ETH zürich

Towards epoxy resins for cryogenic applications

CHART workshop
June 9th, 2022

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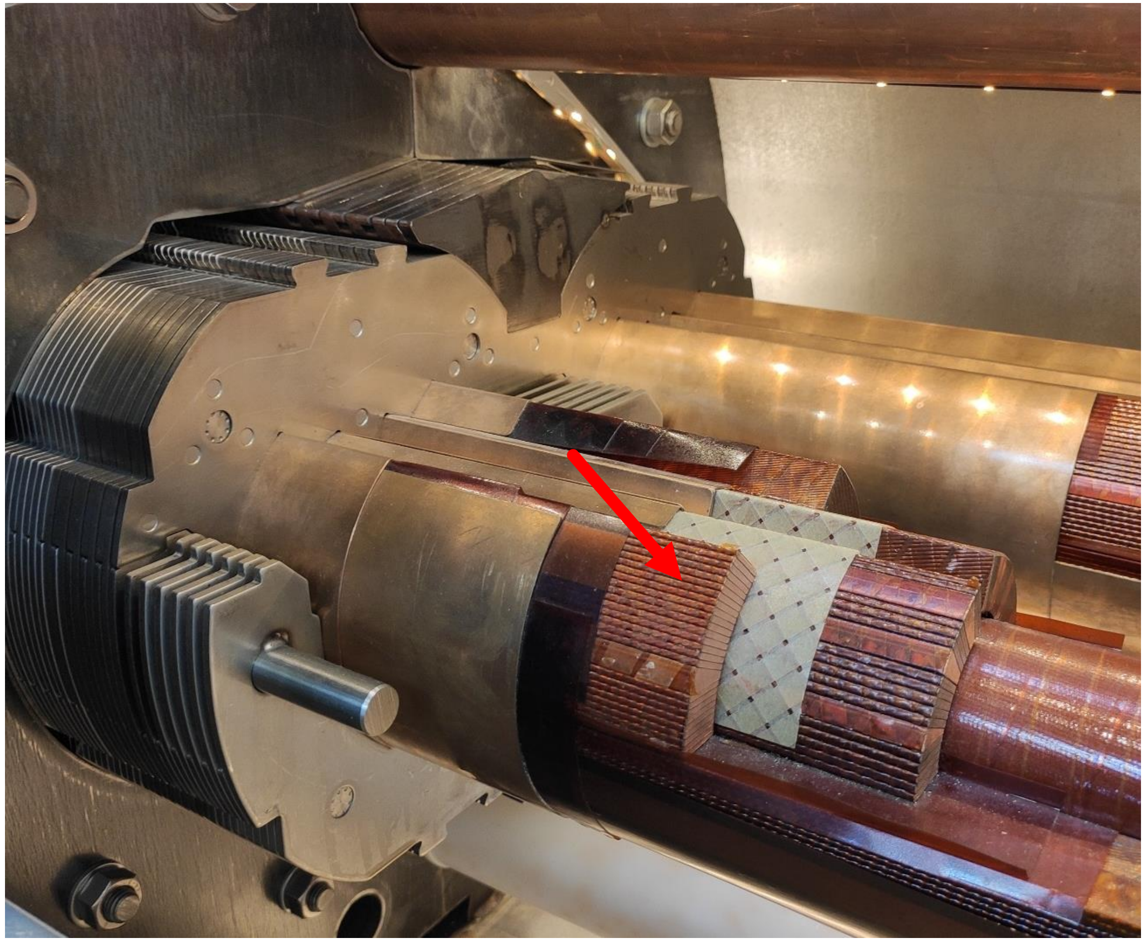
Superconducting electromagnets



- Stresses in epoxy insulation
  - Thermal stresses
  - Lorentz forces

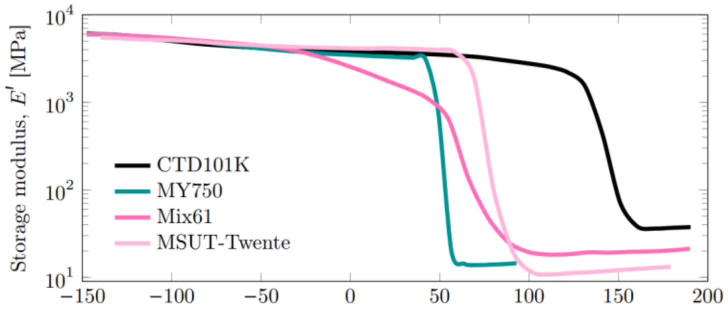
- Cracking / Delamination / Yielding → Quenching of magnet

- Goal: Develop a new epoxy resin
  - Longer pot-life than current resins
  - Good fracture resistance at 4 K (tested at 77 K)
  - Solid at room temperature

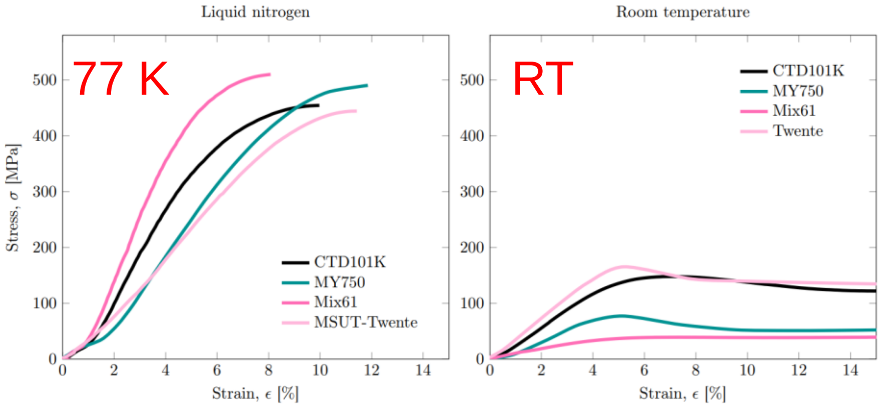
- Develop an understanding
  - Relation between toughness and structure
  - Adhesive properties

Previous Research (André Brem et al.)

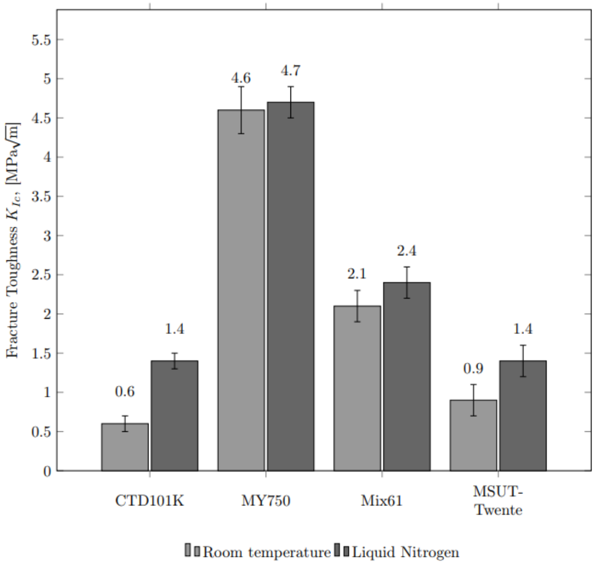
- 4 resin systems
  - Elastic modulus

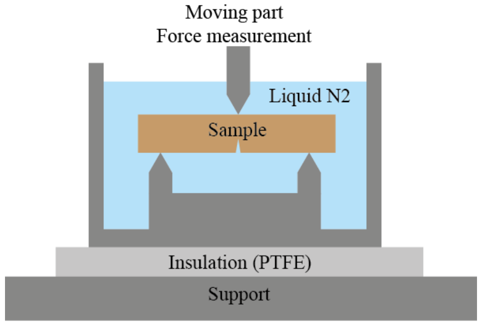


  - Yield in compression



- Fracture toughness
  - Large differences, even at 77K

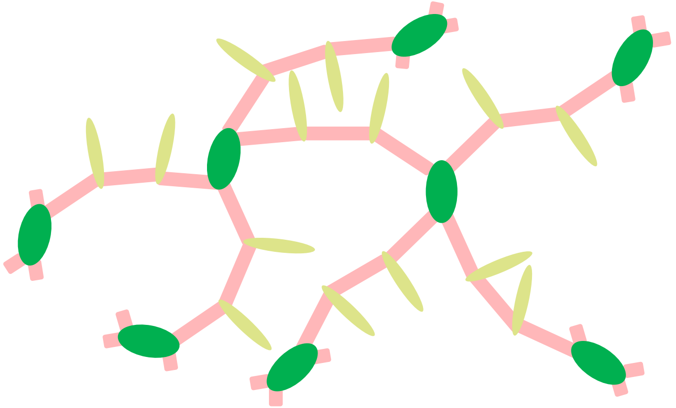




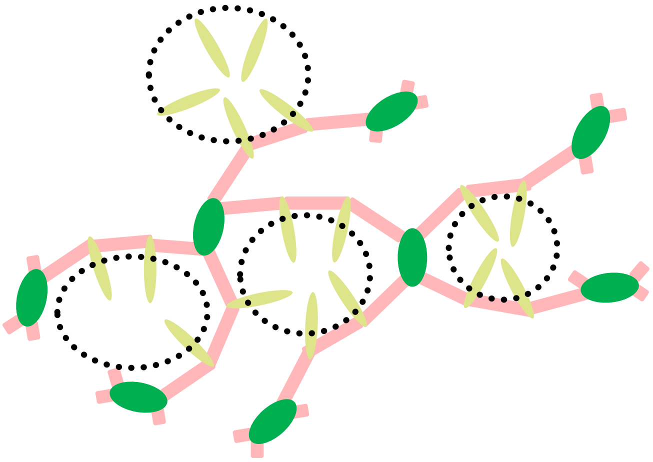
Network design parameters

➢ F = 4	Functionality of hardener	F ∈ {4, 3, 2}
➢ R = 3:2	Ratio DGEBA:Aliphatic amine	R ∈ {1:0, 5:4, 9:8}

Example: F=4, R = 3:2

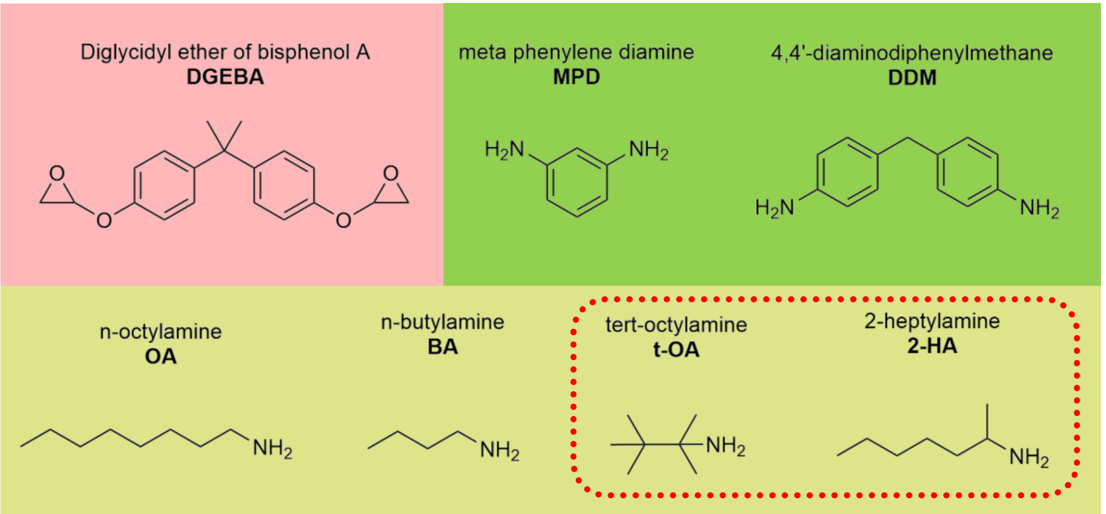


1st hypothesis: Nanodomains



Are there nanodomains and are they responsible for improved properties?

Monomers and reaction mechanism



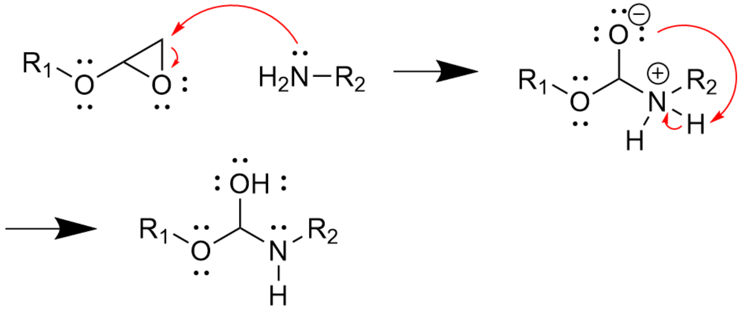
More polar

Less polar / amphiphilic

Sterically hindered

Table 1
Monomers used for synthesizing the epoxy resins. F denotes the functionality of the component. EEW denotes the epoxide equivalent weight (g/mol).

Name	Abbreviation	F	EEW
bisphenol A diglycidyl ether	DGEBA	2	172
meta phenylene diamine	MPD	4	27.0
4,4'-diaminodiphenylmethane	DDM	4	49.6
n-octylamine	OA	2	64.6
n-butylamine	BA	2	36.6
tert-octylamine	t-OA	2	64.6
2-heptylamine	2-HA	2	57.6



Sample overview

Table 2
Sample overview

	System	ID	R	f	KIC (RT)	KIC (LN2)	Tg (max tand)	Density
Var. R	DGEBA, MPD	Base	1:0	4	0.8 ± 0.1	2.0 ± 0.1	160.1	1.217
	DGEBA, BA, MPD	BA-4-5:4	5:4	4	1.2 ± 0.2	3.5 ± 0.6	68.3	1.153
Var. R / Var. f	DGEBA, BA, MPD	BA-4-9:8	9:8	4	1.5 ± 0.1	4.1 ± 0.6	61.4	1.145
Var. f	DGEBA, BA, MPD	BA-2-9:8	9:8	2	1.9 ± 0.2	5.3 ± 0.4	n.a.	1.145
Var. f / Var. sidechain	DGEBA, BA, MPD	BA-3-9:8	9:8	3	1.6 ± 0.1	5.0 ± 1.1	73.0	1.147
Var. sidechain	DGEBA, OA, MPD	OA-3-9:8	9:8	3	1.8 ± 0.1	4.4 ± 0.5	54.4	1.109
	DGEBA, t-OA, MPD	tOA-3-9:8	9:8	3	1.0 ± 0.1	2.7 ± 0.4	100.7	1.108
	DGEBA, 2-HA, MPD	2HA-3-9:8	9:8	3	1.8 ± 0.1	4.7 ± 0.3	72.4	1.115
	DGEBA, BA, MPD	BA-3-5:4	5:4	3	1.6 ± 0.2	4.7 ± 0.3	n.a.	1.153
	DGEBA, OA, MPD	OA-4-5:4	5:4	4	1.5 ± 0.2	4.6 ± 0.4	n.a.	1.115

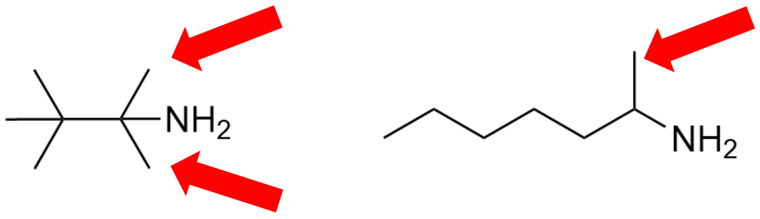
- Addition of Butylamine, Octylamine or 2-Heptylamine → **Improved toughness at 77 K!**
- Due to nanophase separation?

First result: Improved pot-life by sterical hindrance

- Methyl group in β-position → sterical effect!

tert-octylamine
t-OA

2-heptylamine
2-HA



- **Significantly longer pot-life with**
  2-Heptylamine or tert-Octylamine

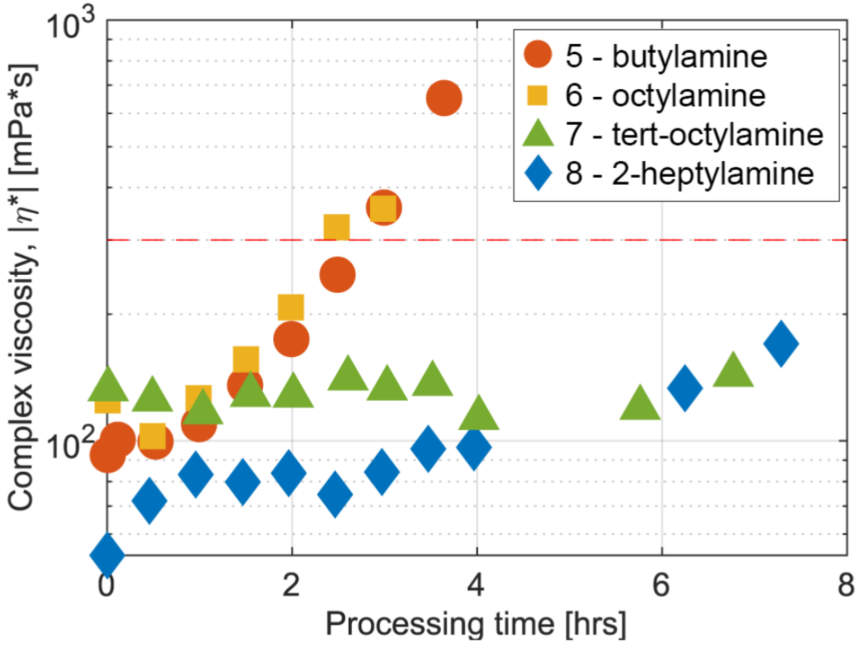
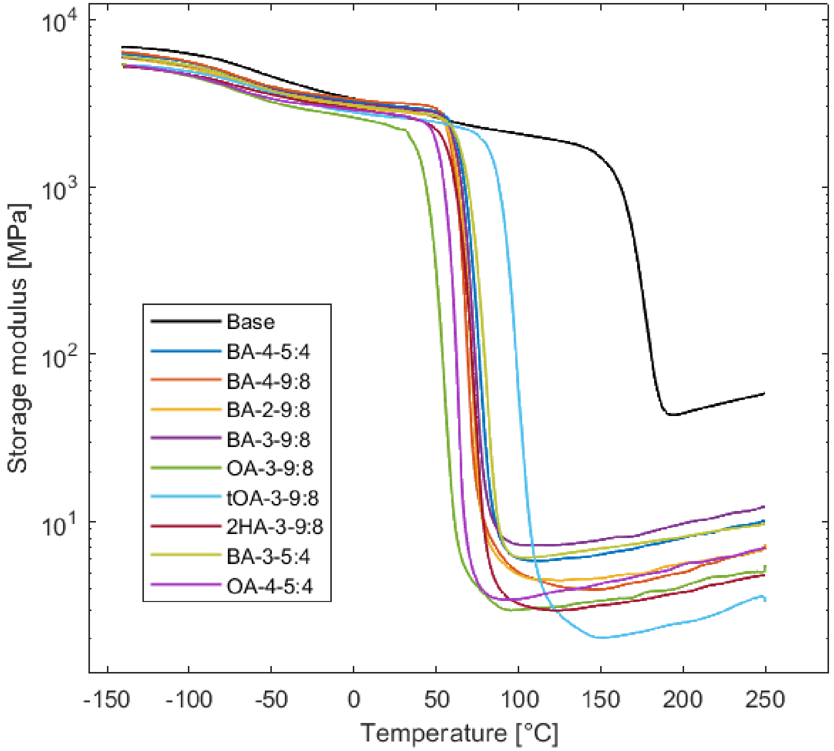
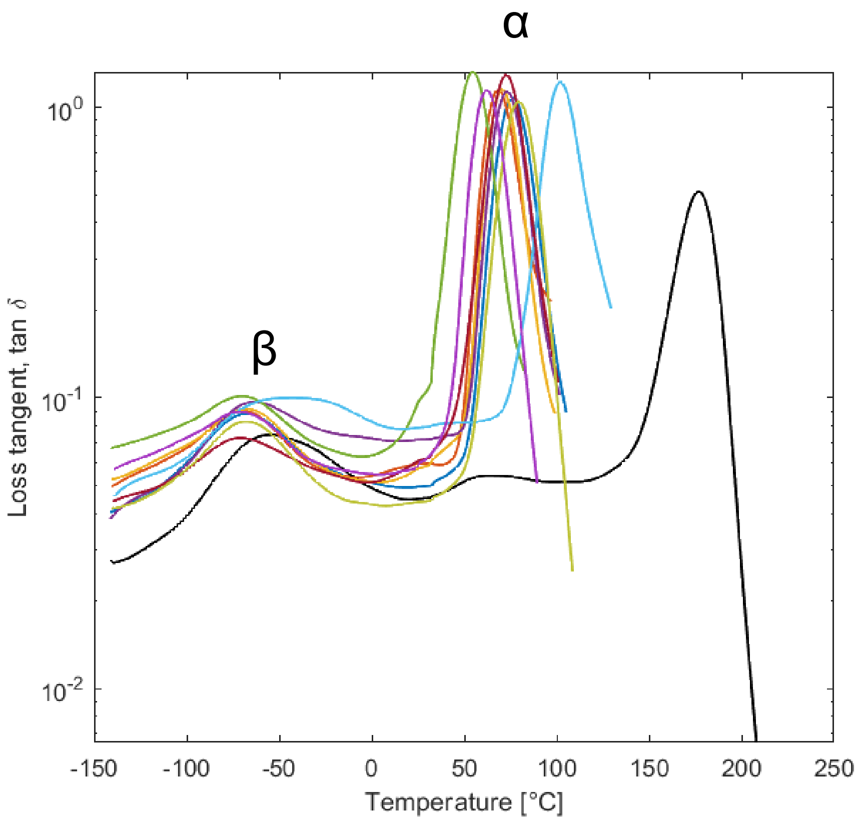


Figure 3: Time dependence of the complex viscosity of as-prepared mixtures stored at 22.5 °C for specified amounts of time. The measurements were done at 22.5 °C.

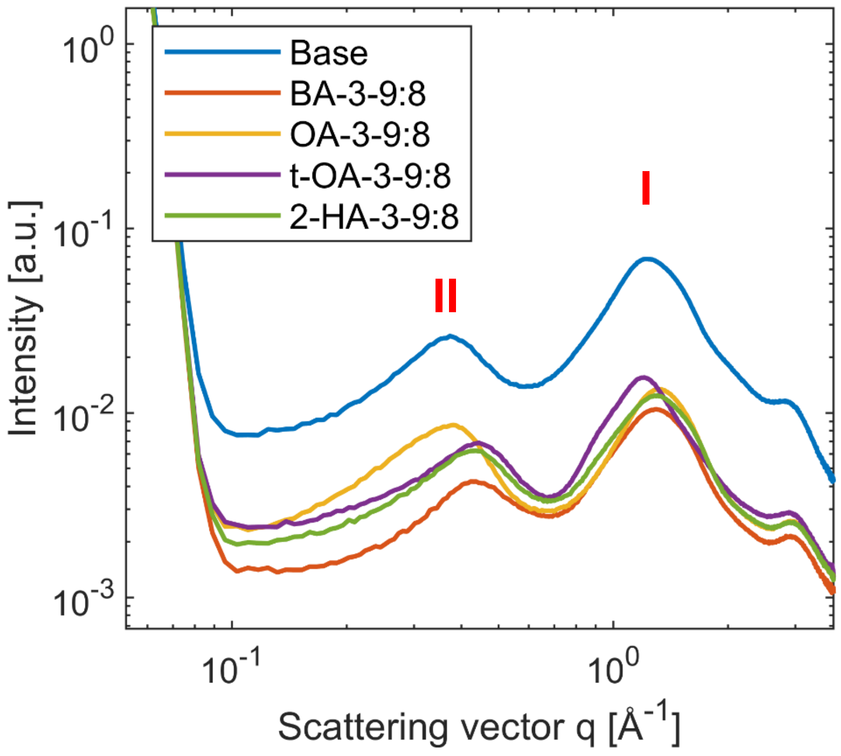
DMTA – No proof for nanophase separation



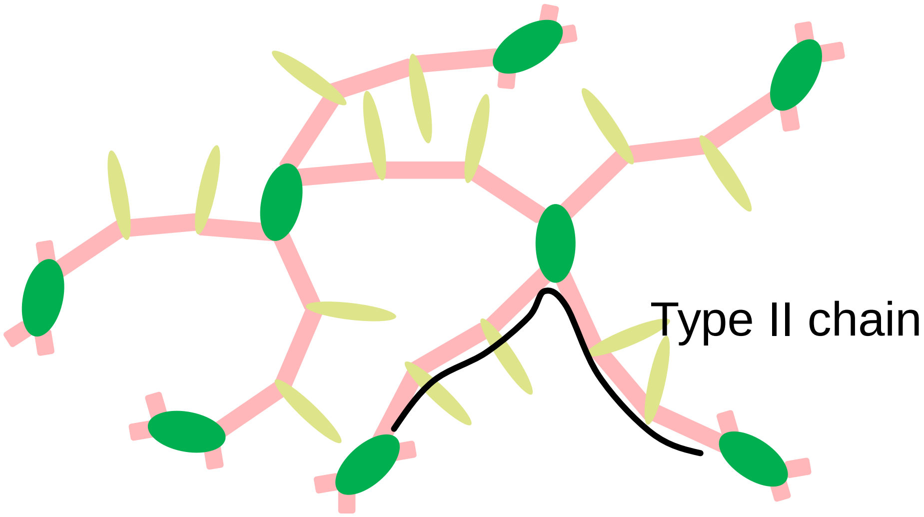


- ➢ Tougher systems seem to have less broad β-relaxation
- ➢ No other relaxations detected – inconclusive with respect to nanophase separation

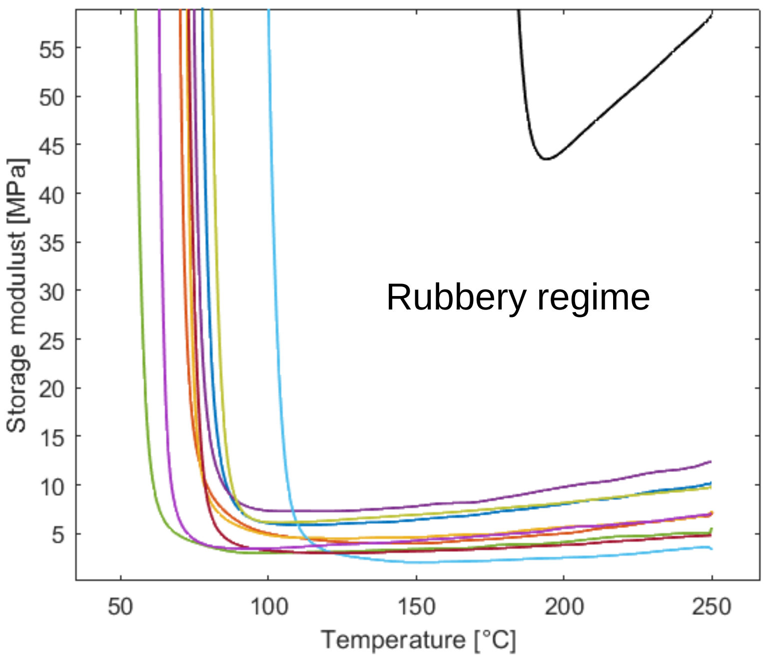
WAXS scattering – Influence of sidechain-type



- Peak I: 1.25 Å^{-1} / 5 Å
  - Amorphous halo (VdW interactions)
- Peak II: 0.4 Å^{-1} / 15 Å
  - Also visible in Base system, ascribed to Type-II chains in the network (Lovell, 1989)
  - Not enough evidence for nanophase separation



DMTA – Extraction of crosslink density



- From rubber elasticity theory:

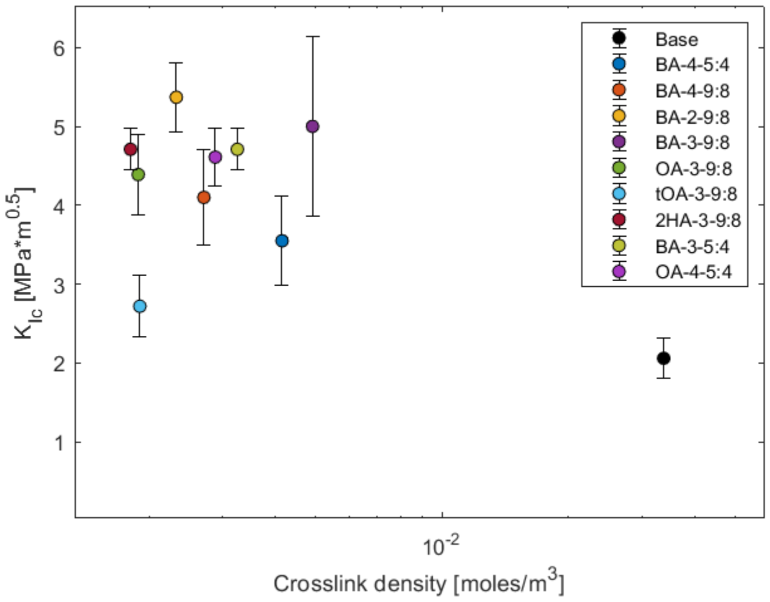
fit from data

$$M_C^{-1} \propto \left(\frac{G_R}{T}\right)\frac{1}{g\rho R} \quad \xrightarrow{\rho_C = M_C^{-1}\rho} \quad \rho_C \propto \left(\frac{G_R}{T}\right)\frac{1}{gR}$$

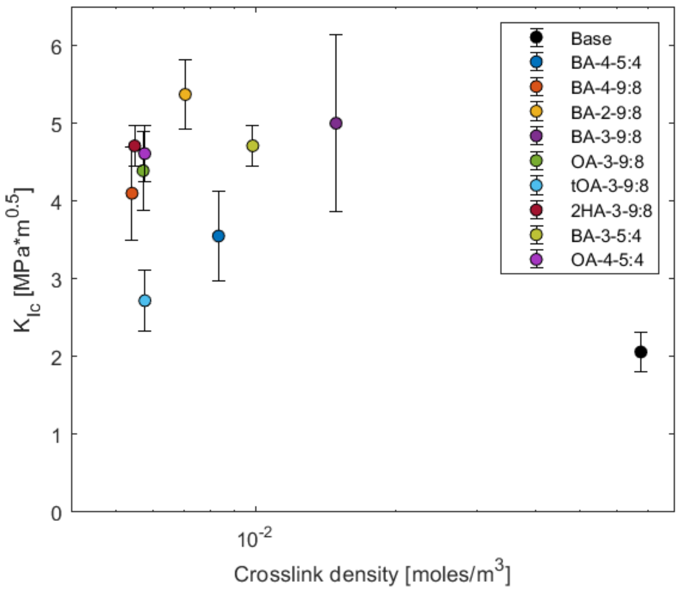
- Variables:
  - M_C Molecular weight between crosslinks [g/mol]
  - g Factor accounting for crosslink mobility
    - g=1 Immobile crosslinks
    - $g=(f_c-2)/f_c$ Mobile crosslinks
  - ρ density [g/cm3]
  - R Ideal gas constant
  - G_R Rubbery modulus [N/mm2]
  - T Temperature [K]
  - ρ_C Crosslink density [mol/cm3]

Dependence of KIC at 77K on measured crosslink density

g=1



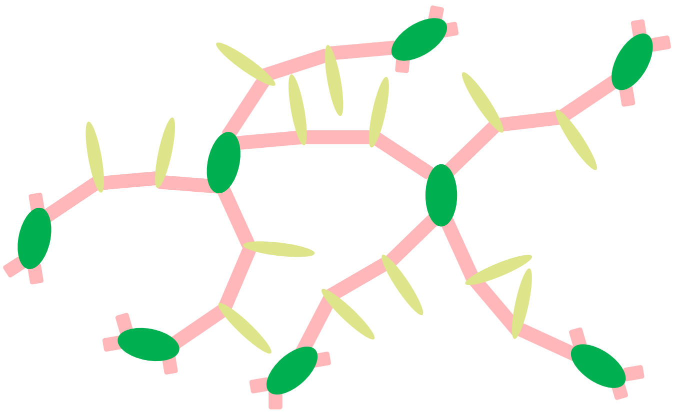
g=(fc-2)/fc



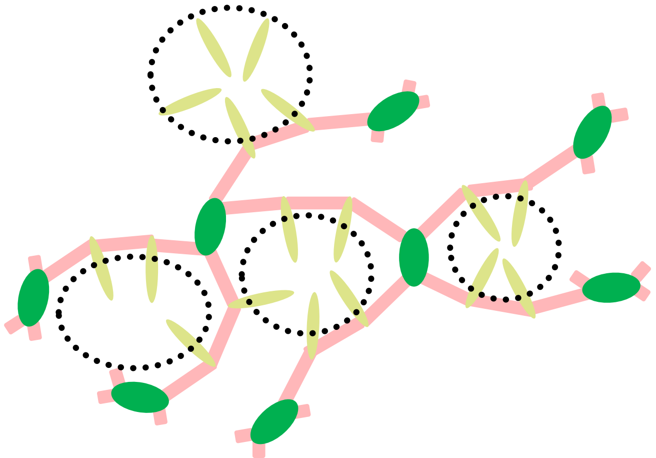
- ➢ The correlation is very weak
- ➢ Crosslink density as reason for improved toughness is also not confirmed

New hypothesis for improved properties

Example: F=4, R = 3:2

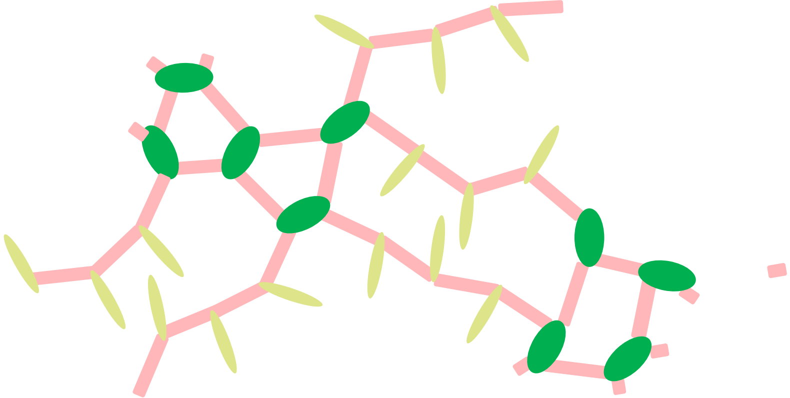


1st hypothesis: Nanodomains



No proof
1. No additional relaxation
2. Very similar WAXS pattern

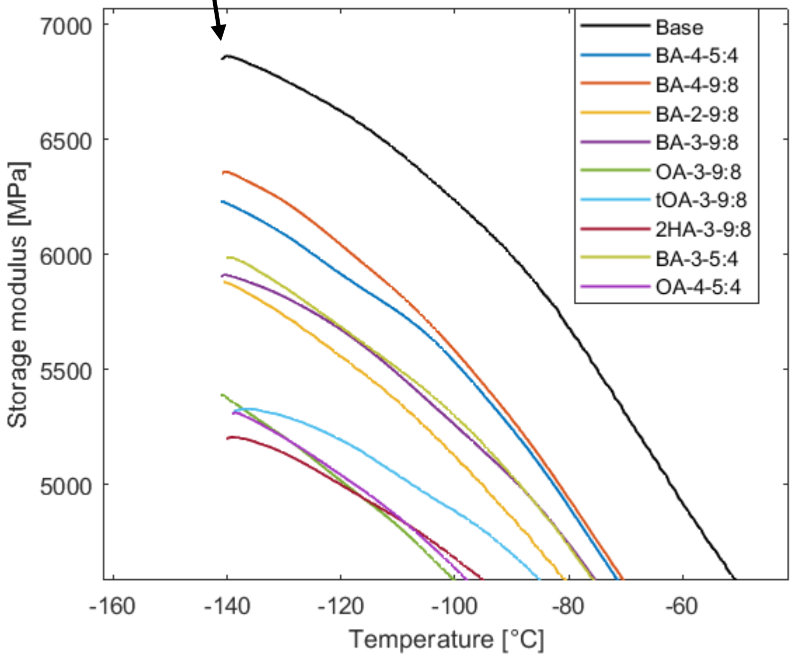
2nd hypothesis: Large scale inhomogeneities

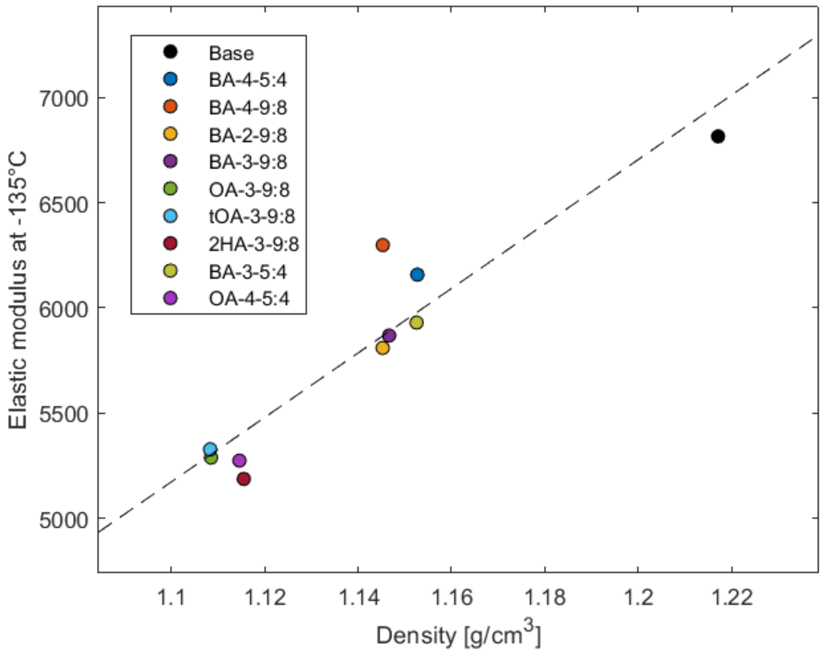


→ SAXS / USAXS measurements planned

Dependence of E‘ at -140°C on measured density

Extraction of moduli





- Lower modulus with more aliphatic side-chains
  - Polyethylene-like chains decrease cohesive energy density

Grüneisens 1st rule (Isotropic van der Waals materials)

$$E_{0K} = 3(1-v)\frac{mn}{4}\frac{E_{\mathrm{coh}}}{V_{0K}}$$

Conclusions

- New, **tough** epoxy resin formulation with **long pot-life**
  - Long pot-life
  - Low viscosity
  - Lower elastic modulus
  - Thermal expansion yet to be measured
- Structure-property relationship for toughness not yet established