichlorohydrin resin, type DGEBA, Mw < 700 g/mol (100 pbw) and the aliphatic polyamine hardener Aradur HY5922 (55 pbw) from Huntsman Corporation. The curing temperature cycle comprises two plateaus 6 h-40 °C and 3 h-80 °C post curing.
4) **Mix61:** Composed of a diglycidyl ether of bisphenol-A (DGEBA) resin, an aromatic hardener of the amine type, a high molecular weight co-reactant of the amine type and a liquid low molecular weight additive. The curing temperature cycle comprises two plateaus 16 h-60 °C and 24 h-100 °C post curing.
5) **CEA mix:** Two-component resin system Huntsman Araldite® CY192-1, a cycloaliphatic epoxy resin (100 pbw), and its corresponding anhydride type hardener, Huntsman Aradur® HY 918-1 (100 pbw), has been used by CEA Saclay for the impregnation of Nb3Sn quadrupole coils. The applied curing cycle recommended by CEA Saclay comprises three isothermal plateaus as follows: 80 °C-24 h, 120 °C-34 h+ 130 °C-12 h.
6) **Araldite F:** used by the company ASG Superconductors S.p.A. for impregnation of magnet coils and consists of the bisphenol A / epichlorohydrin resin (type DGEBA) Araldite F, the carboxylic anhydride hardener Aradur HY 905, and the polyglycol flexibilizer DY 040. The resin, hardener, and flexibilizer are combined in the ratio of 100 pbw : 100 pbw : 10 pbw, respectively. The Araldite F/Aradur HY 905/flexibilizer DY 040 system does not contain the accelerator DY 061, and filler that is recommended by Huntsman. The applied curing cycle comprises two plateaus 100 °C-10h+ 135 °C-48 h.
7) **POLAB Mix:** CERN Polymerlab development. Araldite DY040 is a solvent-free and low-viscous hot-curing flexibiliser liquid used for medium- or high-voltage insulators. POLAB Mix is produced with 10 wt.% DY040 relative to CTD101K epoxy resin. First the CTD101K epoxy resin and hardener are mixed and degassed, and then DY040 is added. This mix is again degassed before the accelerator is added, and a final degassing is executed. The curing temperature cycle comprises two plateaus 5 h-110 °C and 16 h-125 °C post-curing.

T_g and thermal expansion of epoxy resins

- T_g determines the usable temperature range:
  - Structural material usable temperature < T_g
  - Rubber usable temperature > T_g
- Below T_g thermal expansion coefficients of unfilled polymers are similar.
- When T_g is exceeded thermal expansion coefficients increase strongly.

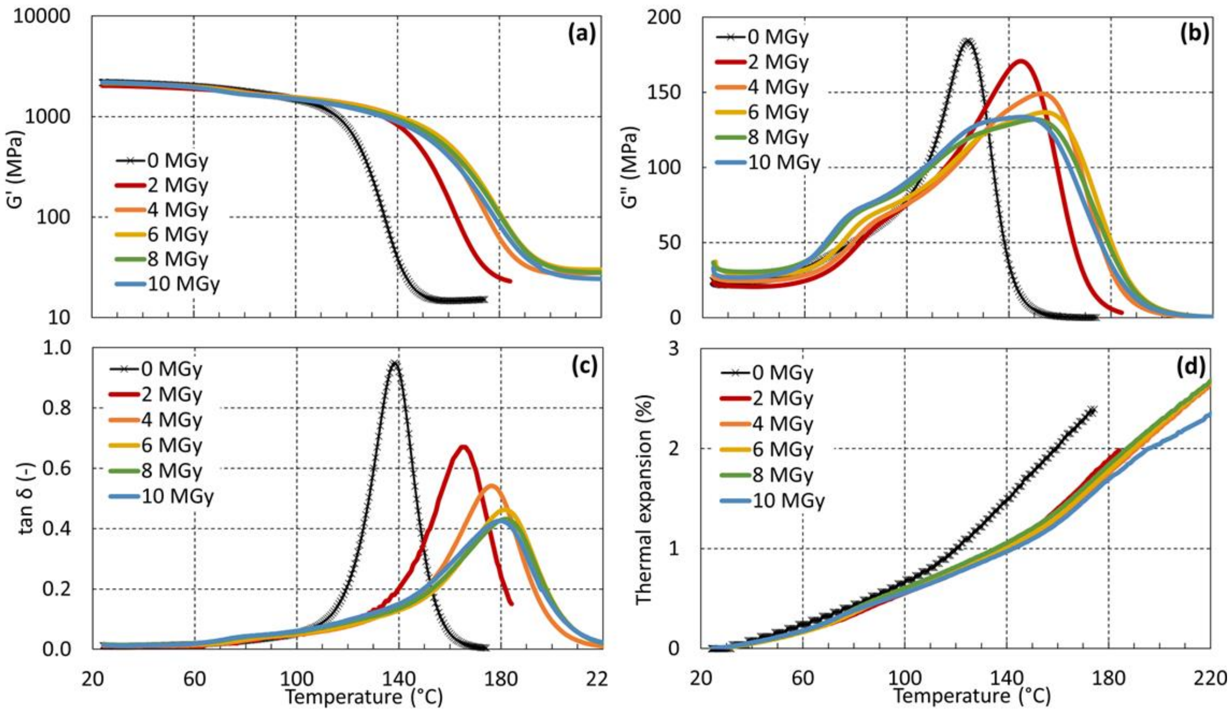


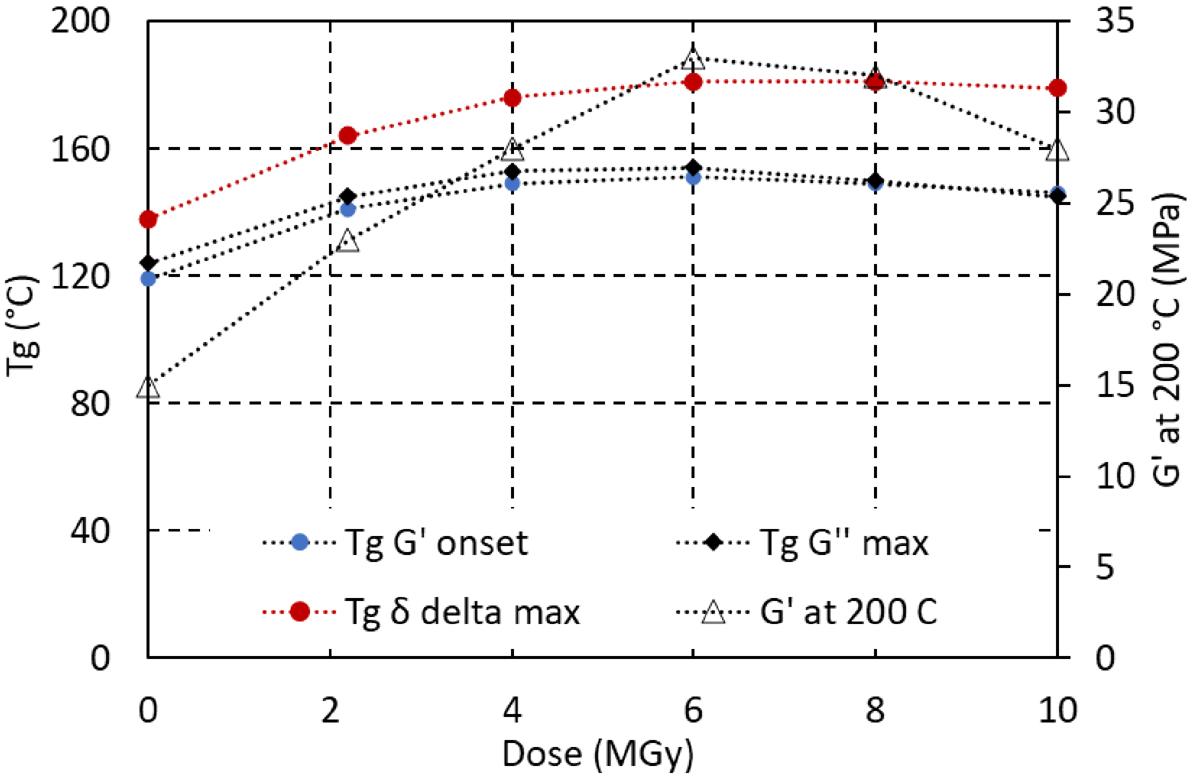


Comparison of (a) the storage modulus G' (T) and (b) thermal expansion evolutions of the non-irradiated epoxy resins of the present study. ***Courtesy N. Martin , EDMS No. 2906914.***

Cross-linking and chain scission in CTD101K

- Increasing T_g of CTD101K indicates that up to 6 MGy formation of new cross links prevails.
- At higher doses, the chain scission rate starts to dominate and T_g decreases.

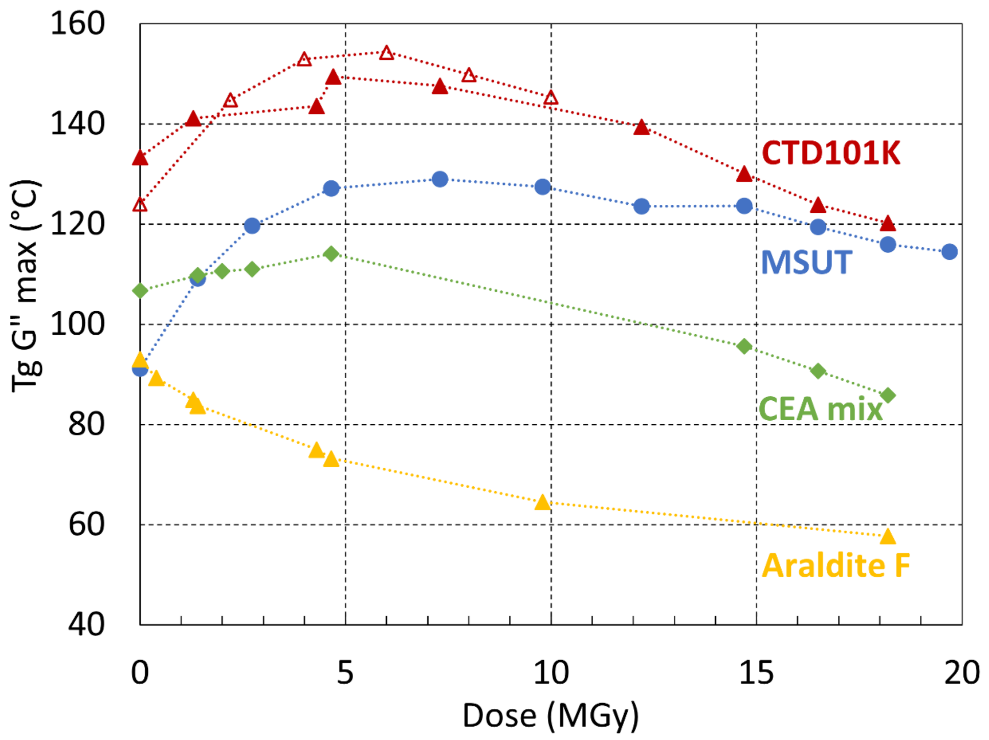


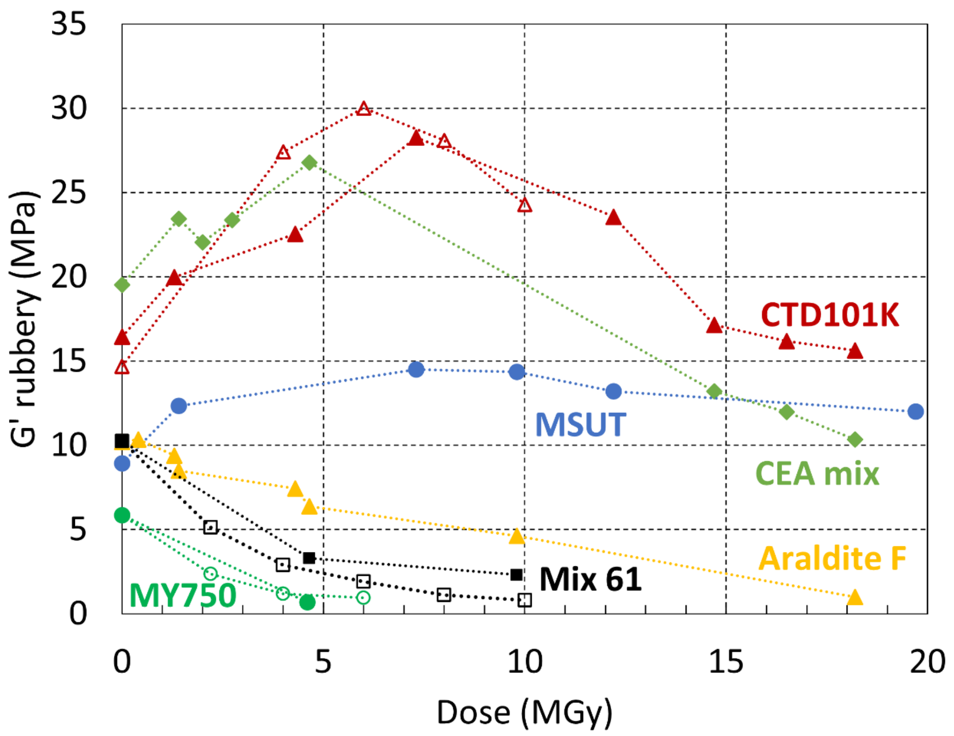


DMA temperature sweeps of CTD101K epoxy resin system after different gamma irradiation doses in ambient air
[https://ieeexplore.ieee.org/document/10319395/]

Effect of irradiation dose in ambient air

- MSUT and CTD101K chain scission rates are comparatively low
- Fastest degradation is observed for Mix 61 and MY750
- Gamma rays and 24 GeV protons have similar effect

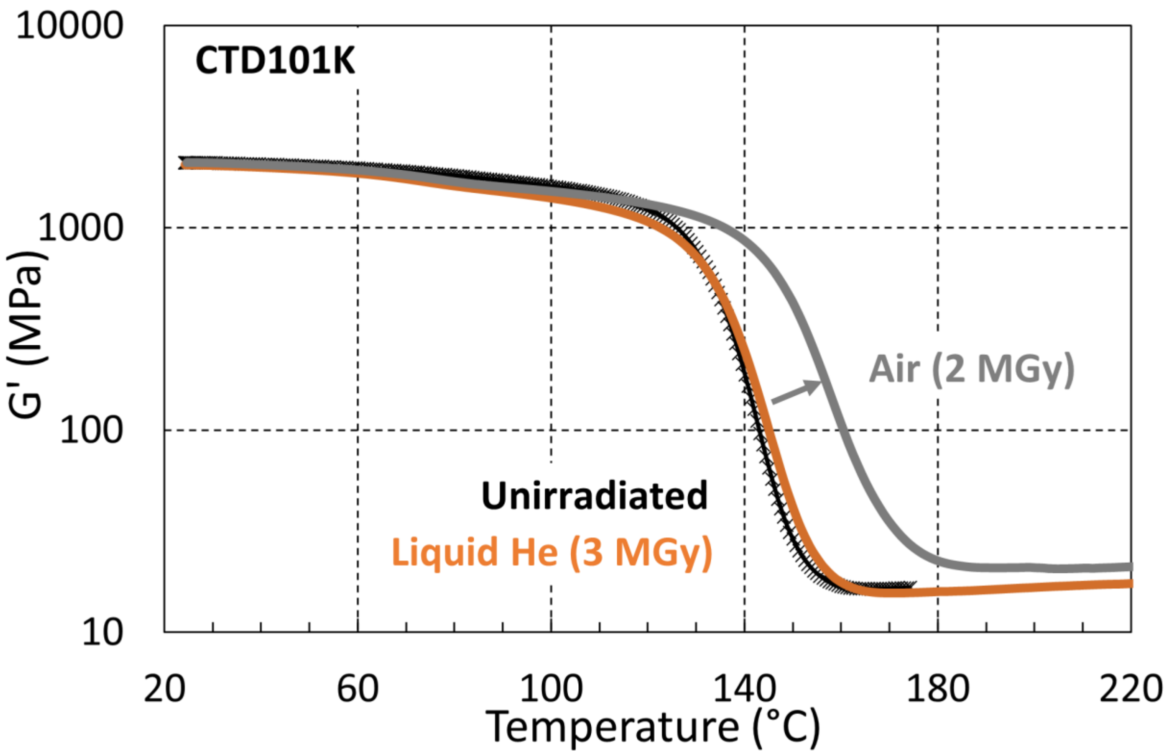




T_g G'' max and (b) $G'_{rubbery}$ as a function of absorbed dose in ambient air (^{60}Co gamma open symbols or 24 GeV proton full symbols).

Irradiation in liquid helium

- To reproduce irradiation conditions in superconducting magnets, at IRRAD samples have been irradiated in liquid helium.
- Identical samples have been irradiated simultaneously in ambient air behind the cryostat.

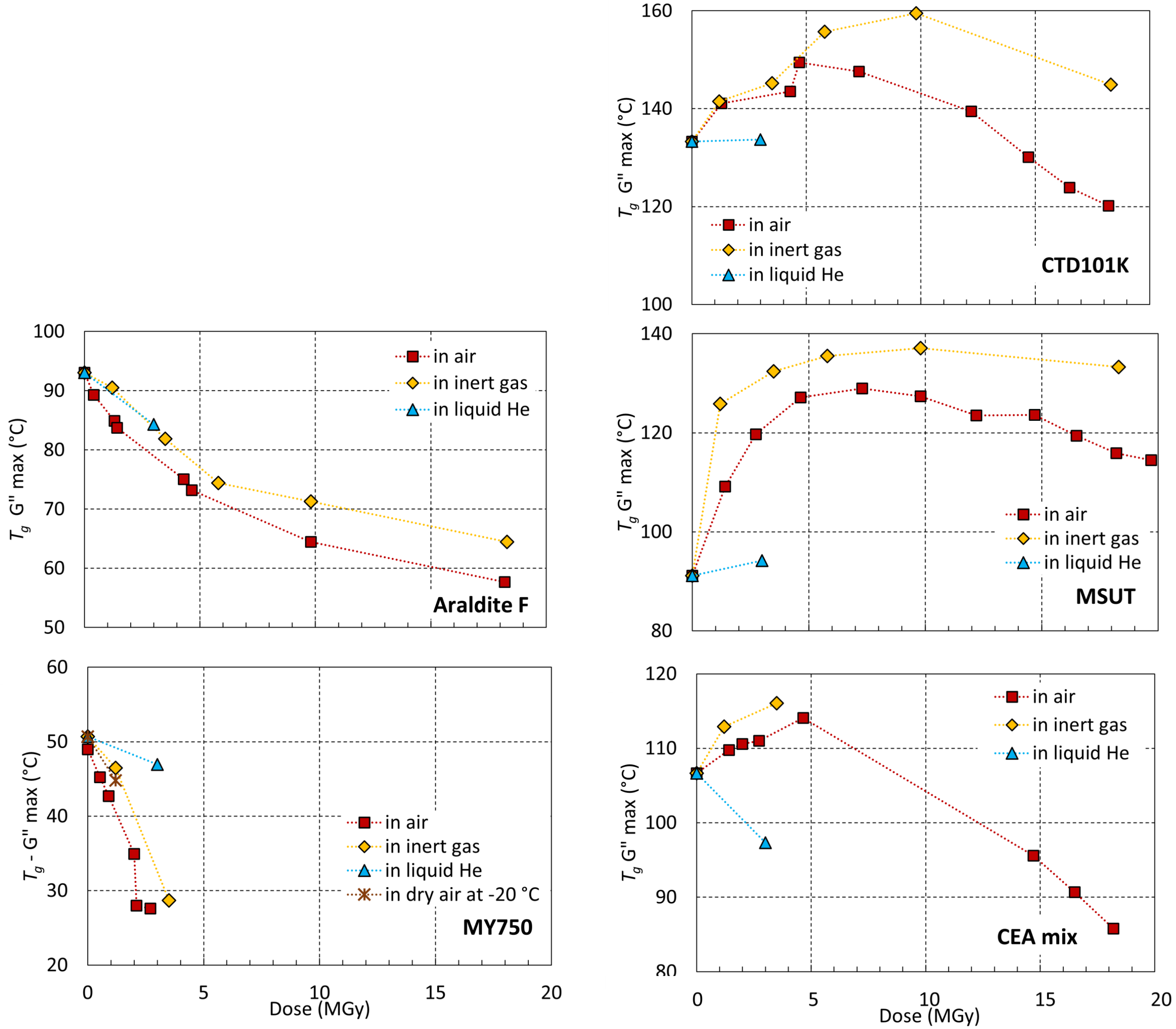


G'(T) of CTD101K before and after proton irradiation in liquid He and in air to about 3 MGy.

Cryostat for proton irradiation in liquid helium

Influence of the irradiation environment

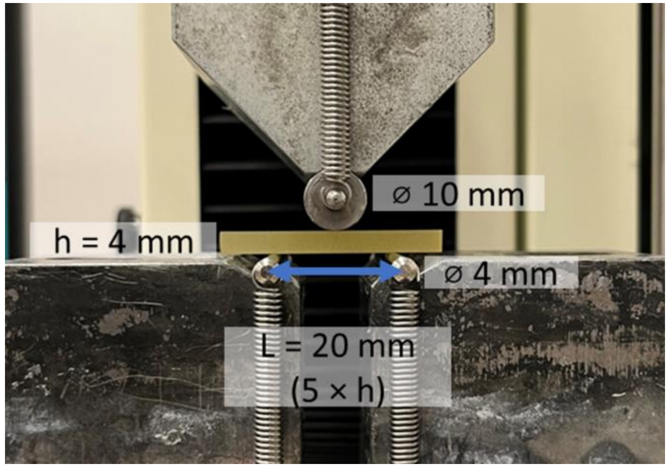
- The presence of oxygen reduces the cross-linking rate.
- Oxygen diffuses into the polymer and reacts with radicals formed by the irradiation, thus preventing their reaction with other molecular chains.
- **Temperature has a strong effect on cross linking rates.** For all epoxies studied, except AralditeF, at cryogenic temperature cross-linking is strongly reduced.
- At least for MY750 there is also a **strong temperature effect on chain scission rates**.



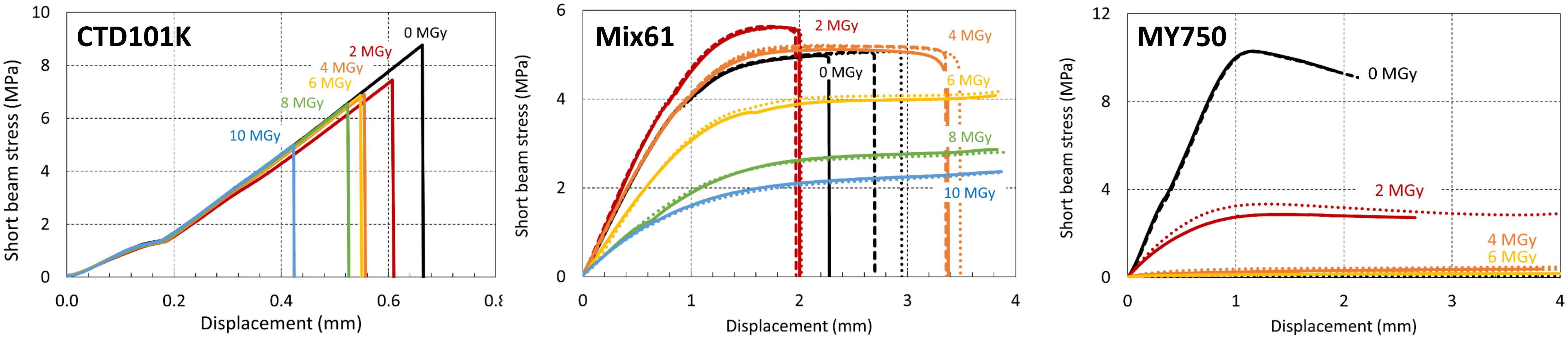
T_g G''_{max} as a function of proton dose absorbed in ambient air, inert gas and in liquid He.

Short beam strength vs dose

- CTD101 – linear elastic behavior; mechanical strength decreases with increasing dose
- Mix61 - initial irradiation induced increase of modulus and strength, above 2 MGy mechanical strength decrease with increasing dose.
- MY750 - drastic reduction of mechanical strength already after 2 MGy. After 4 MGy MY750 cannot transmit substantial loads



3-point bending short beam test configuration.

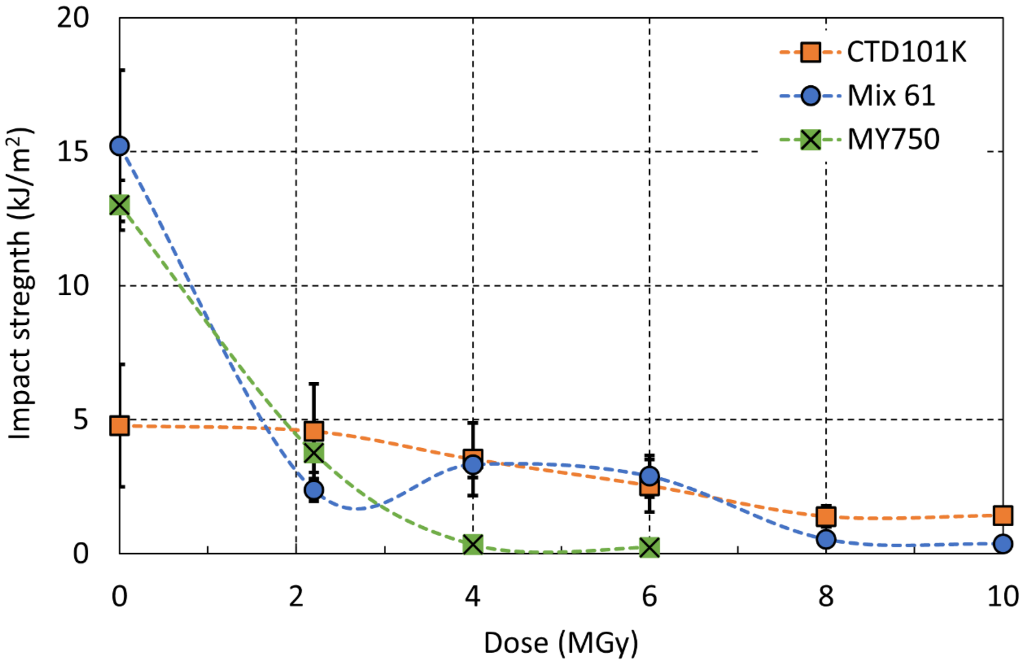


Short beam stress vs displacement of CTD101K, Mix61 and MY750 after different absorbed doses.
[D.M. Parragh et al, https://ieeexplore.ieee.org/document/10319395/]

Impact strength vs dose

Zwick HIT5.5P impact tester for Dynstat tests

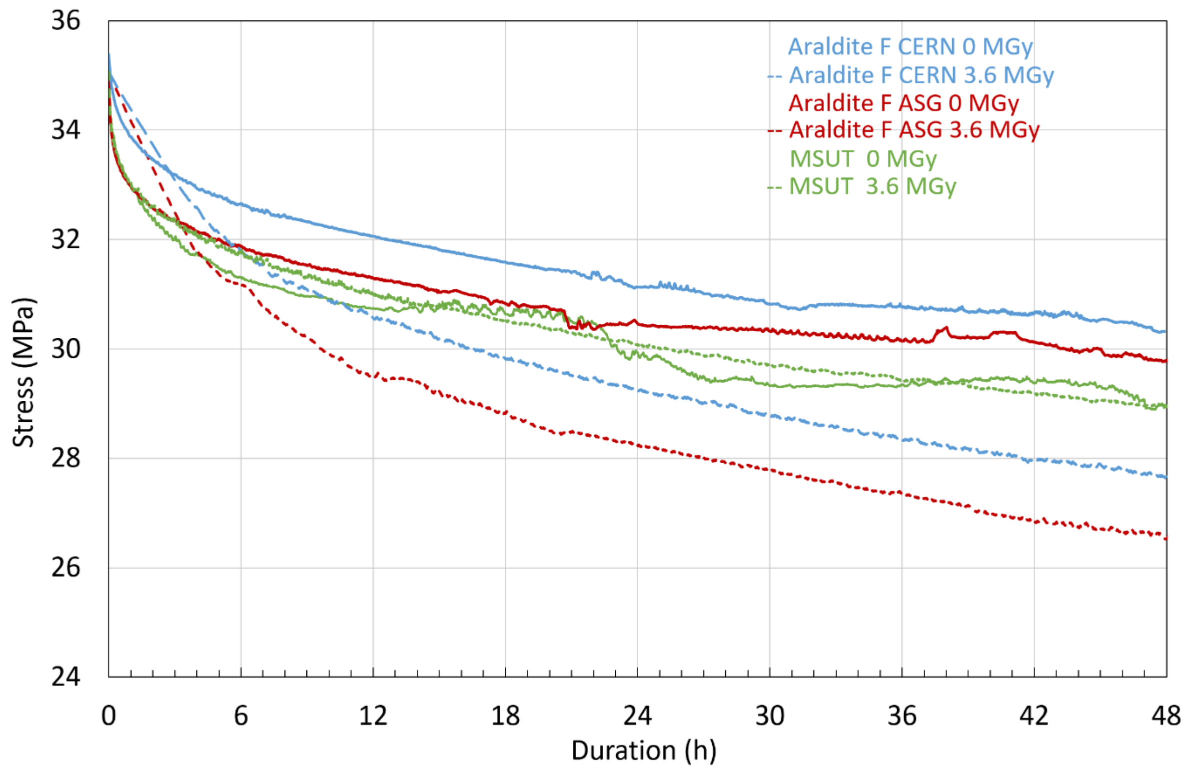
- Dynstat impact tests according to DIN 53435 with a 2 J Dynstat pendulum with unnotched samples.
- Before irradiation Mix61 and MY750 have relatively high impact strength, which is drastically reduced after 2 MGy absorbed dose.



Impact strength of CTD101K, Mix61 and MY750 as a function of absorbed dose.

Effect of irradiation on stress relaxation

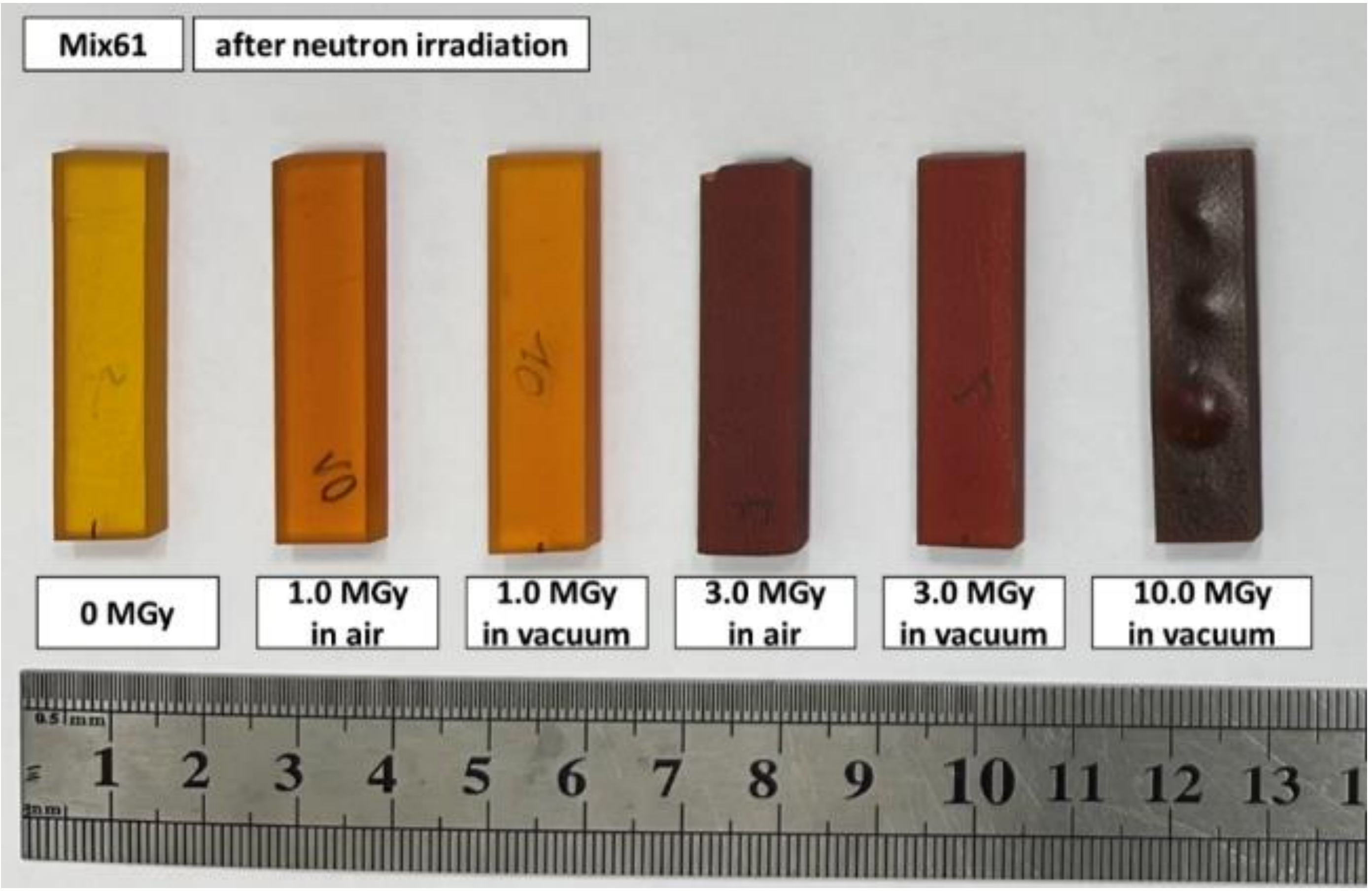
- Stress is measured as a function of duration at constant strain after an initial uniaxial tensile stress of 35 MPa.
- No measurable effect of 3.6 MGy on stress relaxation MSUT.
- Significant effect of 3.6 MGy on stress relaxation of the Araldite F system widely used at CERN (with accelerator DY 061), and the Araldite F system used for impregnation of long superconducting coils (without accelerator DY 061).



Effect of 3.6 MGy gamma dose on stress relaxation behaviour of MSUT and Araldite F ASG and Araldite F CERN. **Courtesy J. Bertsch.** EDMS No. 2963383

Gas evolution during irradiation

- Gas evolution was measured after 10 MGy combined neutron and gamma irradiation under vacuum at Atominstitut of TU Vienna.
- The CTD101K and MSUT epoxy resins exhibit about three times less outgassing as compared to the MY750 and Mix61 epoxy resins.
- After 10 MGy neutron irradiation, bubbles have formed in the Mix61 and MY750 samples (but not in CTD101K and MSUT) [3].



Mix 61 samples after irradiation in air and in vacuum. Bubbles can be seen in the sample after 10 MGy irradiation.

[3] D.M. Parragh et al, https://ieeexplore.ieee.org/document/10319395

Main conclusions of the 1st stage of the polymer lab irradiation study of epoxy resins

- Effect of irradiation source
- The effect of gamma rays and high energy protons is nearly equivalent
- Neutron irradiations are continuing, and neutron irradiated samples being analysed.
- Effect of irradiation environment
- The presence of oxygen in ambient air can reduce cross-linking and chain scission rates. For dose rates in the order of kGy/h for the 4 mm thick samples the effect is comparatively small.
- There is a **strong influence of the irradiation temperature**. To precisely predict the effect of irradiation on polymers in superconducting magnets, irradiations at cryogenic temperature are required.
- Epoxy resins for high irradiation applications
- **DMA results suggest that MSUT, CTD101K and POLAB Mix are the most radiation hard epoxy resin systems studied so far.**
- MY750 and Mix61 are not recommended for use in irradiation environments

Case study II

Radiation hardness of POLAB Mix epoxy resin system with improved toughness at cryogenic temperature

Driving question:

- Does the addition of flexibiliser DY040 change the good radiation hardness of the CTD101K epoxy system?

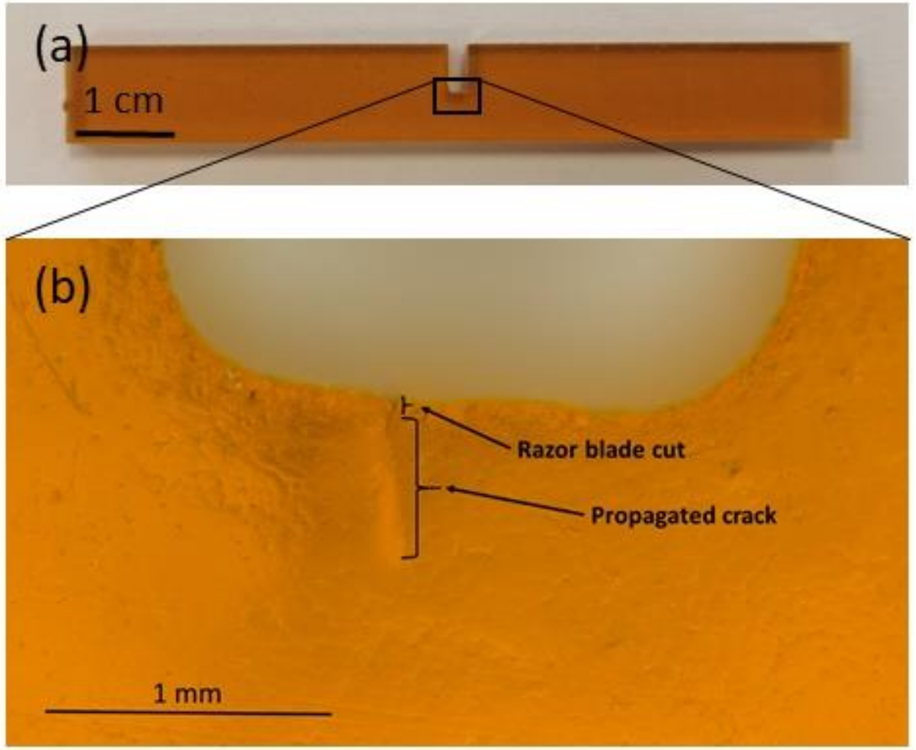
POLAB Mix for impregnation of superconducting magnet coils

- Cracking of the impregnation resin can generate superconductor instabilities.
- The fracture toughness of the epoxy resins for coil impregnation is considered to be a relevant parameter that influences magnet quench behaviour.
- For its good processing capabilities (low viscosity and long pot-life) and relatively high radiation resistance the CTD101K three component epoxy system is the baseline impregnation system for the HL-LHC superconducting magnets.
- A drawback of the three-component CTD101K epoxy system is its relatively low fracture toughness as compared to the fracture toughness of alternative resins studied for superconducting magnet coil impregnation.
- The CERN polymerlab has developed an epoxy system with improved fracture toughness at cryogenic temperature by adding the flexibiliser Araldite DY040 as forth component to the CTD101K system. This four-component epoxy system is referred to as POLAB Mix.
- Before POLAB Mix could be used to impregnate Nb_3Sn magnet coils [7], it had to be verified that the radiation hardness of the CTD101K system is not degraded by adding the flexibiliser.

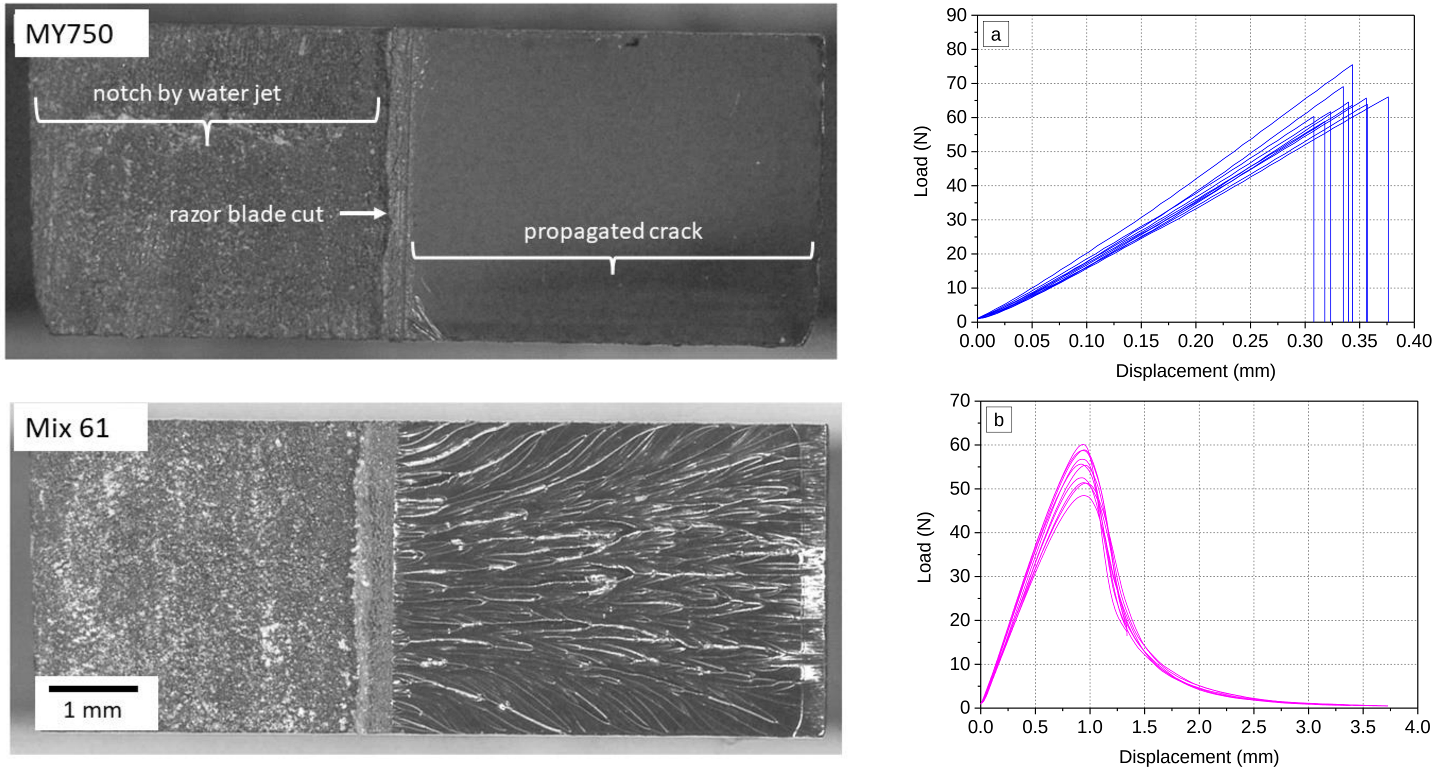
[7] A. Haziot, "Fusillo A Curved-Canted-Cosine-Theta (CCCT) Dipole Demonstrator at CERN", https://indico.cern.ch/event/1271260/contributions/5338190/attachments/2705968/4698855/230831%20-%20MSC%20Seminar%20-%20final.pdf

Fracture toughness measurements

- Flexural fracture toughness tests in accordance with ISO 13586, "Plastics — Determination of fracture toughness (G_{IC} and K_{IC}) — Linear elastic fracture mechanics (LEFM) approach"
- K_{IC} and G_{IC}, can be calculated for materials exhibiting linear-elastic behaviour and unstable crack propagation.



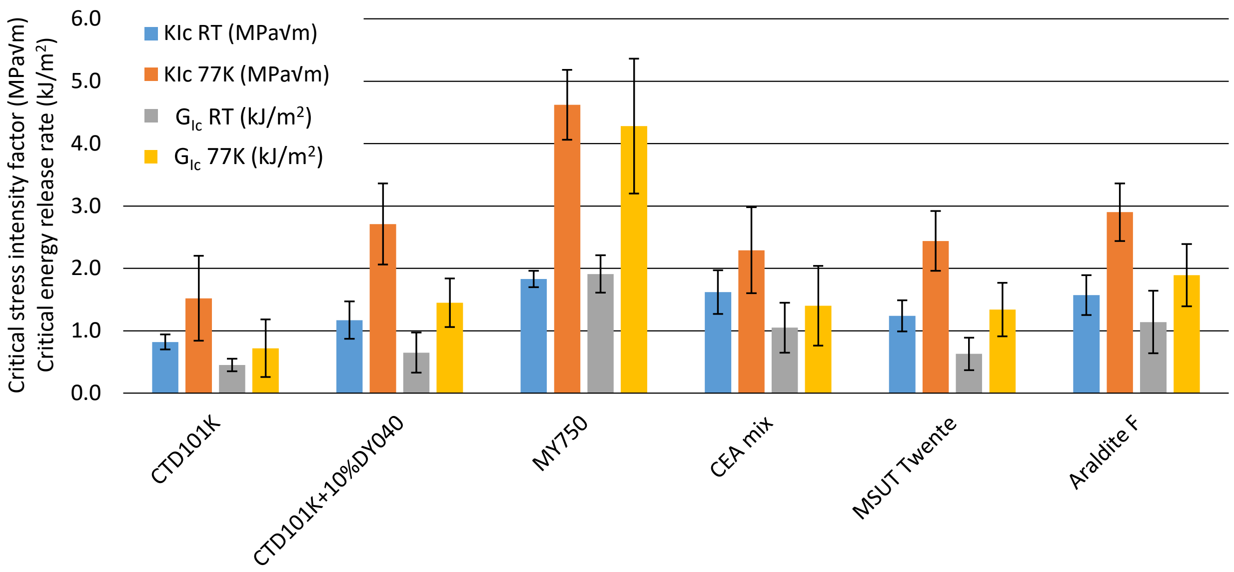
Single edge notched bending (SENB) sample with notch, and propagated crack prior to bending test.



Fracture surfaces and load–displacement diagrams. (a) MY750 exhibits unstable and (b) Mix 61 stable crack propagation [8].

Comparison of epoxy resins fracture toughness

- The fracture toughness of the CTD101K epoxy resin system can be improved by adding 10 wt.% of the flexibiliser Araldite DY040.
- The effect is particularly strong at cryogenic temperature, and at 77 K the fracture toughness can be increased by 80 % from K_{IC} = 1.5 MPa√m to K_{IC} = 2.7 MPa√m [8].
- POLAB Mix fracture toughness is comparable to that of the CEA mix, MSUT and Araldite F ASG epoxy resins systems.
- These systems have the highest fracture toughness of epoxy resins that can be used for impregnation of large coils.
- MY750 has superior fracture toughness, but cannot be processed in long coils, and it is not radiation resistant.

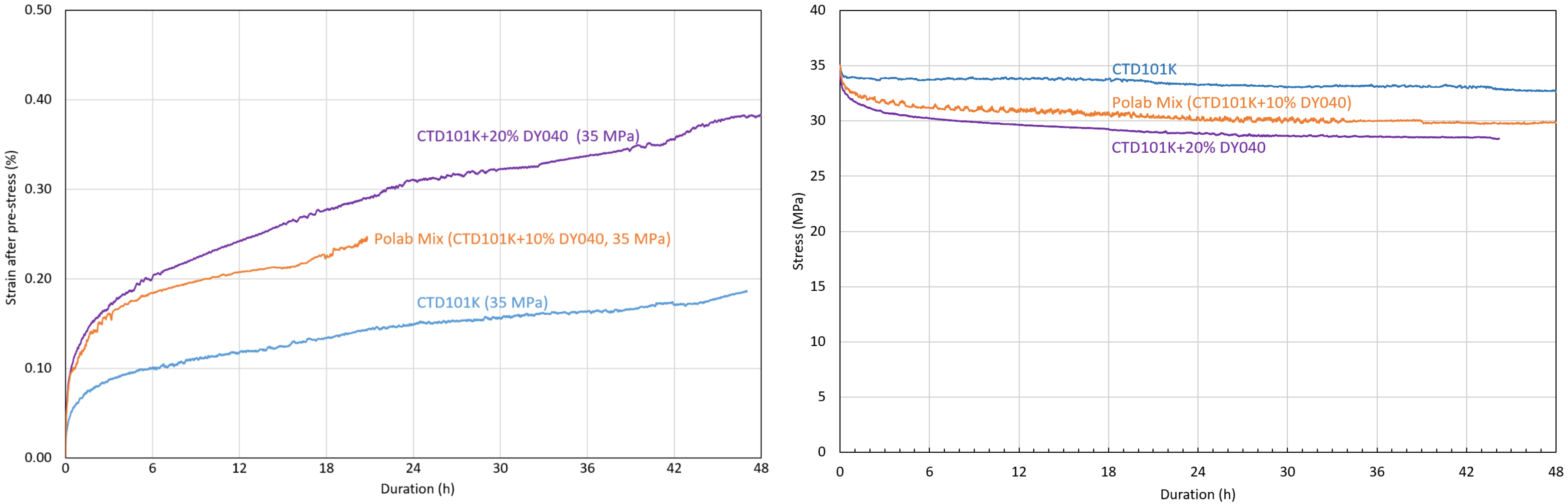


Comparison of the critical stress intensity factor K_{IC} at RT and 77 K of CTD101K, POLAB Mix (CTD101K+10%DY040) and other epoxy resins.

[8] A. Gaarud, D. Mate Parragh, S. Clement, C. Scheuerlein, R. Piccin, R. Lach, "Improved fracture toughness at cryogenic temperature of irradiation hard epoxy system for superconducting coil impregnation", submitted to Cryogenics, (http://ssrn.com/abstract=4478135)

Effect of flexibiliser content on creep and stress relaxation of the CTD101K system

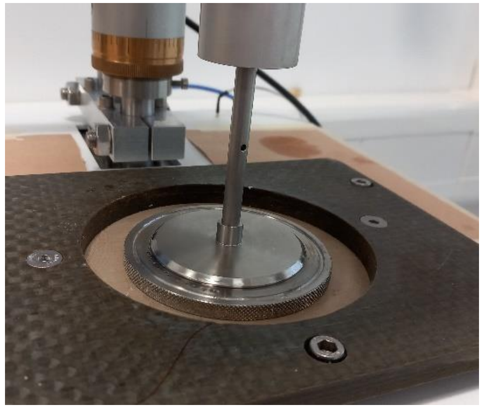
- Addition of the flexibiliser increases creeping at constant 35 MPa tensile stress and stress relaxation at constant tensile strain after loading to 35 MPa.

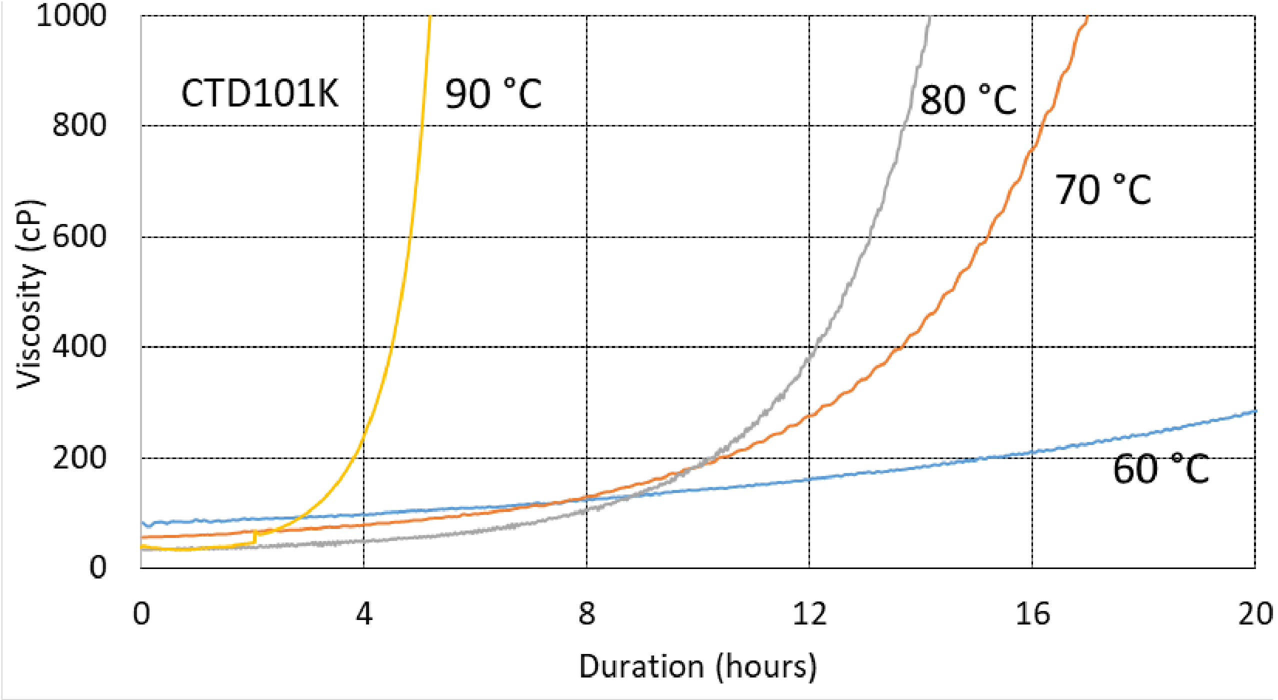


Comparison of (a) creep (strain as a function of duration at a constant stress of 35 MPa) and (b) stress relaxation (stress as a function of duration at constant strain) of CTD101K, POLAB Mix, and CTD101K+20%DY040. **Courtesy J. Bertsch, EDMS 2963385.**

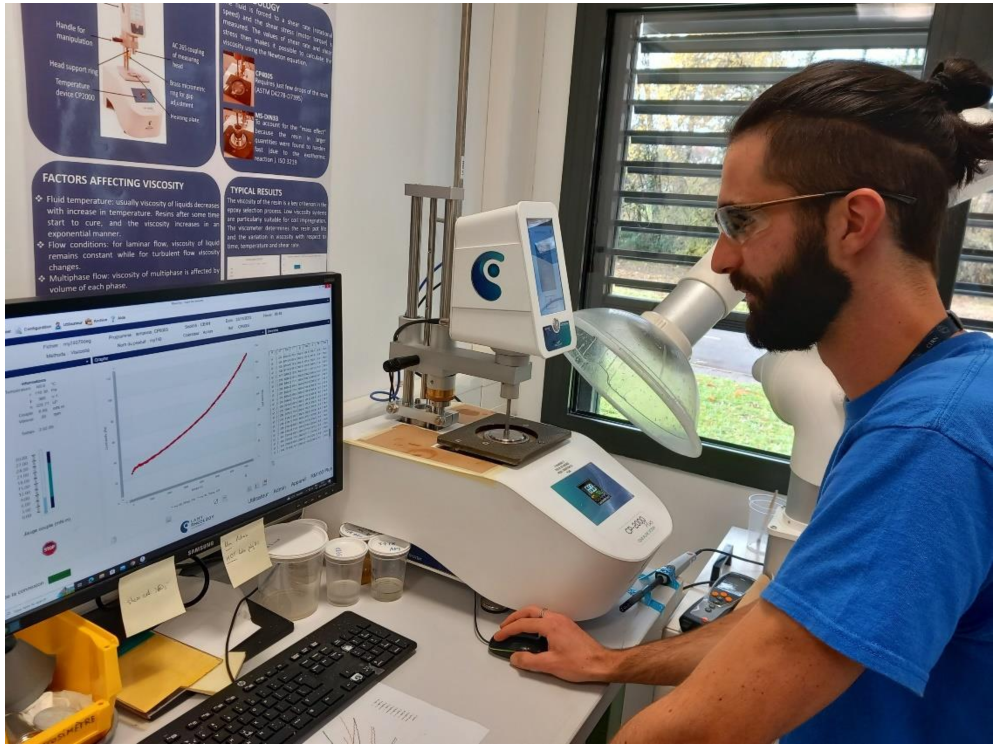
Viscosity of the CTD101K three component mix

- Epoxy resins are thermosets whose precursors are liquid and enable processing like vacuum impregnation of magnet coils.
- Viscosity of the liquid sample at a fixed temperature is measured over time to monitor curing and to characterise the pot life of the epoxy mix.





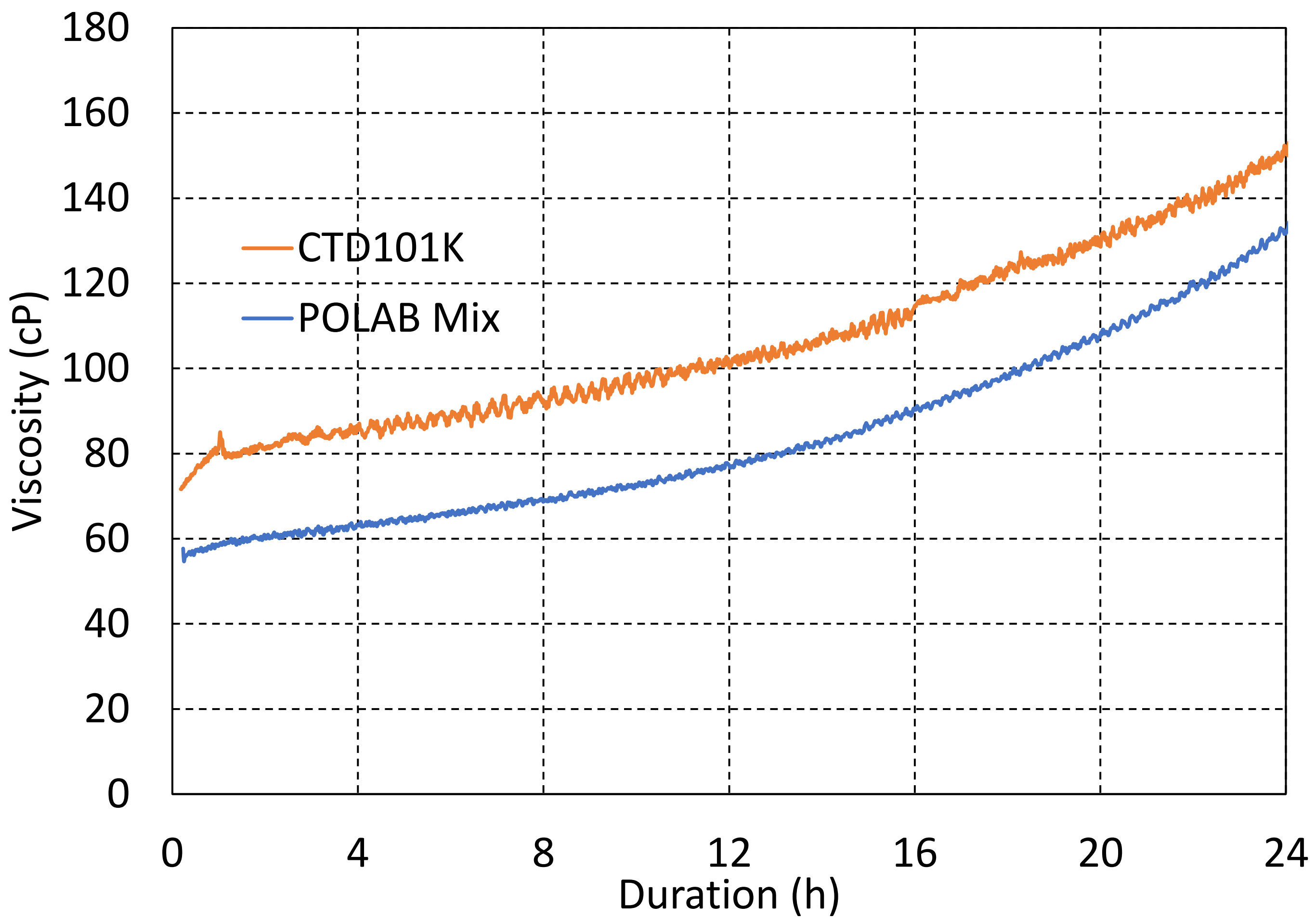
Viscosity evolution of CTD101K as a function of duration at different temperatures. **Courtesy B. Verma**. *EDMS No. 2607624.*



Lamy Rheologie RM100 CP2000 rotating plate rheometer.

Viscosity of POLAB Mix

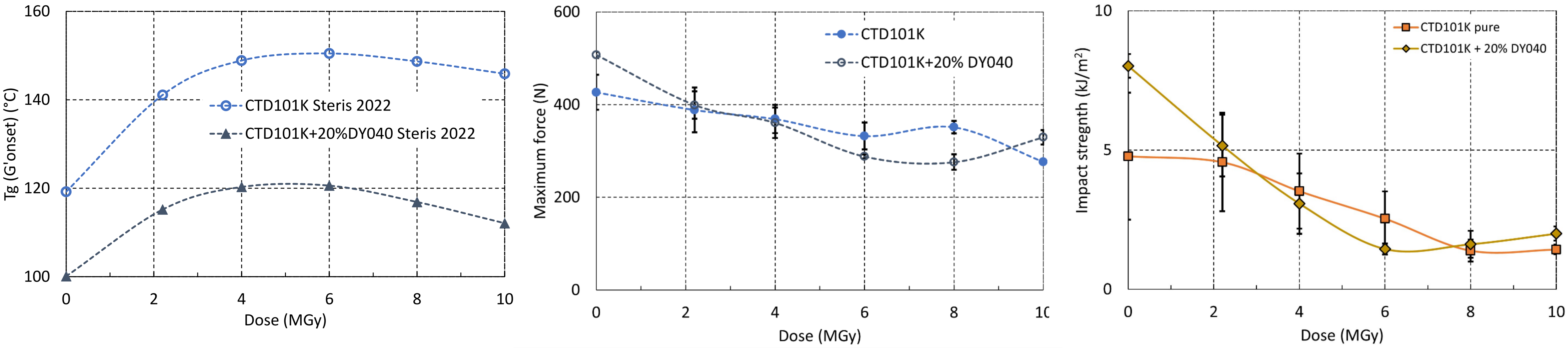
- The excellent processibility of CTD101K is not affected by the addition of 10wt.% flexibiliser DY040.



Viscosity evolution of CTD101K and POLAB Mix as a function of duration at 60 °C. **Courtesy C. Urscheler.**

Effect of gamma irradiation on CTD101K and CTD101K+20% DY040 epoxy resin systems mechanical properties

- Gamma irradiation in ambient air up to 10 MGy at Gammatec facility.
- Comparison of T_g, short beam strength and impact strength as a function of absorbed dose shows that addition of the flexibiliser does not negatively affect the good irradiation resistance of the CTD101K system.



Comparison of (a) T_g, (b) short beam strength and (c) Dynstat impact strength as a function of ^{60}Co dose evolution of CTD101K three component and CTD101K+20wt.% DY040 four component resin systems.

Main conclusions POLAB Mix

- The fracture toughness of the CTD101K epoxy resin system for impregnation of superconducting magnet coils can be improved by adding 10 wt.% of the flexibiliser Araldite DY040.
- Creeping and stress relaxation of POLAB Mix are slightly increased with respect to CTD101K.
- Processability (viscosity and pot-life) of POLAB Mix is comparable to that of CTD101K.
- **Adding the flexibiliser does not significantly change the irradiation induced aging behaviour. POLAB Mix is a valid alternative to the standard formulation of CTD101K.**
- POLAB Mix irradiation up to 30 MGy is ongoing.

Case study III

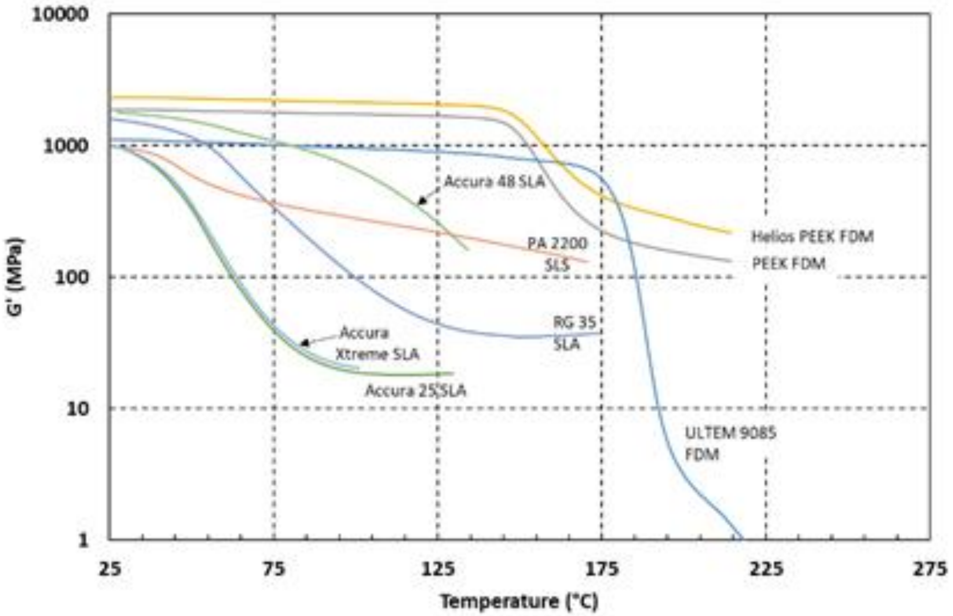
Radiation hardness of 3D printable resins

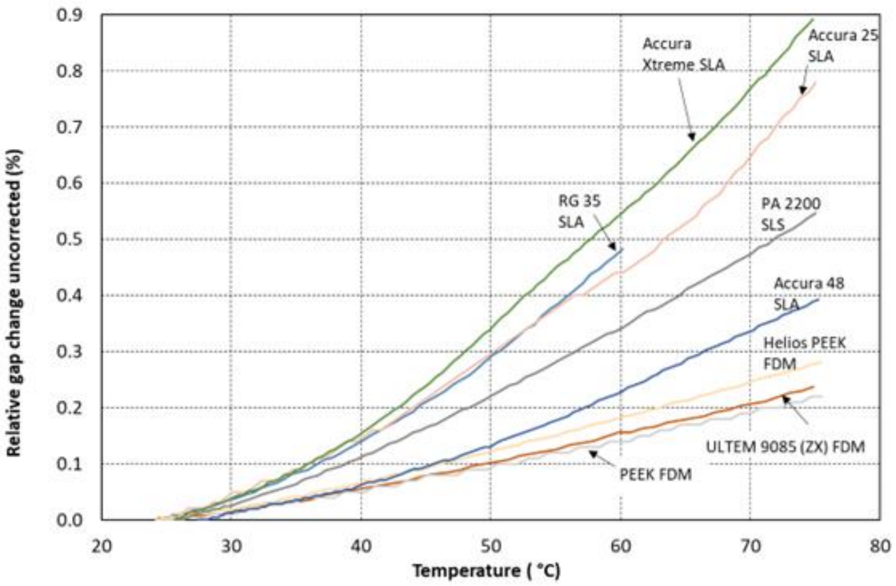
Driving questions:

- Which materials are suited for application in irradiation environment?
- What is the effect of irradiation on the mechanical anisotropy of FDM printed resins?

T_g and thermal expansion of 3D printable resins

- 3D printed samples studied are produced by three processes:
  - stereolithography (SLA)
  - selective laser sintering (SLS)
  - fused deposition modelling (FDM).
- SLA printable resins have comparatively low T_g , T_g of the FDM resins studied exceeds 150 °C.
- Differences in thermal expansion coefficients are mainly due to the different T_g.

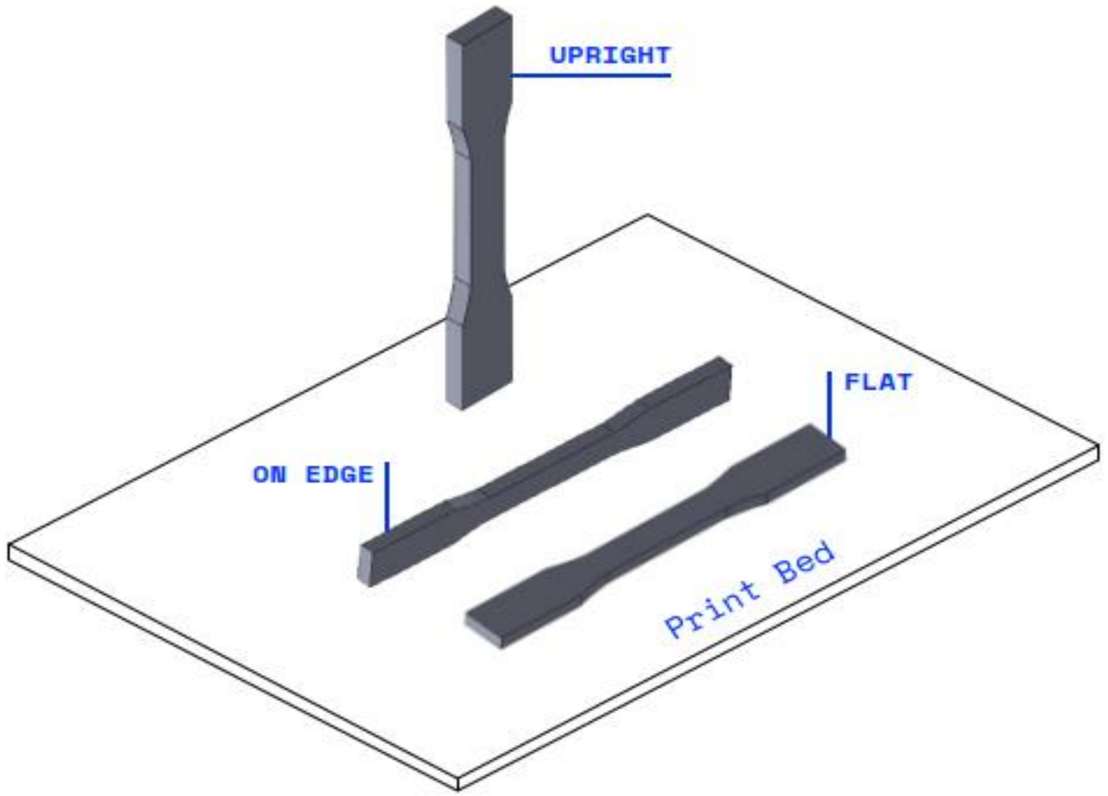




Comparison of (a) the storage modulus G' (T) and (b) thermal expansion evolutions of the non-irradiated 3D printable resin sof the present study. ***Courtesy N. Martin , EDMS No. 2906914.***

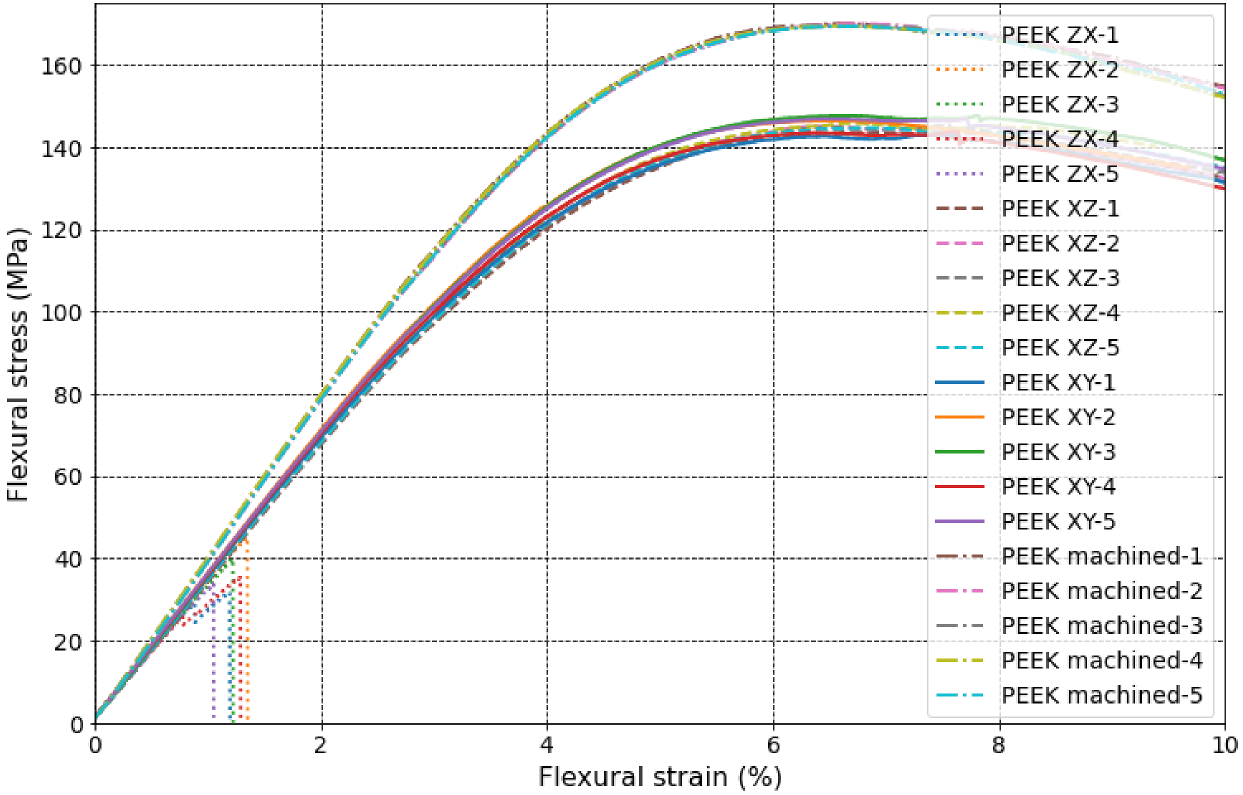
Definition of 3D printing directions

- Mechanical properties of FDM printed materials are strongly anisotropic.
- When reporting a mechanical test result the printing direction needs to be provided:
  - XY: Flat
  - XZ: On edge
  - ZX: Upright



PEEK RT flexural stress-strain curves

- **Strongly anisotropic mechanical properties; samples built in ZX direction fracture at comparatively low stress (minimum measured value for 5 samples is 32 MPa)**
- **Samples built in XZ and XY direction did not break up to 10% flexural strain.**
- **Samples built in XZ and XY directions reach about 70% of the bulk PEEK's maximal stress**



Fracture surface ZX direction

Sample built in XZ-direction after test

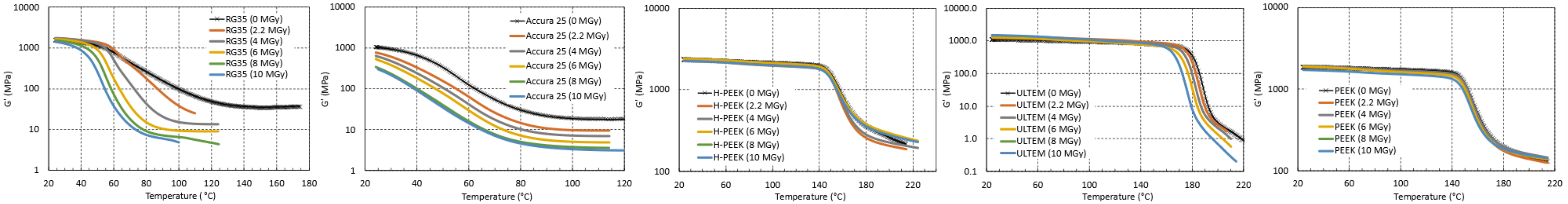
Sample built in XY-direction after test

From A. Gaarud" Thermomechanical properties and fracture behaviour of polymers" presentation at the SMT section meeting of 21 Jul 2022, EDMS No. 2816645

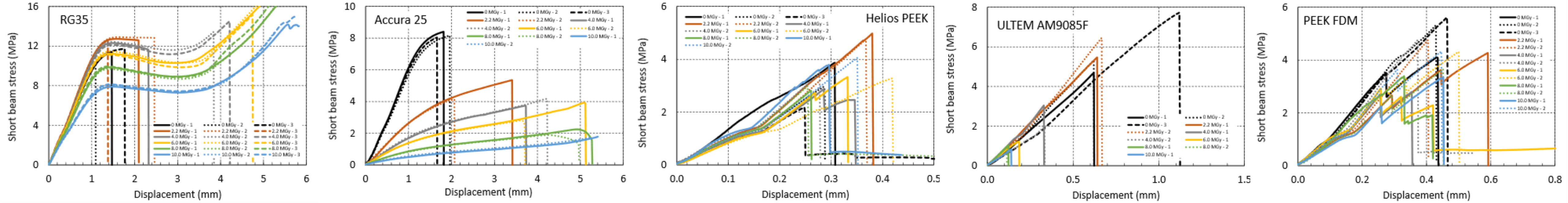
3D printed materials gamma irradiation results

- SLA samples have isotropic materials properties
- FDM samples have been tested in the week ZX direction

Dynamic mechanical analysis



Short beam test



RG35-SLA **Accura 25-SLA** **Helios PEEK-ZX** **ULTEM AM9085F-ZX** **PEEK-ZX**

From D. M. Parragh ” Irradiation study update: a brief overview” presentation at the Polymer laboratory meeting of 23 Nov 2023

Main conclusions irradiation induced aging of 3D printable resins

- **Of the SLA 3D printed materials irradiation tested so far, RG35 has outstanding mechanical properties before and after irradiation.**
- FDM printed PEEK and ULTEM 9085 have very good radiation resistance in the favourable printing directions.
- The effect of irradiation on the mechanical anisotropy of FDM printed polymers is being studied.

Case study IV

MCBC/MCBY magnet constituent materials

Driving questions:

- Is there an irradiation induced change of thermomechanical properties of MCBC and MCBY corrector magnet polymer constituents that could explain changing training behaviour of these magnets in the LHC?
- Is there an irradiation induced degradation of the dielectric properties of the Nb-Ti wire PVA enamel insulation?

MCBC/MCBY magnet constituent materials

Studied samples

- PVA enamel insulated MCBY rectangular Nb-Ti wire.
- Coil block samples cut from a pre-series MCBC coil impregnated with Araldite GY 285/Texaco D400.
- Isopreg 2704 used for the MCBC/MCBY outer insulating layer

For more details see references [1] and [2].

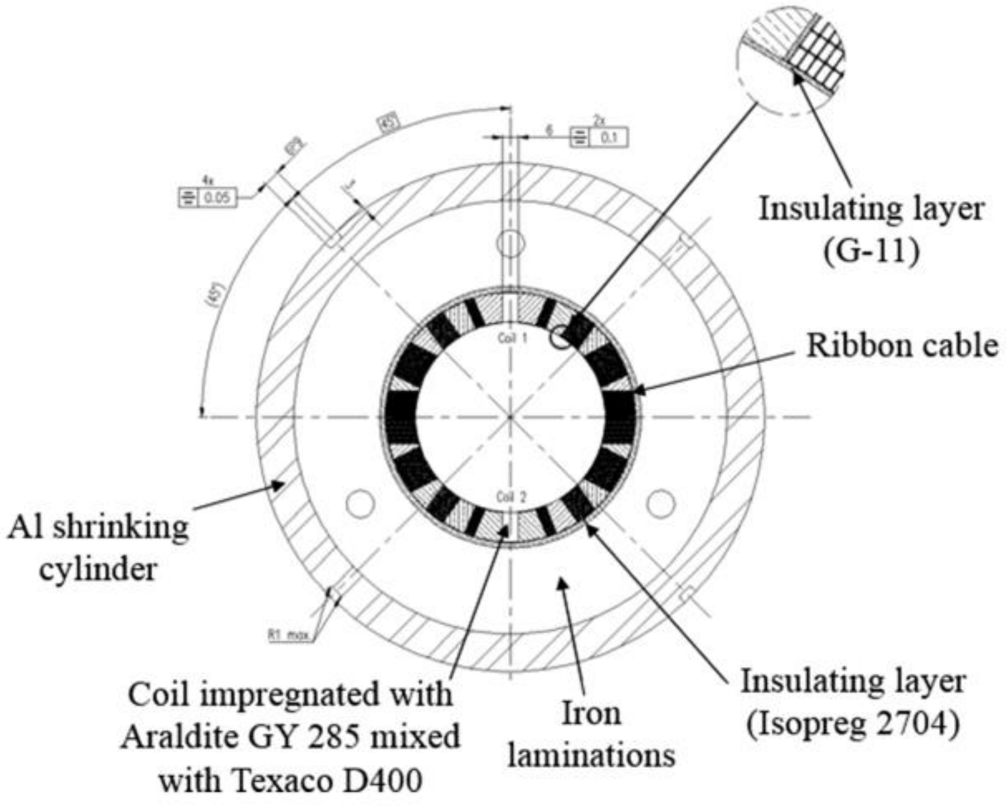


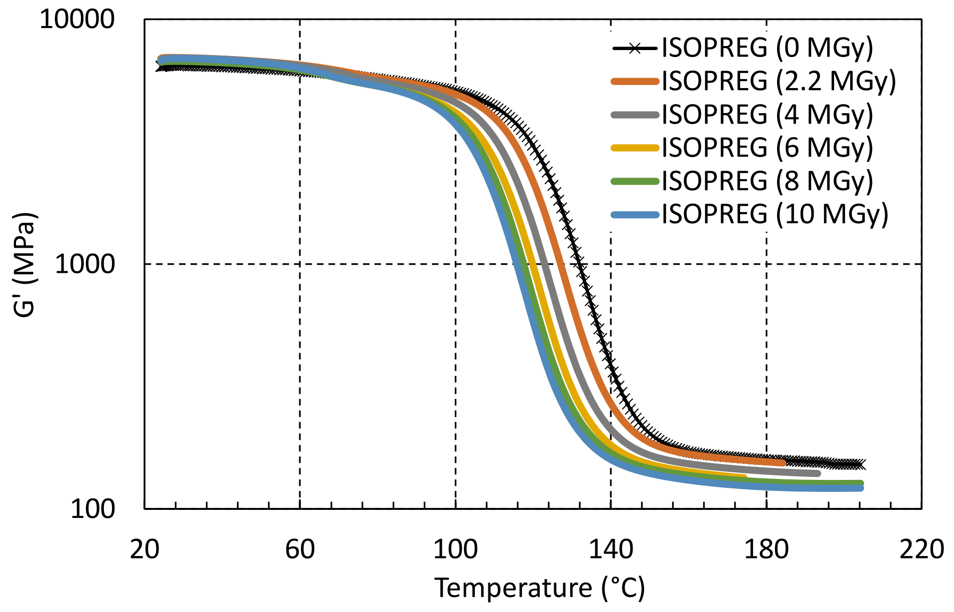
Fig. 2. Components of the MCBC and MCBY magnets inside the aluminum shrinking cylinder.

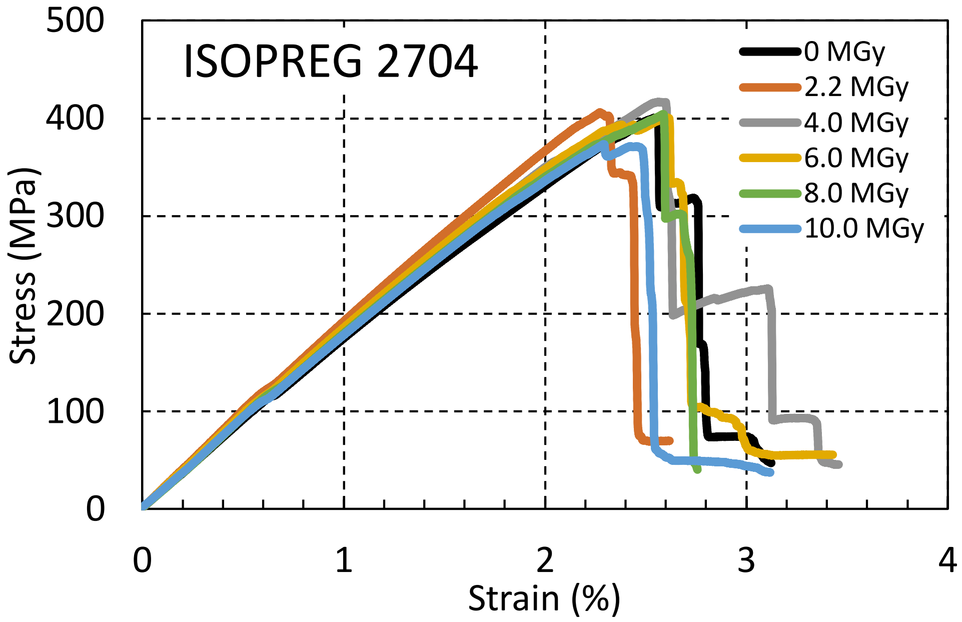
[1] D. Schörling et al., "The MCBC and MCBY LHC magnet consolidation",https://indico.cern.ch/event/802179/contributions/3334608/attachments/1802572/2940567/Schoerling_MCBCY_V4.pdf

From : [2] A. louzguiti, et al. "Design of Radiation Hard Spare Units for the Orbit Corrector Dipoles of LHC", IEEE Trans. Appl. Supercond. 30(4), 2020

ISOPREG 2704 flexural test results

- ISOPREG 2704 sheet from Isovolta, 15 h-120 °C curing, glass fibre volume fraction V_f=60 %, [0,90] fibre orientation (half of the fibres are oriented in the load direction).





(a) Storage modulus (G') and flexural stress-strain curves of ISOPREG 2704, V_f=60 %, [0,90] *after different dose levels.*

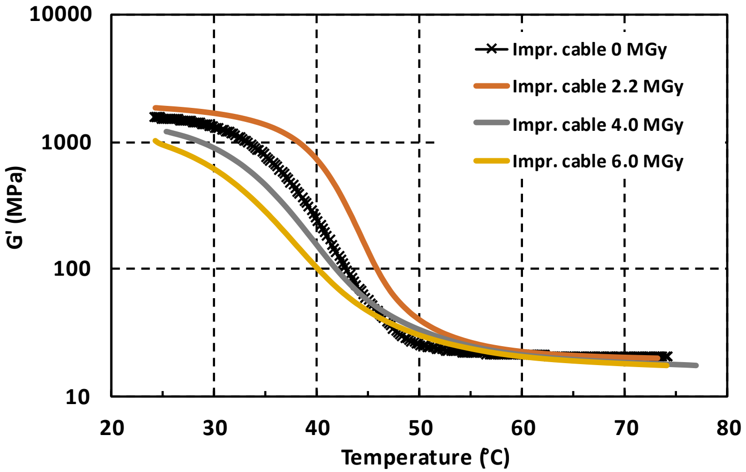
- After 10 MGy T_g is reduced by 16 °C with respect to T_g of the unirradiated sample.
- In the [0,90] test configuration the fibre mechanical properties dominate the composite properties.
- No significant effect of 10 MGy ^{60}Co gamma irradiation on the mechanical properties of ISOPREG 2704, (V_f=60 %, [0,90]).

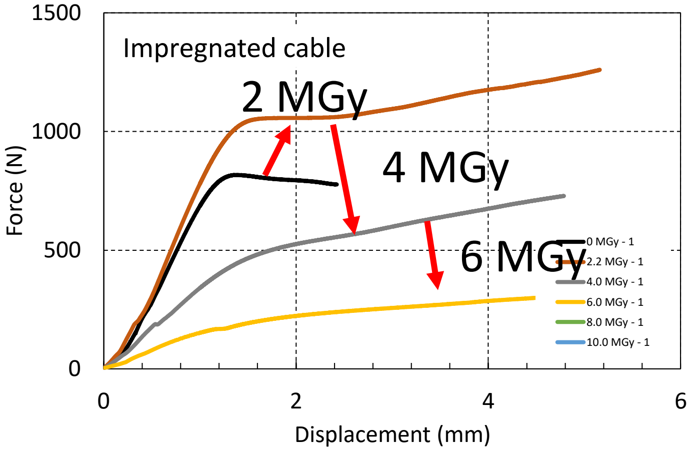
D.M. Parragh, "Effect of gamma irradiation on the thermomechanical properties of MCBY corrector magnet constituent material ISOPREG 2704, CERN Polymer lab test report, EDMS No. 2816963, (2023)

Araldite G 285 + Jeffamine D400 epoxy resin system

- DMA and short beam tests with impregnated cable samples, gamma irradiation in air.
- Improvement of mechanical properties after 2 MGy.
- Strong degradation after 4 MGy

Ribbon cables impregnated with Araldite G 285 + Jeffamine D400 *before and after irradiation up to 6 MGy.*

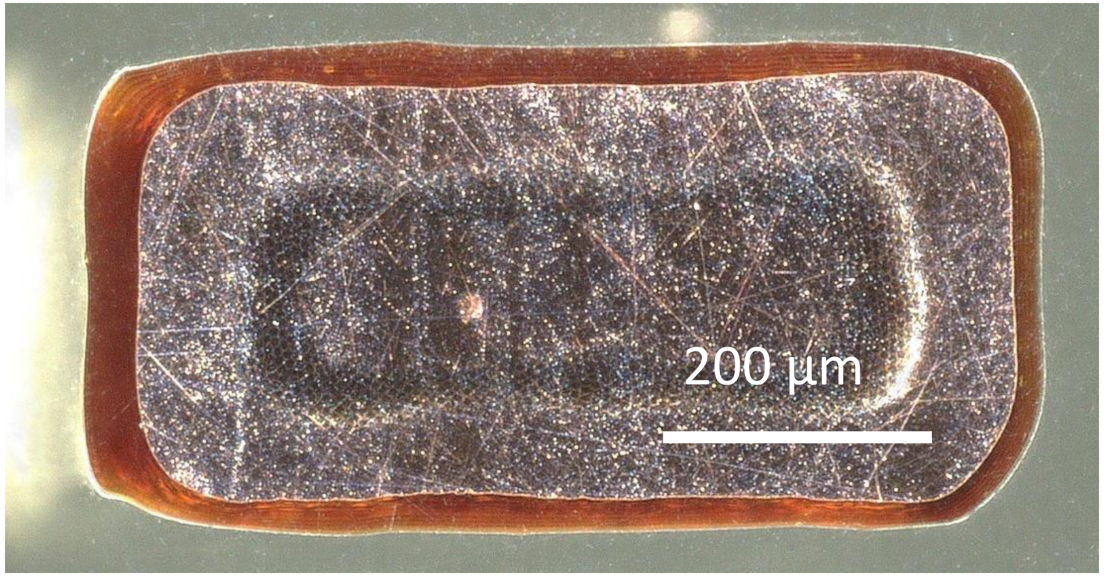




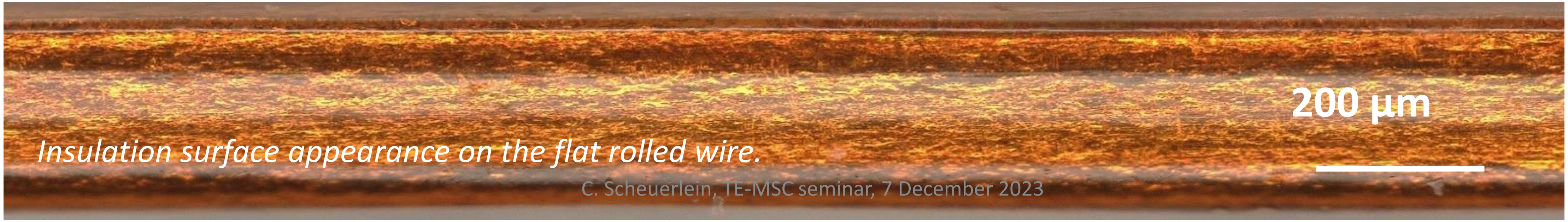
(a) G'(T) and (b) short beam bending force vs displacement of Araldite G 285 + Jeffamine D400 *before and after irradiation up to 6 MGy .*

PVA enamel insulated Nb-Ti/Cu wire

- PVA insulation is applied on the round wire and afterwards the wire with insulation is rolled to the final rectangular shape.



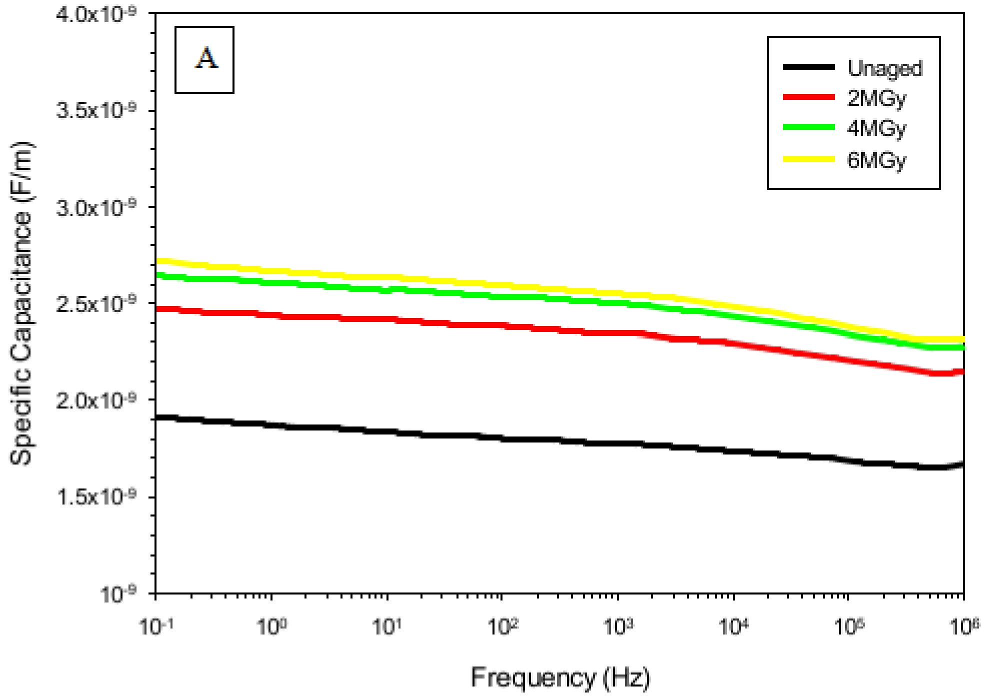
Flat rolled wire cross section. Courtesy of S. Pfeiffer, EN-MME.



Insulation surface appearance on the flat rolled wire.

Dielectric spectroscopy

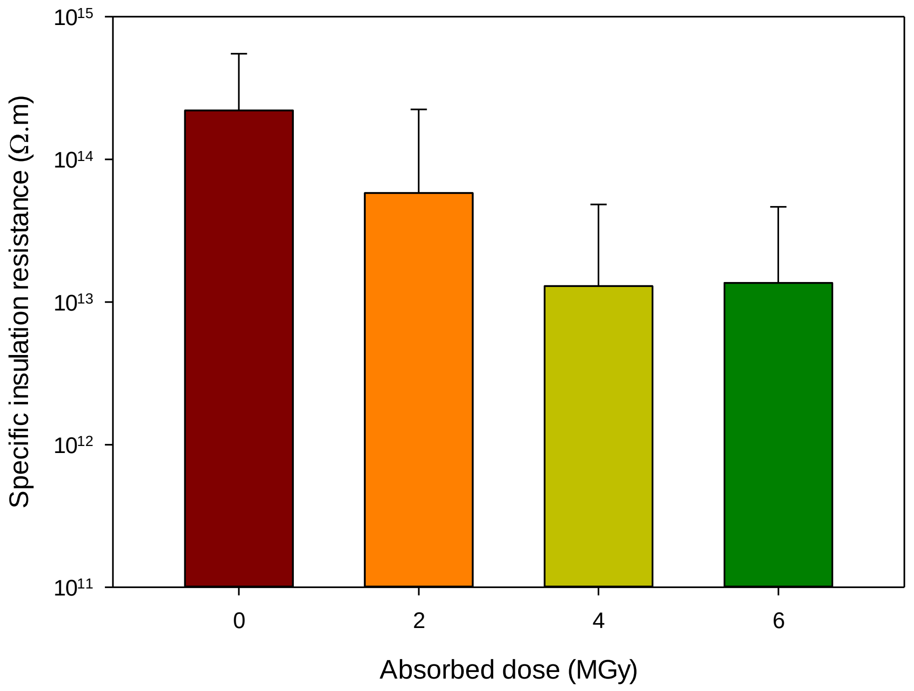
- Specific capacitance values increase with increasing dose throughout the studied frequency range.
- The biggest increase is recorded between the unirradiated and the 2 MGy aged sample.
- The increase of capacitance is probably due to arise of polar species. It may also partly be caused by densification of the insulation.



Specific capacitance as a function of frequency for different aging levels.
Courtesy S. Vincenco Suraci and D. Fabiani, University of Bologna.

Insulation resistance

- According to the IEC/IEEE 62582-6 part 6 “Insulation resistance standard”
- Set-up consists of picoamperemeter (Keysight B2981A) and a voltage generator Keithley 2290E-5 5kV).
- DC voltage was applied to the conductor while the current was recorded through the external painted electrode.
- Leakage current values are acquired at 500 V until the reaching of the steady-state value or after 24h from the beginning of the test.
- Leakage current measurements indicate a significant reduction of insulation resistance after 2 MGy and a further reduction after 4 MGy.



Specific insulation resistance before and after gamma irradiation up to 6 MGy.
Courtesy S. Vincenco Suraci and D. Fabiani, University of Bologna.

DC breakdown

- Tests were performed on at least three wire samples per each aging level.
- Breakdown voltage data were statistically analyzed through Weibull distribution according to IEC 62539 “Guide for the statistical analysis of electrical insulation breakdown data”.
- Results are not conclusive.
- Many more tests would be needed to obtain statistically meaningful results.

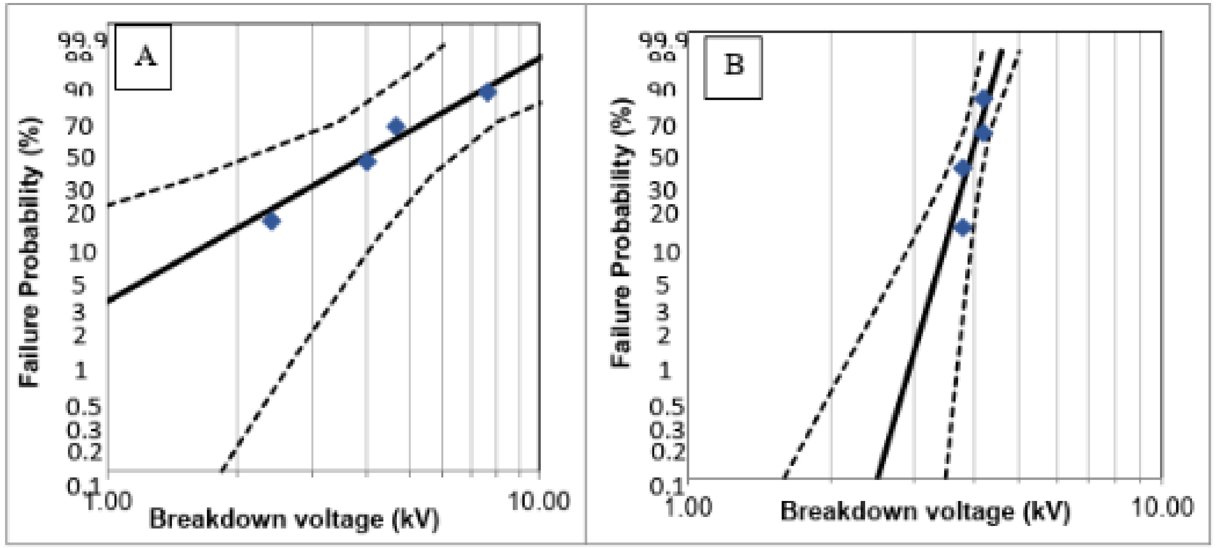


Figure 10 Weibull plots of breakdown voltage for tested samples.

Conclusion MCBY corrector magnet constituents

- Superconducting wire PVA insulation
  - **Dielectric spectroscopy is sensitive to assess radiation induced aging of the PVA enamel wire insulation.**
  - Significant reduction of insulation resistance after 6 MGy irradiation.
  - An irradiation induced reduction of breakthrough voltage cannot be detected.
  - **Resistance measurements and dielectric spectroscopy are non-destructive methods that could be envisaged to monitor radiation-induced ageing.**
- Coil impregnation epoxy resin
  - Significant effect of 6 MGy irradiation on the ambient temperature mechanical properties of the MCBC coil Araldite G 285 + Texaco D400 impregnation.
- Coil to ground insulation
  - Negligible effect of 10 MGy irradiation on the mechanical properties of the outer insulation layer (ISOPREG 2704).

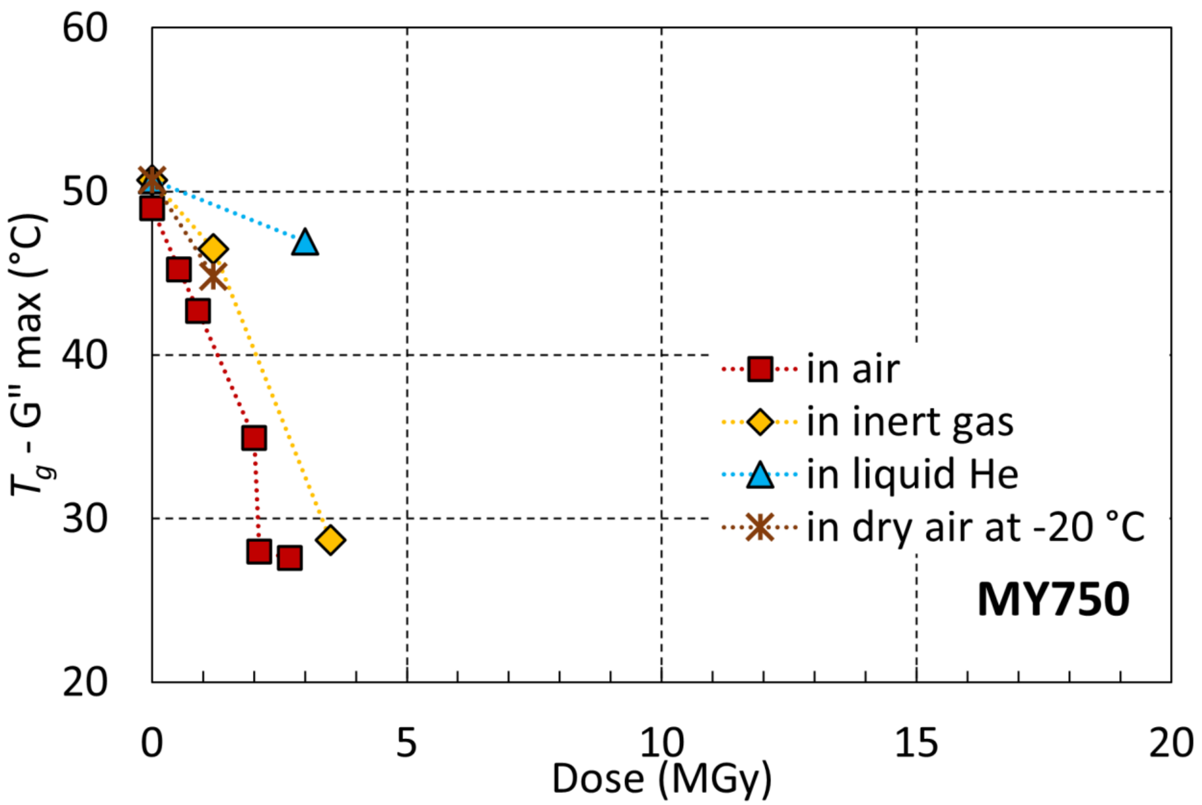
Outlook

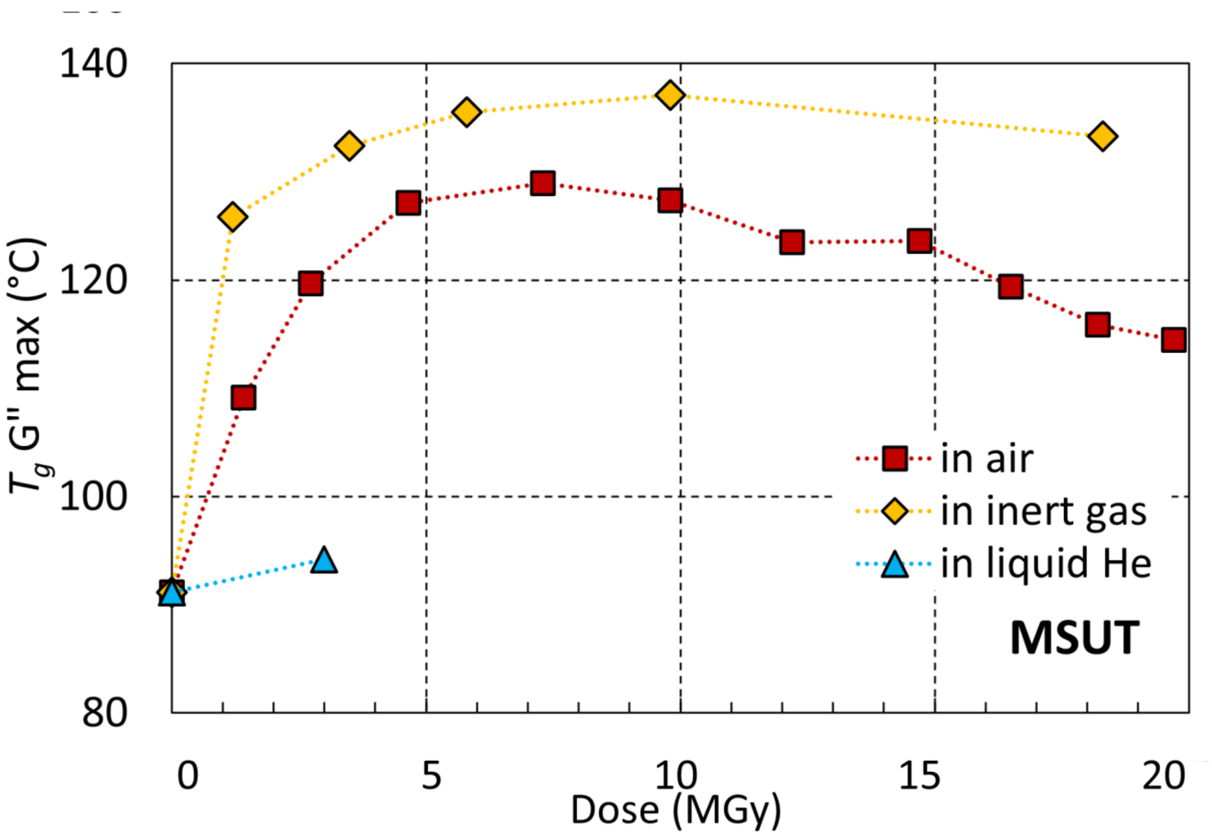
- Driving questions for the 2^{nd} stage of the polymer lab irradiation study:
  - What is the dose limit of the polymers and insulation systems of accelerator magnets under relevant irradiation conditions?
    - In magnets already installed in the LHC (correctors and triplets)
    - In new magnets for the CERN accelerator complex, e.g. for PS Booster
    - In magnets for the HFM project
  - What are the most irradiation resistant insulation systems for future accelerator magnets?
    - What is the effect of reinforcing fibres and fillers in composites?
    - How is the irradiation behaviour of epoxy systems affected by additives, hardener, binders, … ?
    - How is the aging of mechanical, dielectric and thermal properties related?

Ongoing and planned irradiations

- Ambient temperature irradiations
  - **Gamma irradiation up to 30 MGy** at Steris Gammatec, large sample volume for thermal, mechanical and dielectric testing of unfilled resins and reinforced composites. Irradiation started in November 2023 with a dose rate of **2.5 kGy/h**. Irradiated materials include:
    - LHC and HL-LHC magnet constituents
    - HFM candidate materials
    - Candidate resins for PCB booster magnets
    - 3D printable materials for different applications in magnets and detectors
    - Polyurethanes
  - **Proton irradiation to >50 MGy at CERN IRRAD of the most radiation hard epoxy systems, including MSUT, CTD101K and Polab Mix.** During 2024 and 2025 runs.
  - Mixed field neutron irradiations at CERN spallation source NEAR nTOF, continue irradiation of reference samples in 2024 and 2025 (about 2 MGy per year)
  - Much higher dose rates could be achieved at a reactor (e.g. 100 MGy could be achieved at Triga Mark II of ATI Vienna in <6 months)

Influence of the irradiation temperature





T_g G''_{max} of MY750 and MSUT as a function of proton dose absorbed in ambient air, inert gas and in liquid He.

Irradiations at cryogenic temperature

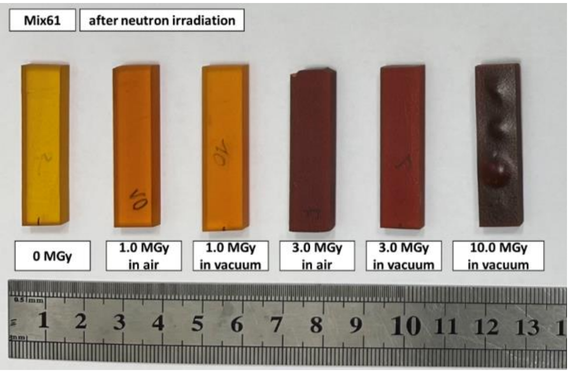
- IRRAD low temperature irradiations have shown the **strong influence of the irradiation temperature** on aging rates. To precisely predict the effect of irradiation on polymers in superconducting magnets, irradiations at cryogenic temperature are required.
- **Proton irradiation in liquid helium** will be continued during the 2024 and 2025 IRRAD runs (up to 3 weeks irradiation, corresponding with 3 to 4 MGy per year)
- **Cryocooled set-ups enable cold irradiations** and to study the change of functional materials properties under the irradiation conditions in superconducting accelerator magnets.
- During 2024 and 2025 develop and commission a new set-up for cold irradiations of a large sample volume in a gamma ray facility to 30 MGy.
- First cold irradiations at a gamma ray facility should start in 2025.

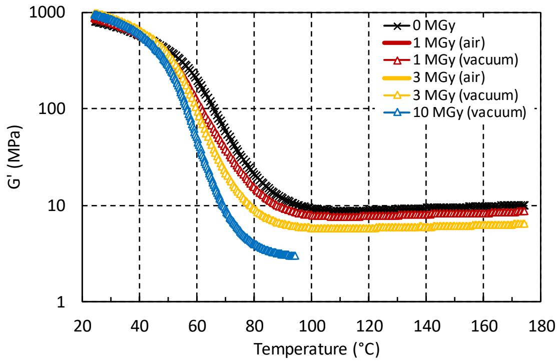
Thank you for your attention

Extra slides

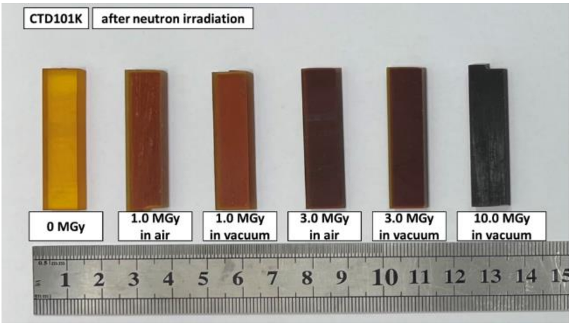
Neutron irradiation of epoxy resins: DMA results

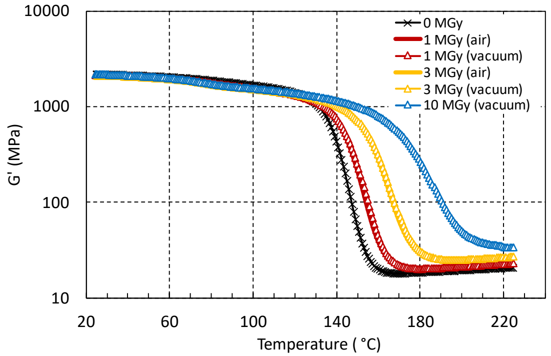
- Effect of neutron irradiation dose and environment on the visual and mechanical properties
- Dose steps about 1 MGy, 3 MGy, 10 MGy, neutron and gamma irradiation at ATI Vienna



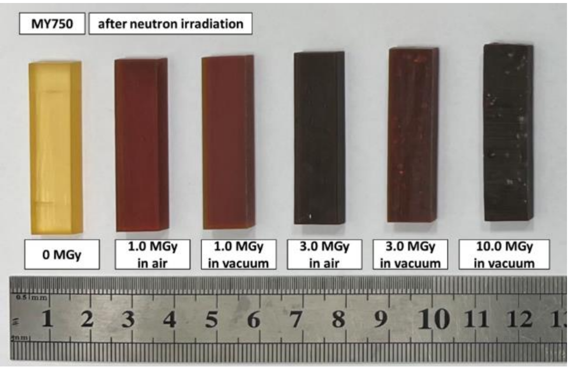


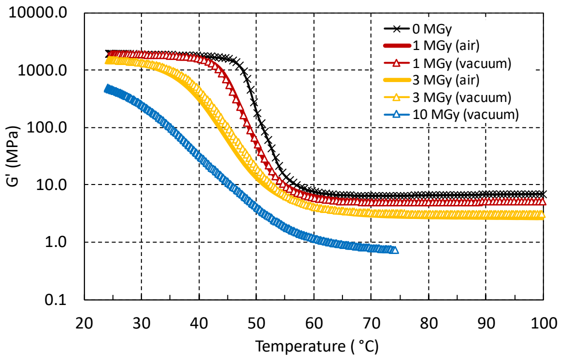
Mix61

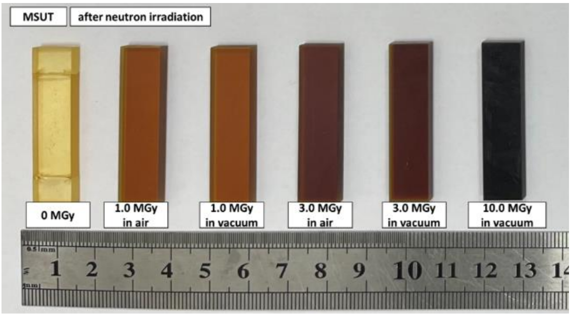


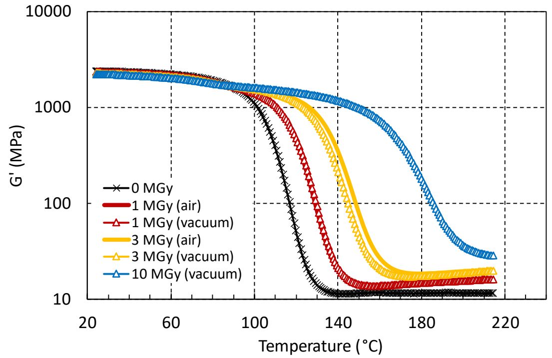


CTD101K







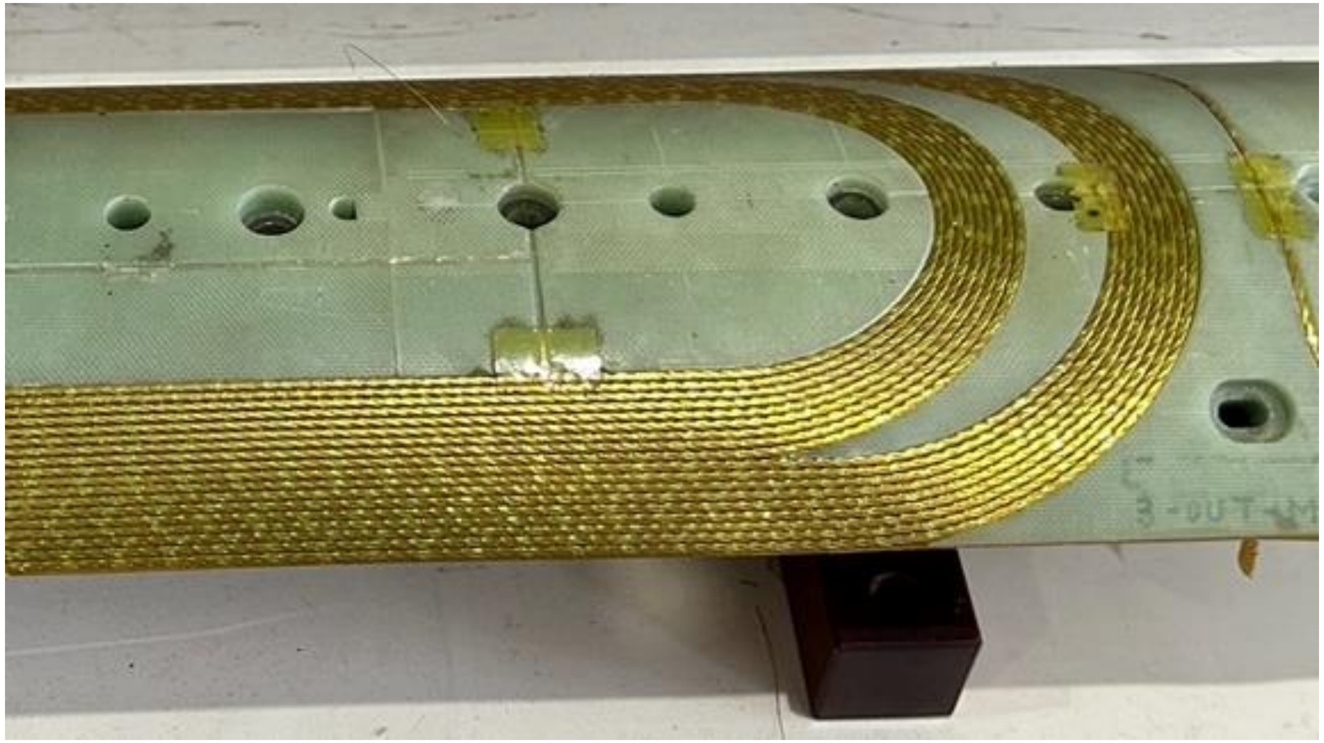


MY750

MSUT

From D. M. Parragh " Irradiation study update: a brief overview" presentation at the Polymer laboratory meeting of 23 Nov 2023

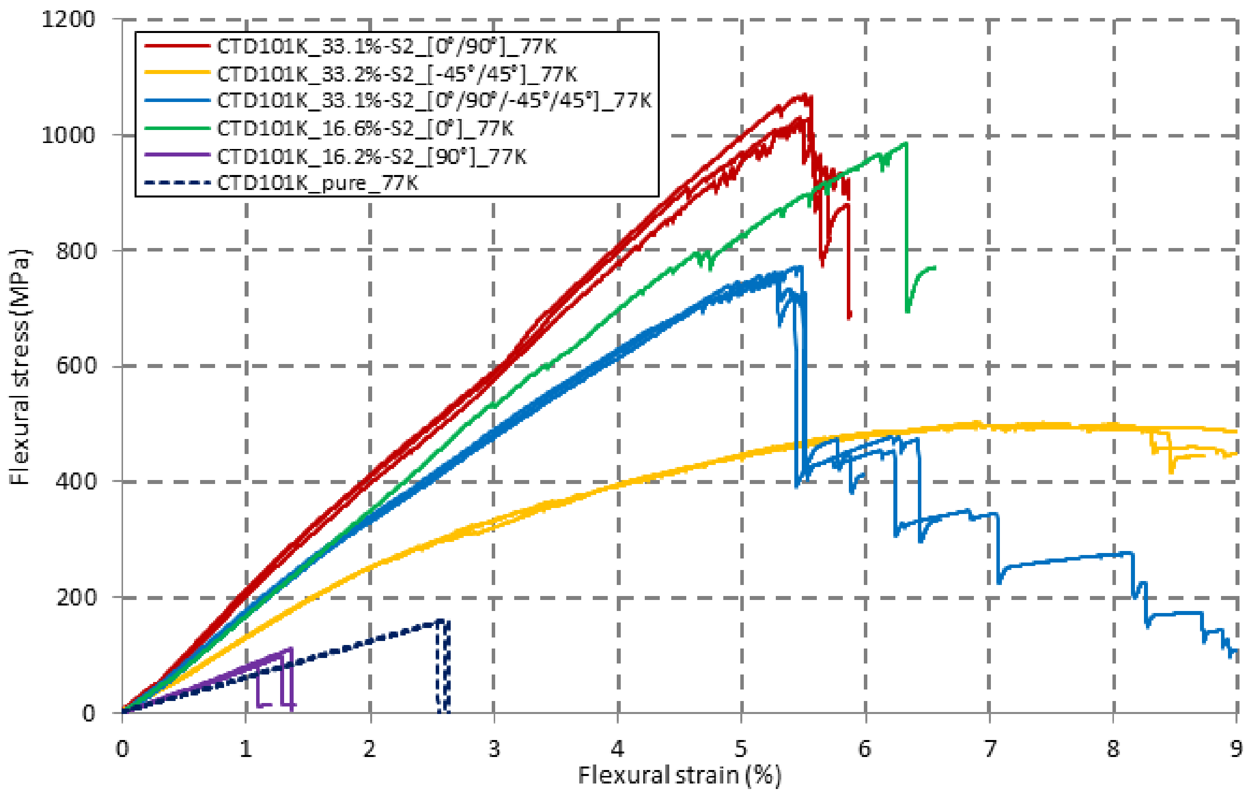
MQXA coil end spacer materials being irradiated to 30 MGy



LHC inner triplet magnet constituents made of EP GC3 (also known as G11-CR) being irradiated to 30 MGy. Samples were cut out from (a) MQXA coil with end spacers produced by KEK and (b) tube from which MQXA coil end spacers have been produced by FNAL.

Effect of fibre orientation to the load direction

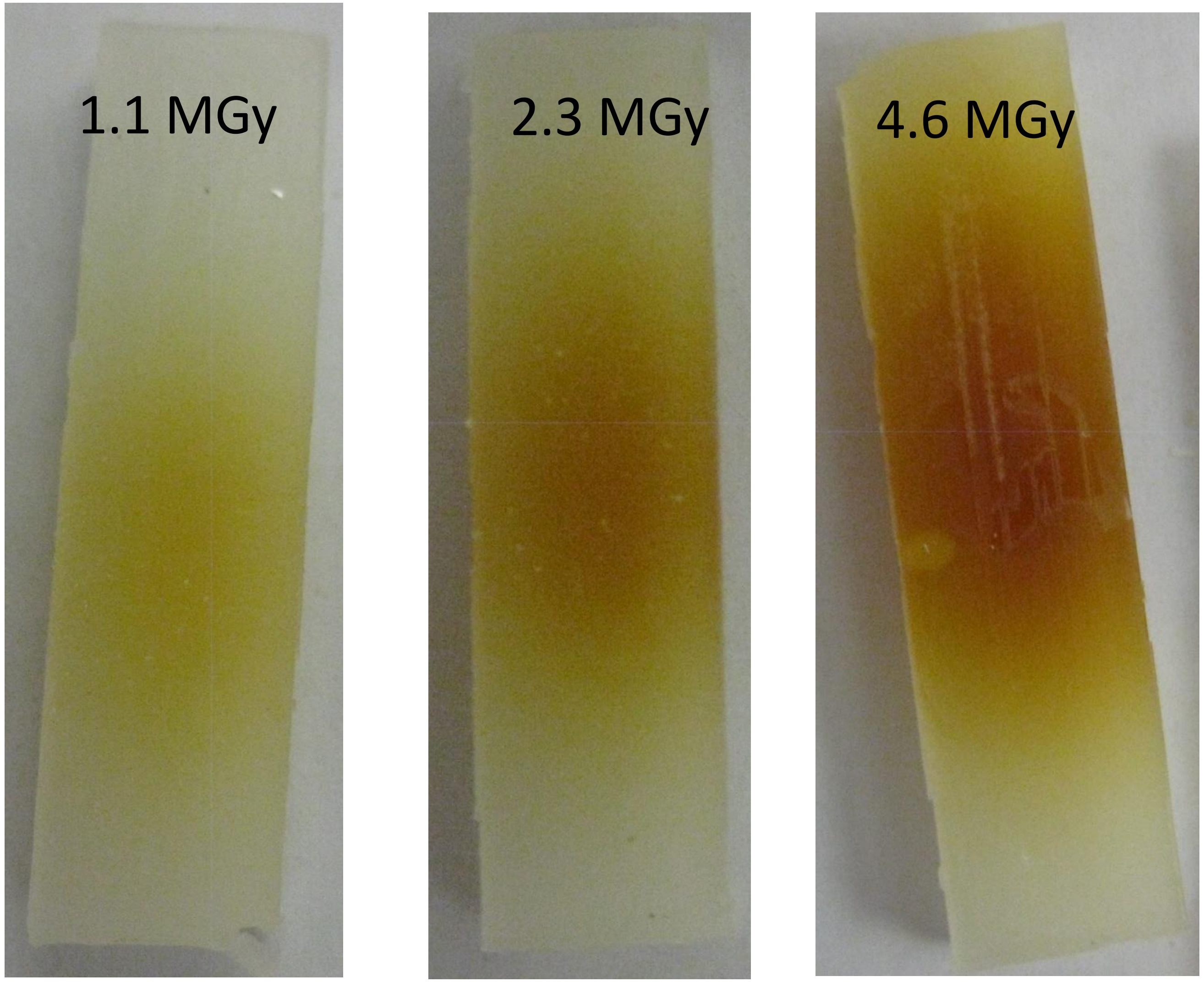
- Most irradiation studies are performed using fibre reinforced composites with [0,90] samples, with the samples mechanically loaded in the fibre orientation.
- In this configuration the test result is determined by the strength of the fibres, and less sensitive to epoxy resin radiation damage.
- In the 2nd stage of the irradiation study, selected fibre reinforced composites will be characterised in different test configurations relevant for their application in superconducting magnets.



77K flexural stress vs flexural strain curves of S2-glass reinforced CTD101K specimens of layups [0°/90°], [90°], [0°], [-45°/45°/0°/90], [-45°/45], and pure CTD101K. **Courtesy P. Wiker.** EDMS 2592927.

Wax

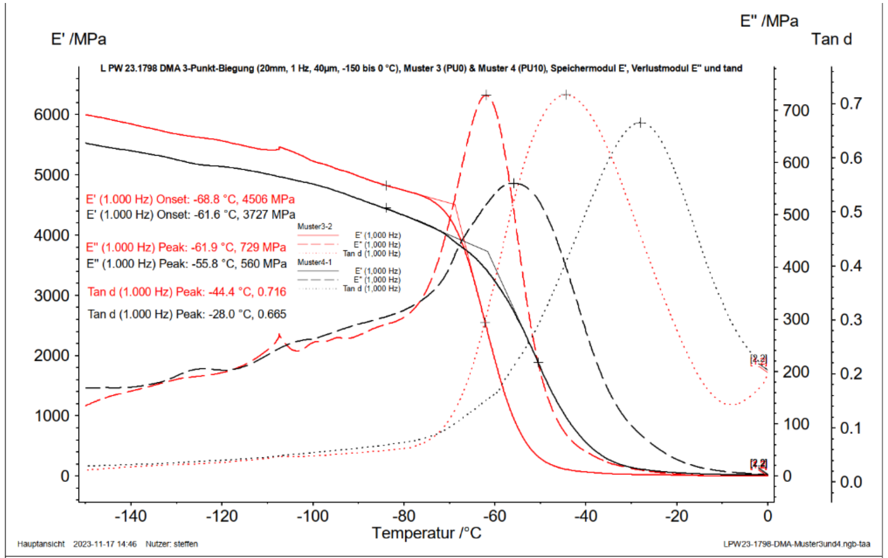
- Wax has been successfully used superconducting magnet coil impregnation.
- Wax samples are provided by A. Brem, PSI.
- Mechanical and dielectric testing methods to assess irradiation damage of wax are to be developed.
- We try to assess irradiation effects from
    - Visual appearance
    - Compression behaviour/hardness
    - Outgassing
    - Volume changes



Visual aspect of Paraffin wax Polarit G 54/56 °C after 24 GeV proton irradiation in ambient air (samples provided by A. Brem, PSI)

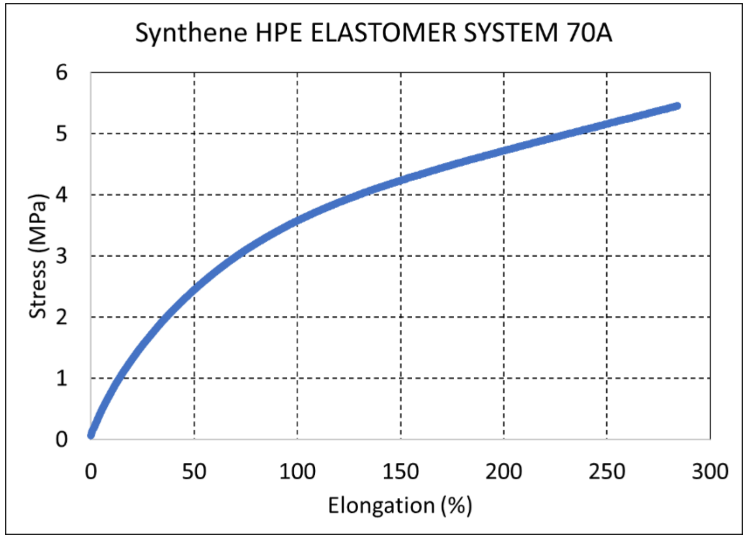
Irradiation induced aging of polyurethane for potential use in the jacks for magnet alignment

- Usable temperature range of polyurethane in jacks for magnet alignment is above T_g (T_g <RT).
- To carry high loads above T_g, polyurethane is to be loaded in nearly hydrostatic conditions.
- For studying irradiation damage the strain at fracture under uniaxial tensile loading before and after gamma irradiation in ambient air is compared.

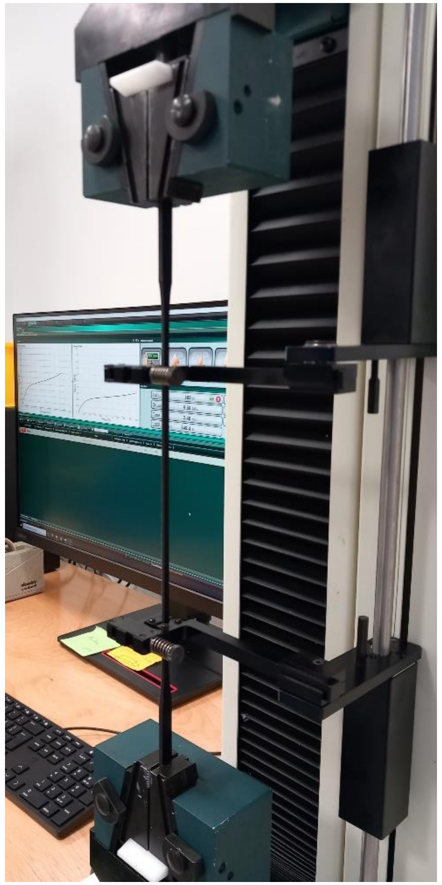


[#] Gerät	Datei	Datum	V..	Probe	Probenabm./mm	S..	Bereich	F	Kalibrierungen	Glättu...
[1.2] DMA 2...	LPW23-1798-DMA-3PB-20mm-1Hz--150-100C-Muster3-2.ngb...	2023-11-...	#..	Muster...	20.000x10.034x4....	2...	-150.0°C/2.0(K/min)/100....	1	2023_04_27D... .em2+2023_05_17D...	1e-00...
[2.2] DMA 2...	LPW23-1798-DMA-3PB-20mm-1Hz--150-100C-Muster4-1.ngb...	2023-11-...	#..	Muster...	20.000x9.977x4.006	2...	-150.0°C/2.0(K/min)/100....	1	2023_04_27D... .em2+2023_05_17D...	1e-00...

E'(T) and E''(T) of HPE70A.
T_g E' onset = -69 °C.



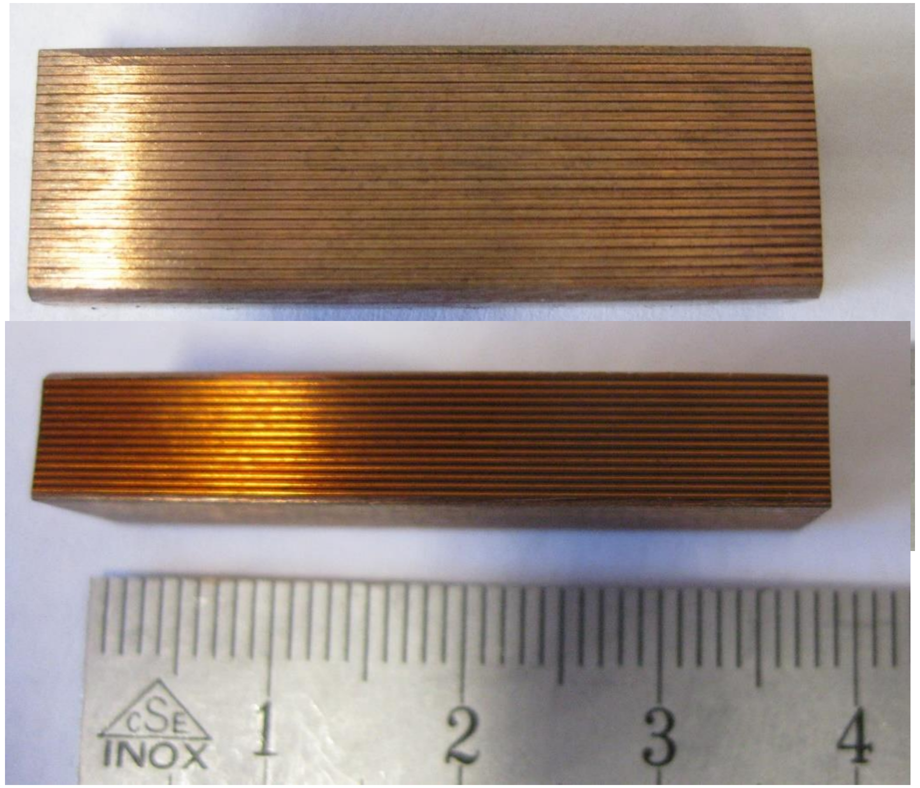
Tensile stress as a function of elongation of HPE70A. ***Courtesy J.-S. Rigaud.***



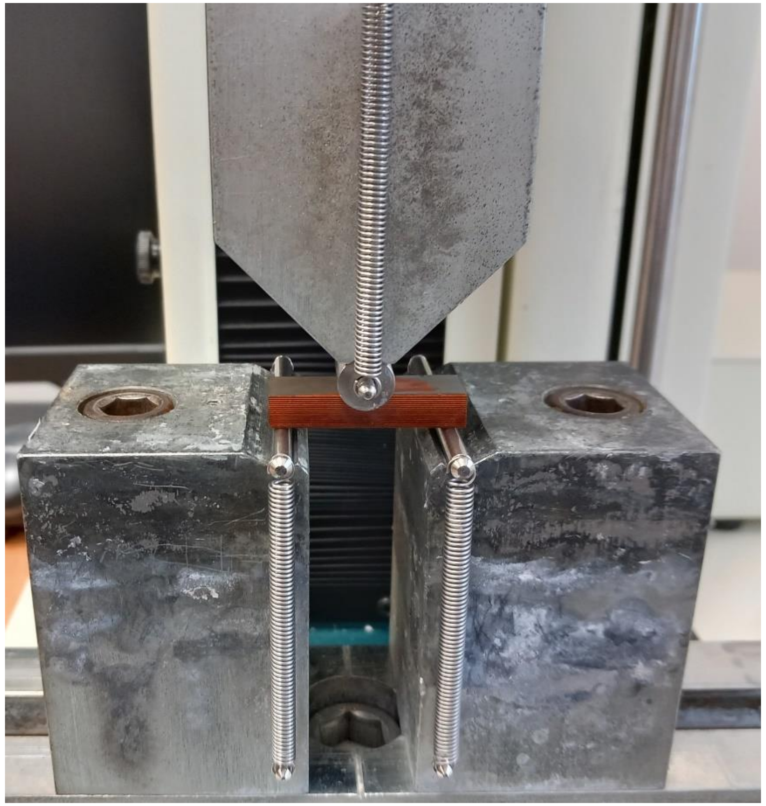
HPE 70A / 12h-40°C, EDMS No. 2957859, E' onset =-69 °C, E'' max = -62 °C, tan delta max = -44 °C
UR 3450 / 12h-40°C, EDMS No. 2957420, E' onset =-62 °C, E'' max = -56 °C, tan delta max = -28 °C

Coil block samples cut from pre-series MCBC coil

- Coil block samples were cut from a pre-series MCBC coil (courtesy F. Wolf).
- The effect of irradiation on the coil block samples impregnated with the Araldite GY 285/Texaco D400 epoxy system has been tested by short beam tests of samples that were irradiated up to 8 MGy.



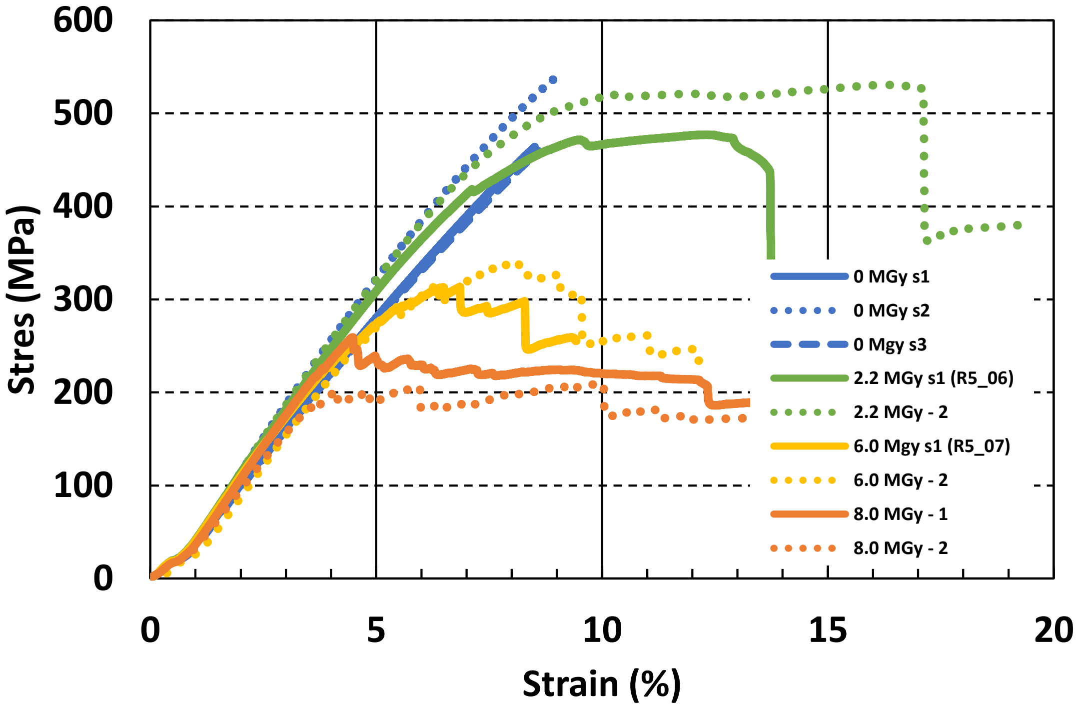
MCBC coil block sample.



Short beam test of MCBC coil block sample.

MCBY coil block sample impregnated with Araldite G 285 + Texaco D400

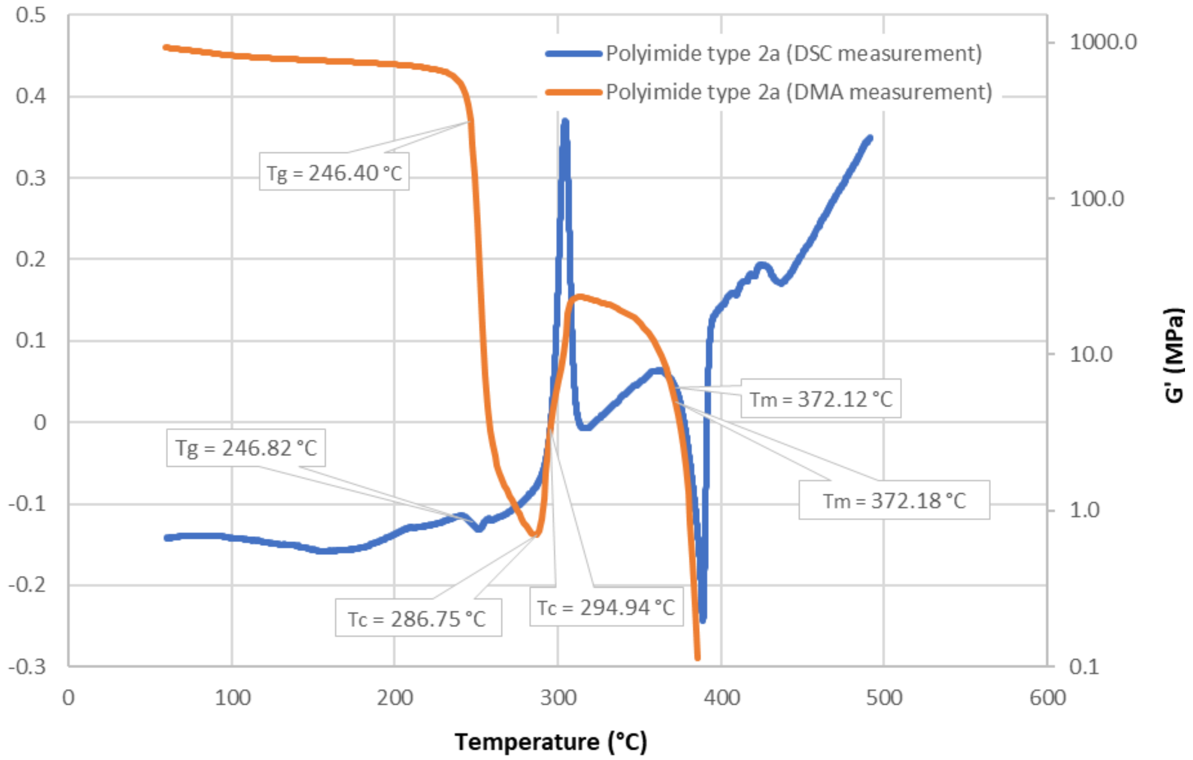
- Coil block samples were tested in short beam configuration (Nb-Ti/Cu wires are aligned parallel to the load direction).
- Unirradiated sample short beam strength exceeds the stress range accessible with the 5 kN test machine.
- Short beam strength decreases with increasing dose, indicating an irradiation induced degradation of the epoxy matrix.
- 3-point bending is not representing the load case in the magnets.
- Transverse compressive stress-strain behaviour is probably much less influenced by degradation of the epoxy matrix.



Short beam bending stress – strain curves of MCBC coil block samples before and after irradiation to 8 MGy. Courtesy of D.M. Parragh.

Differential Scanning Calometry (DSC)

- Glass transition is often hardly detectable in DSC.
- Crystallisation causes a sharp endothermic peak in DSC, and a strong increase of G'.
- Crystallinity of thermoplastics can have a strong influence on the aging behaviour.
- The polymer's percent crystallinity can be derived from DSC.



Comparison of DSC and DMA temperature sweep of extruded polyimide.

DSC courtesy D. Ternova, DMA courtesy N. Martin. EDMS No. 2885849, (2023)