Epoxy Chemistry

Research update
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Pascal Studer

Laboratory for Soft Materials

Current research topics

- Characterisation of Araldite CY192-1 / HY918 system

- Phenoxy resins
  - Linear polymers which potentially exhibit high fracture toughness at cryogenic temperatures

- High Tg-epoxy (Tg > 140°C)
  - For engineering a specific epoxy composite with UHMWPE

- High K_{1c}-epoxy by adding reactive diluents to high Tg epoxy

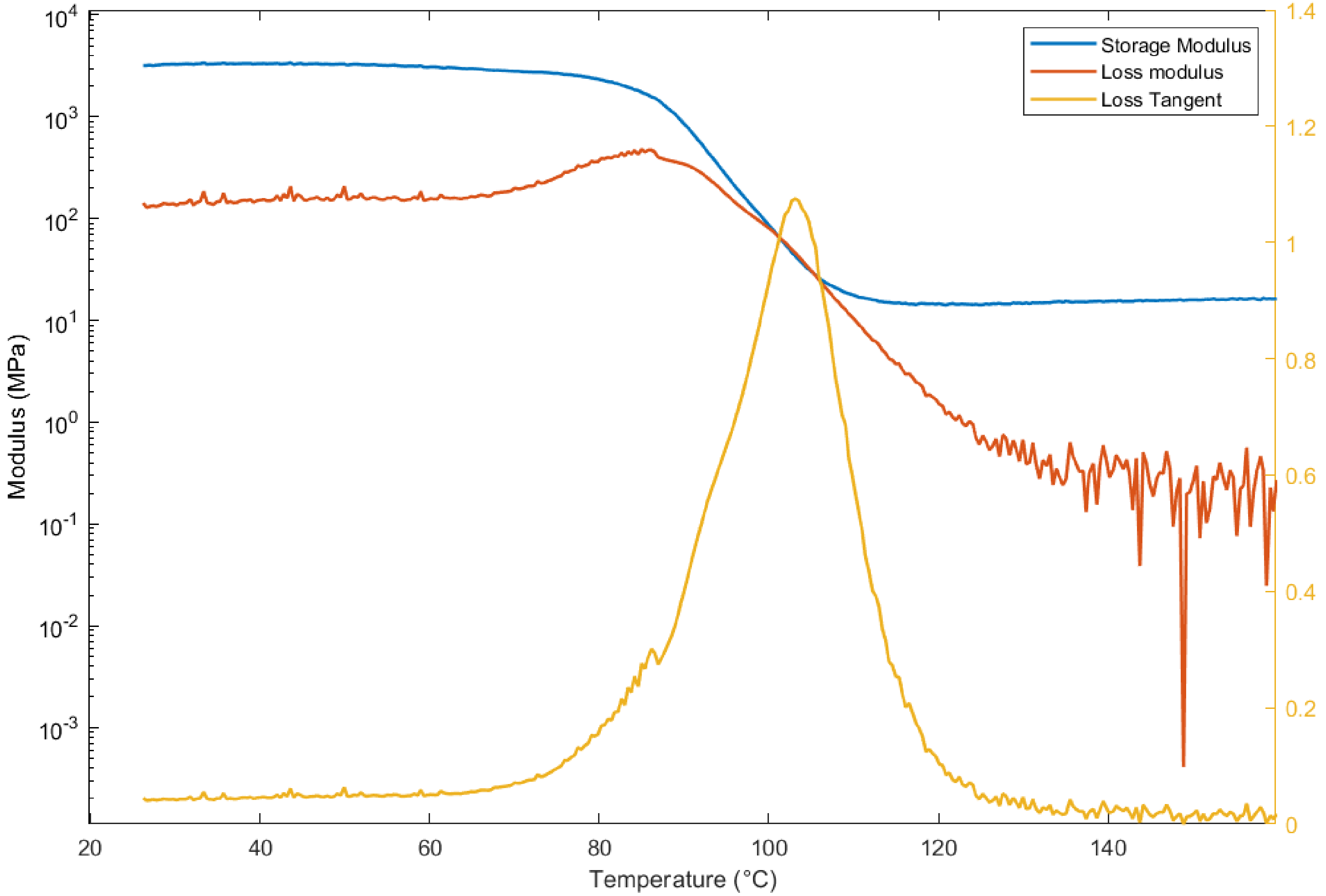
Araldite CY192-1 / HY918

- T_g: 89°C by DSC (inflection point)
- Fracture toughness: KIc
  - Significant increase at lower temperature, but still low compared to MY750!

RT	LN2
0.87	2.79
0.92	2.07
0.86	2.57

Araldite CY192-1 / HY918

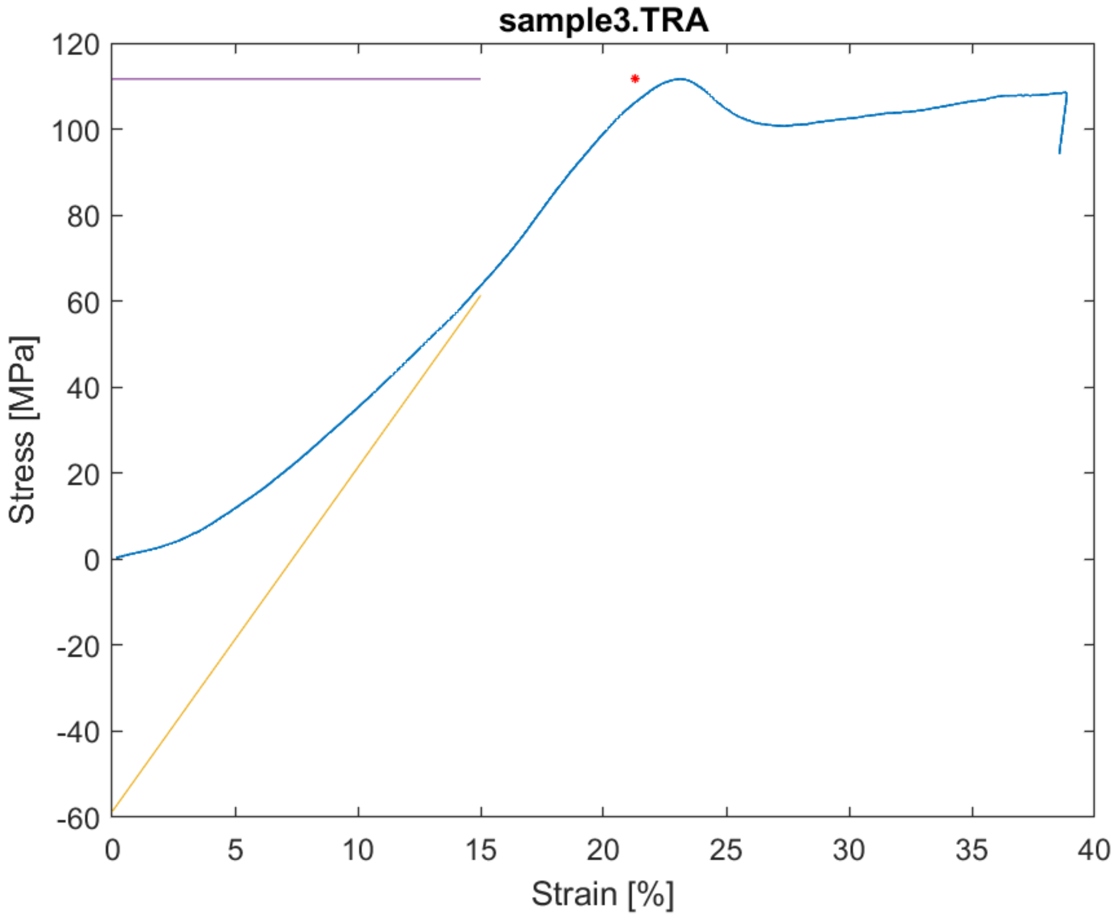
- DMTA
  - 3-point bending, 1 Hz, 0.02% strain, 2°C/min
  - E‘ at 25°C: 3.2 GPa
  - Tg from max(tanδ): 103°C
- Flexural bending:
  - E‘ at 25°C: 3.06 GPa



Araldite CY192-1 / HY918

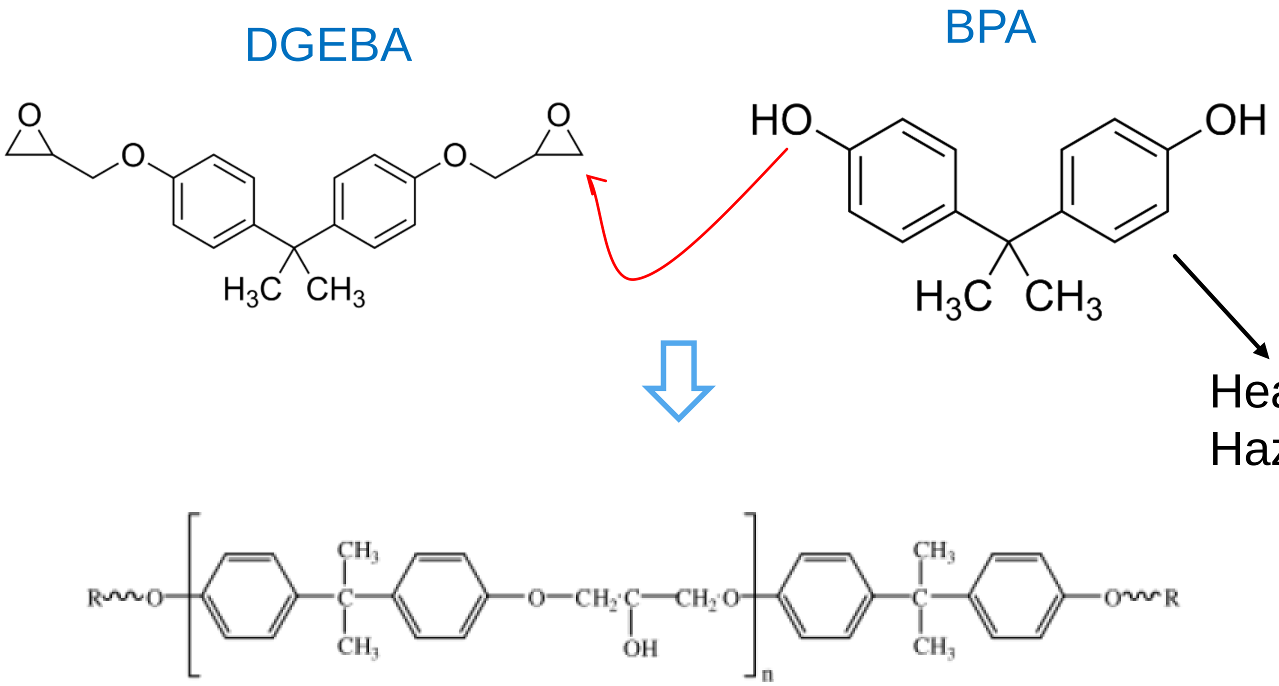
- Compression testing at $0.1s^{-1}$
  - Brittle fracture in LN2
  - At RT:

Yield strain (%)	Yield stress (Mpa)
22.1	116.3
21.3	111.6
20.3	109.0



Phenoxy resins

- Phenoxy resins are mainly linear
  - Increased fracture toughness at cryogenic temperatures



Health Hazard!

D: DGEBA + BPA
E: DGEBiphenyl + BPA
F: Novolac + BPA

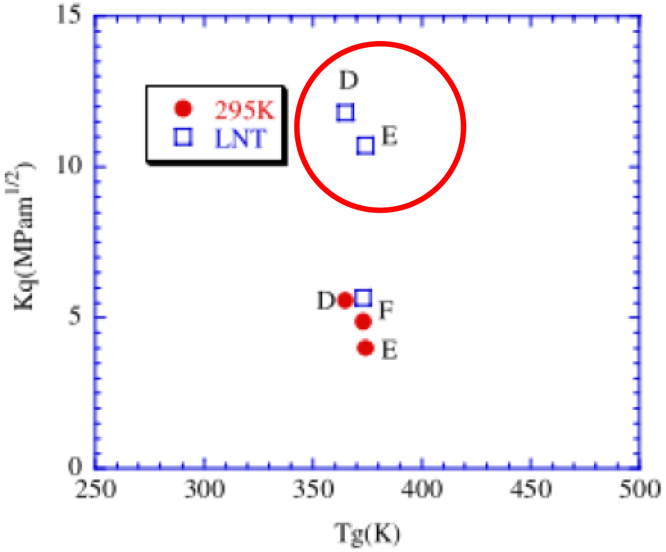


Fig. 9. Relationship between K_q and T_g.

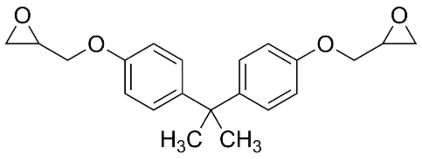
Epoxies for cryogenic use: Ueki et al., Cryogenics, 2004, DOI: 10.1016/j.cryogenics.2004.07.002

Phenoxy resins

- Starting system

Lower melting point (110°C)
Less toxic
Lower viscosity

Resin
DGEBA
(A)



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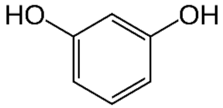
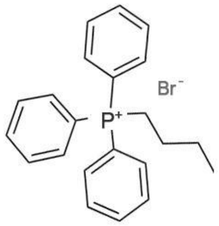
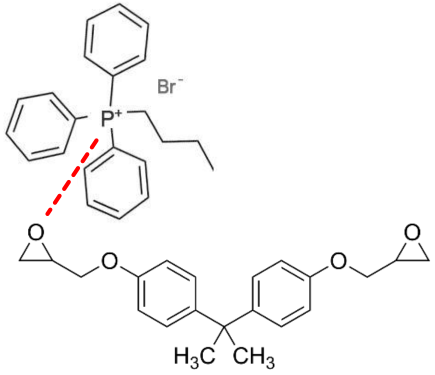
Hardener
Resorcinol (RSO)
(B)



Latent catalyst
Butyl triphenyl phosphonium bromide
(C)



  - Example: 14.72g DGEBA, 4.74g RSO, ~6.8mg catalyst
  - A and B: equimolar amount



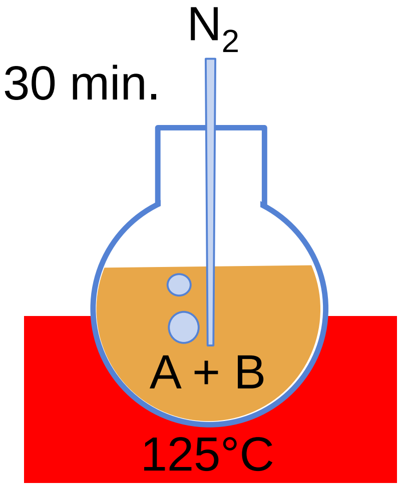
DMATL.

Example synthesis: Shih et al., J. appl. Polym. Sci., 1999, ISSN: 00218995

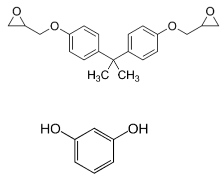
Phenoxy resins

- Current processing method

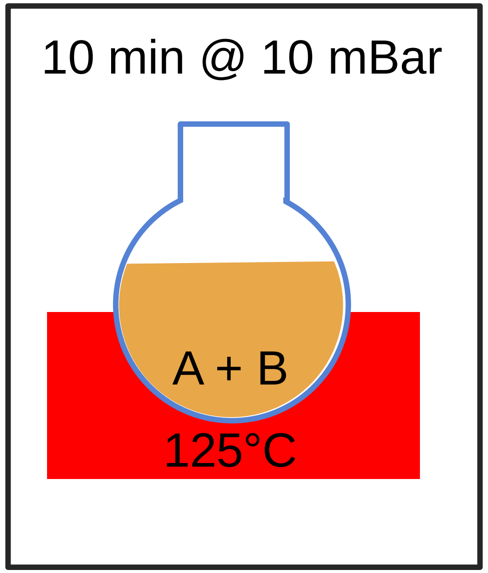
Liquify mixture



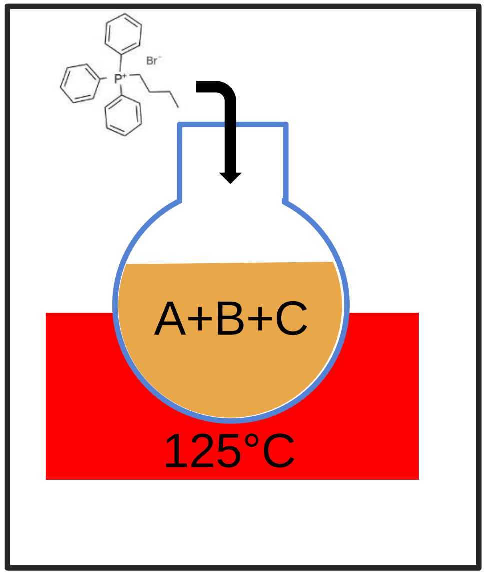
30 min.



Degas

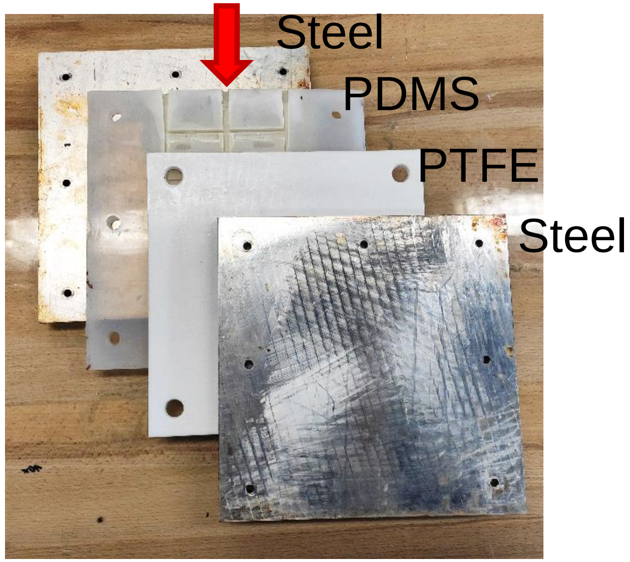


Add catalyst



(Catalyst stored in vacuum @ 50°C)

Fill mold



Mold preheated to 130°C

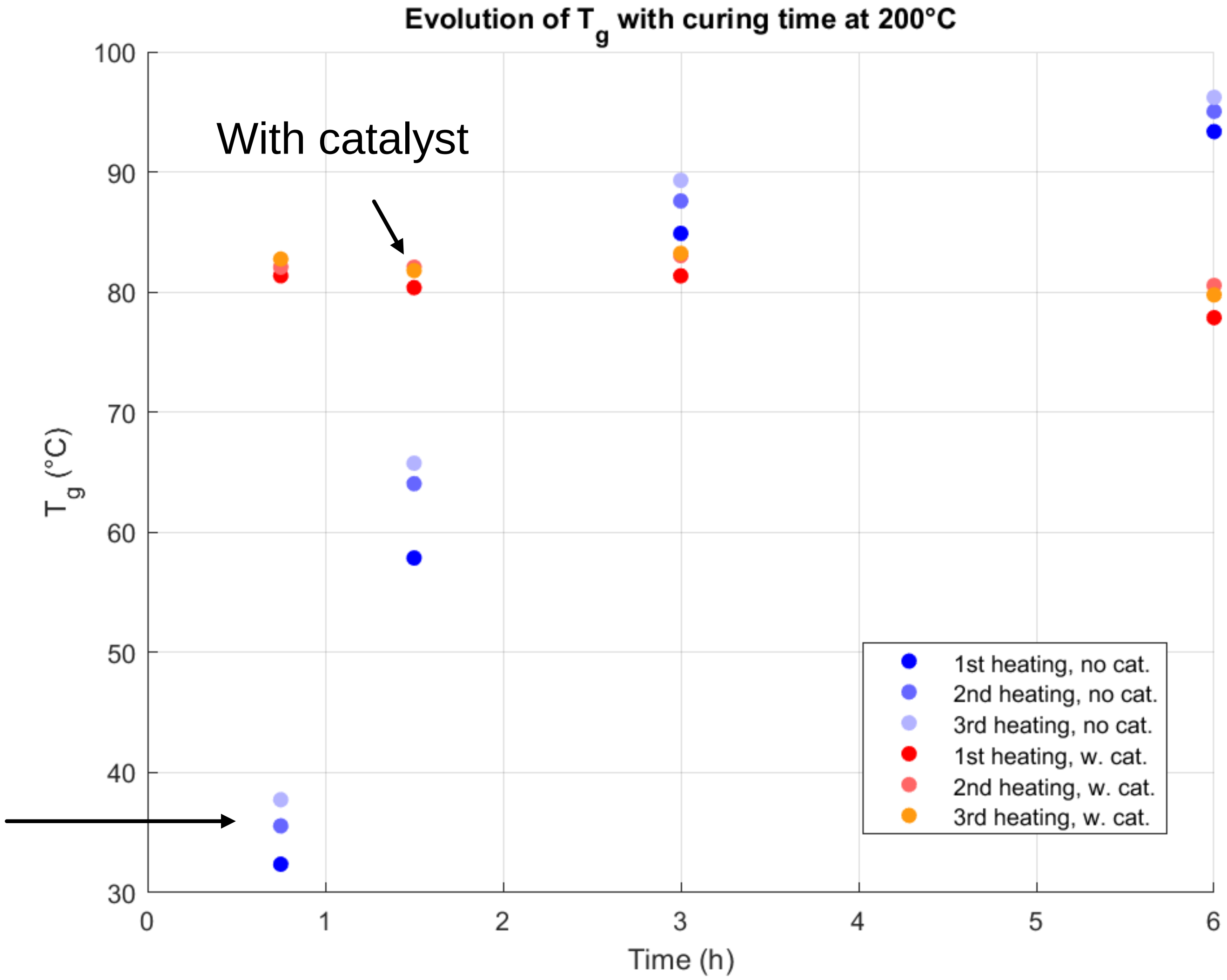
Cure

~30 min @ 200°C

Example synthesis: Shih et al., J. appl. Polym. Sci., 1999, ISSN: 00218995

Phenoxy resins

- Results
  - Effect of catalyst on curing times
  - More catalyst results in higher Tg



With catalyst

Without catalyst

Phenoxy resins

- Problem: Bubbles in the samples
  - Water bubbles due to condensation of hydroxy-groups?
    - No, mass loss during curing insignificant
      - 4.0 Mass. ‰ without catalyst
      - 1.9 Mass. ‰ with catalyst
  - Catalyst interaction with PDMS mold?
    - No, samples cured without catalyst also have bubbles!
    - Without catalyst: Longer curing time (~6h)
  - Residual gas in the mixture?
    - Probably no
      - When degassing at 10mbar, first strong bubbling, then less and less
      - Going to lower pressures, mixture begins boiling
      - Resorcinol: Vapour pressure P=3.35 mBar @ 125°C (Antoine Equation)

- Trying a lower curing temperature…

Phenoxy resins

- T_{Cure} = 165°C
- Samples for DSC study

Non-catalyzed

1h 2h 4h 7h 14h

catalyzed

1h 2h 4h 7h 14h

1,6-Hexanediol
Instead of
Resorcinol

14h 14h

Liquid

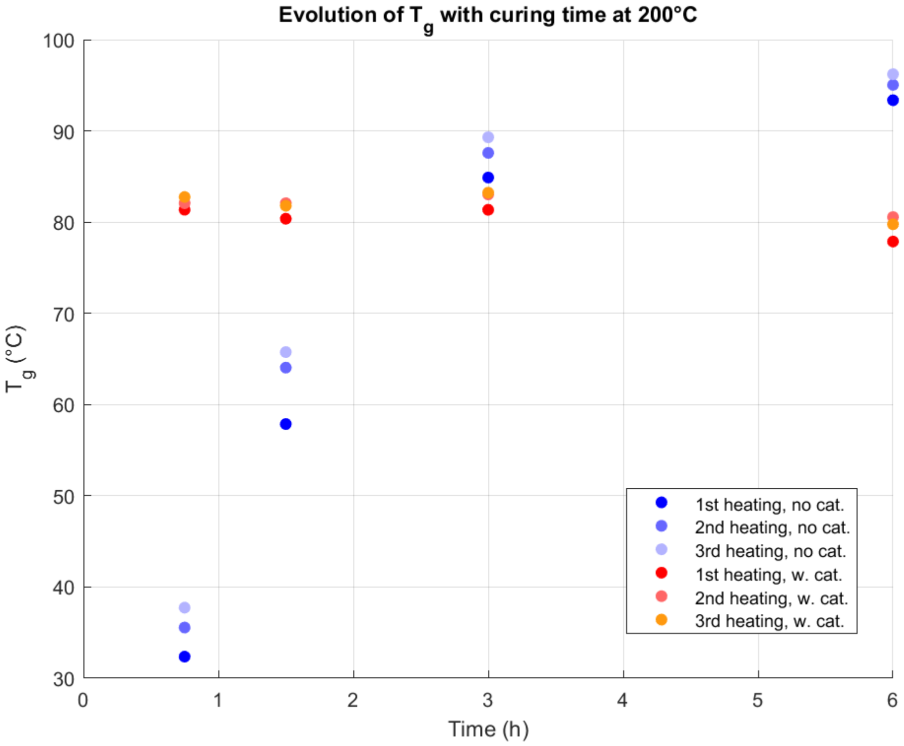
„Honey-like“

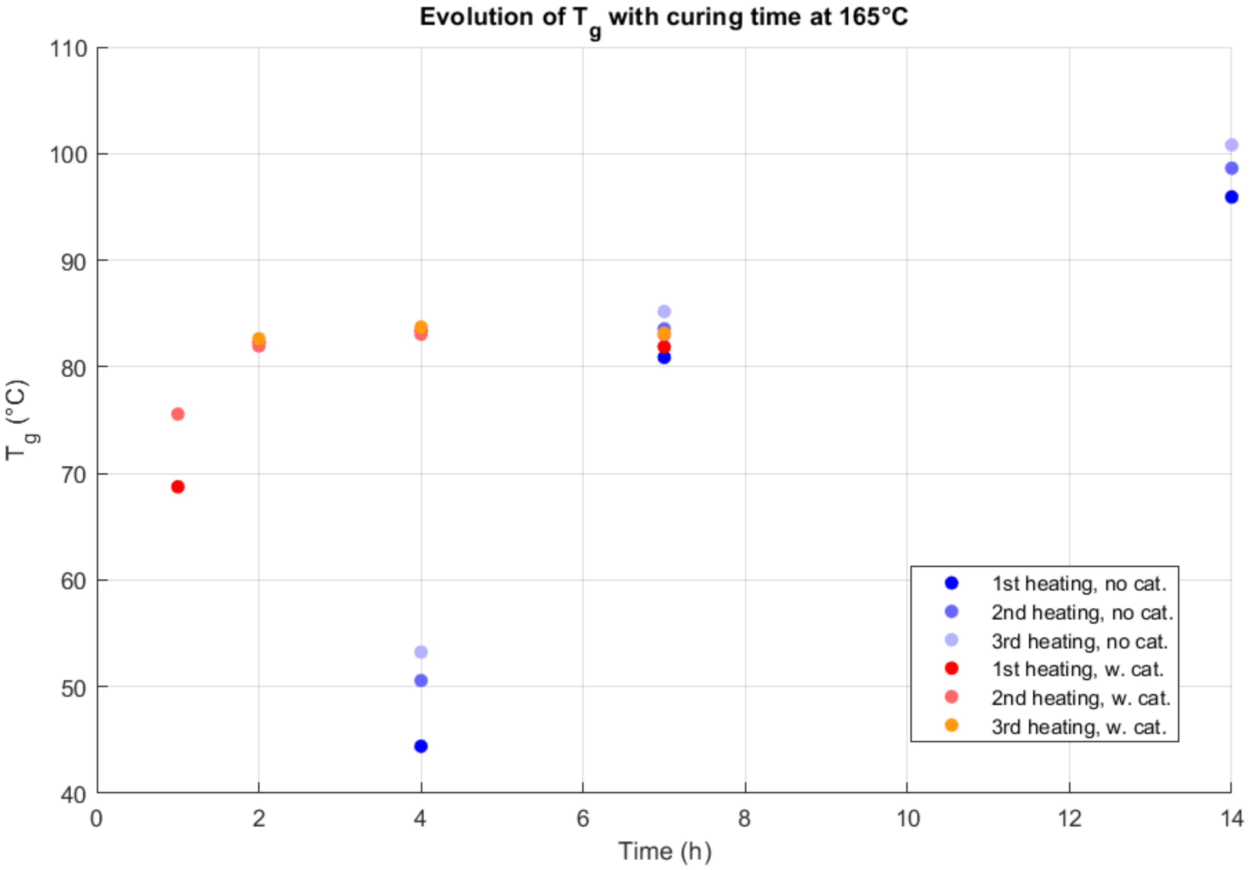
liquid

Phenoxy resins

- T_{Cure} = 200°C

T_{Cure} = 165°C → almost no bubbles!





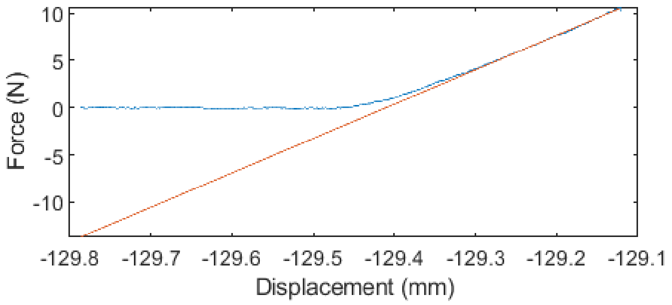
Phenoxy resins – characterization

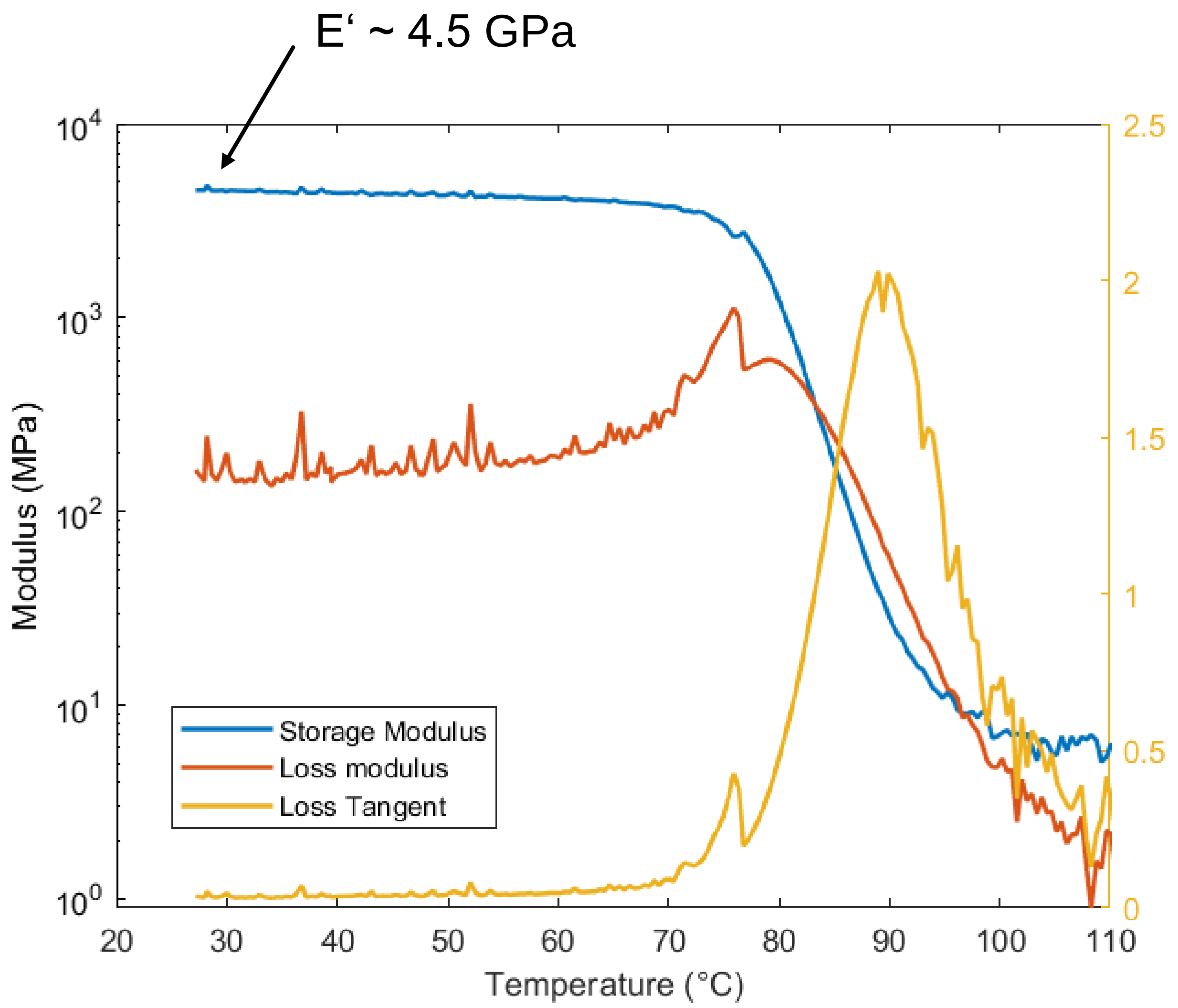
- Single-etch notch bend specimens
    - W x H x L ~ 5mm x 9mm x 40mm
    - Tested with 200N loadcell @ Zwick
- Calculated KIc values (MPa*m$^{0.5}$)

RT	LN2
1.09	1.62
1.23	1.55
0.86	1.46
1.08	1.46
0.63	

Phenoxy resins – characterization

- Bending specimens
    - W x H x L ~ 4mm x 3mm x 40mm
- DMTA with ARES-G2
    - 1 Hz
    - 0.005 % strain amp.
    - Temperature sweep @ 3°C/min
- Flexural modulus with Zwick
    - E‘ @ RT: 3.4 Gpa
    - W x H x L ~ 5mm x 5mm x 60mm

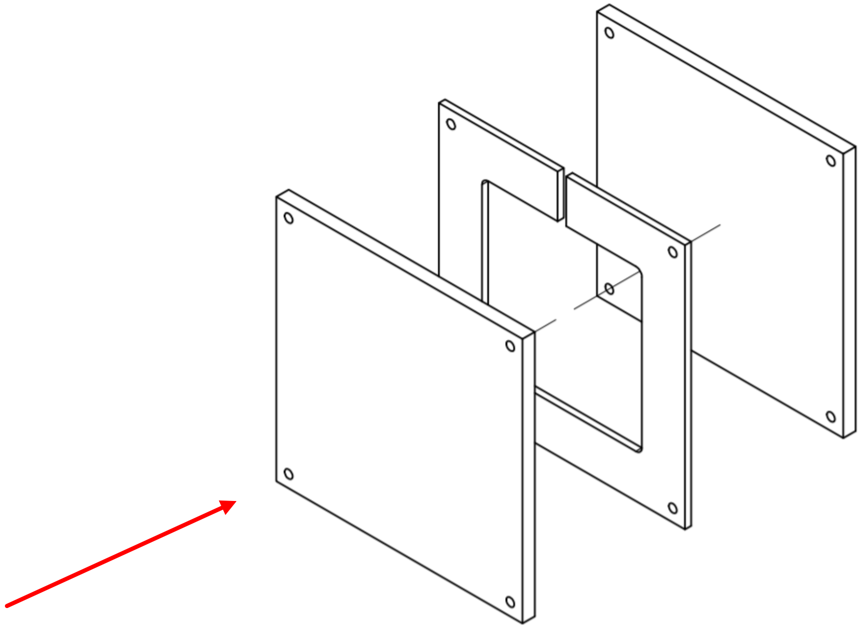


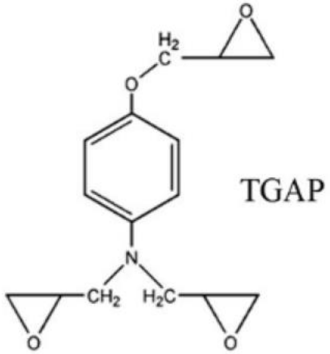

E‘ ~ 4.5 GPa

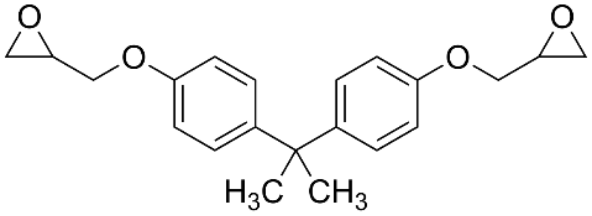
Phenoxy resins – Continuation

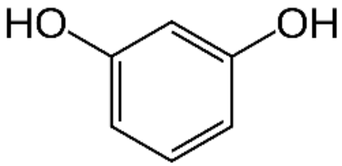
- Lower Tg (~80°C) compared to samples cured in glass vial (~100°C)
- Modulus seems dependent on sample dimensions
- Still some bubbles, especially in thin samples
- Dimension tolerances of samples could be better
- Fracture toughness much lower than expected

- → move away from silicone mold
- → make PTFE mold for plates for water-jet cutting, design in progress







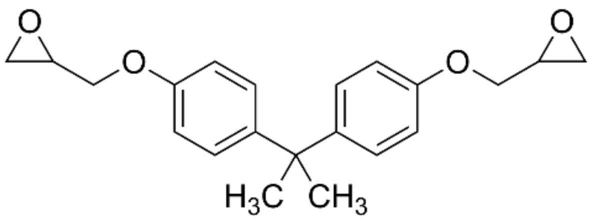


Phenoxy resins – Continuation

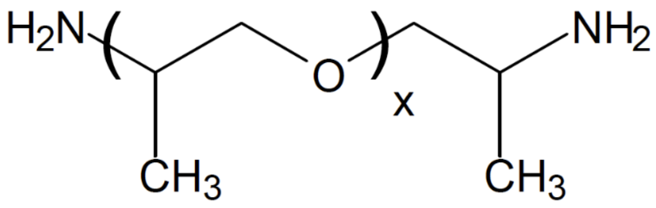
- Advantage of phenoxy chemistry: Long curing time
- Imitate the network structure of tough resins
  - Use long difunctional monomers in network
  - Or slightly crosslink the linear network using TGAP (trifunctional)

Epoxy cured
With
Jeffamine

DGEBA (F=2)



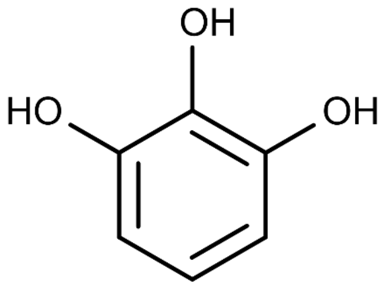
Jeffamine (F=4)



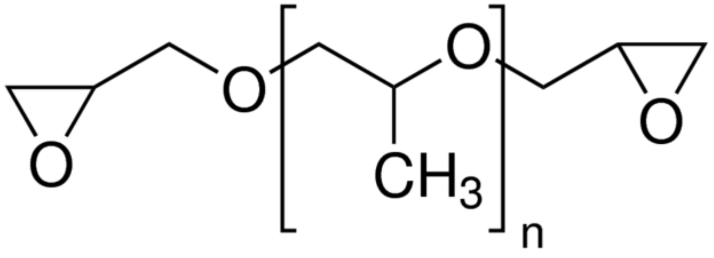
x ≈ 6.1

Phenoxy
pendant

Pyrogallol (F=3)

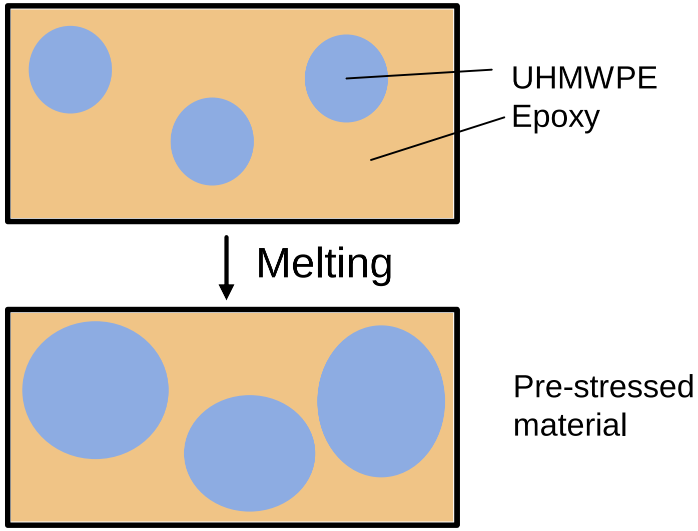


Poly(propylene glycol) diglycidyl ether (F=2)



High T_g epoxy composite

- Idea

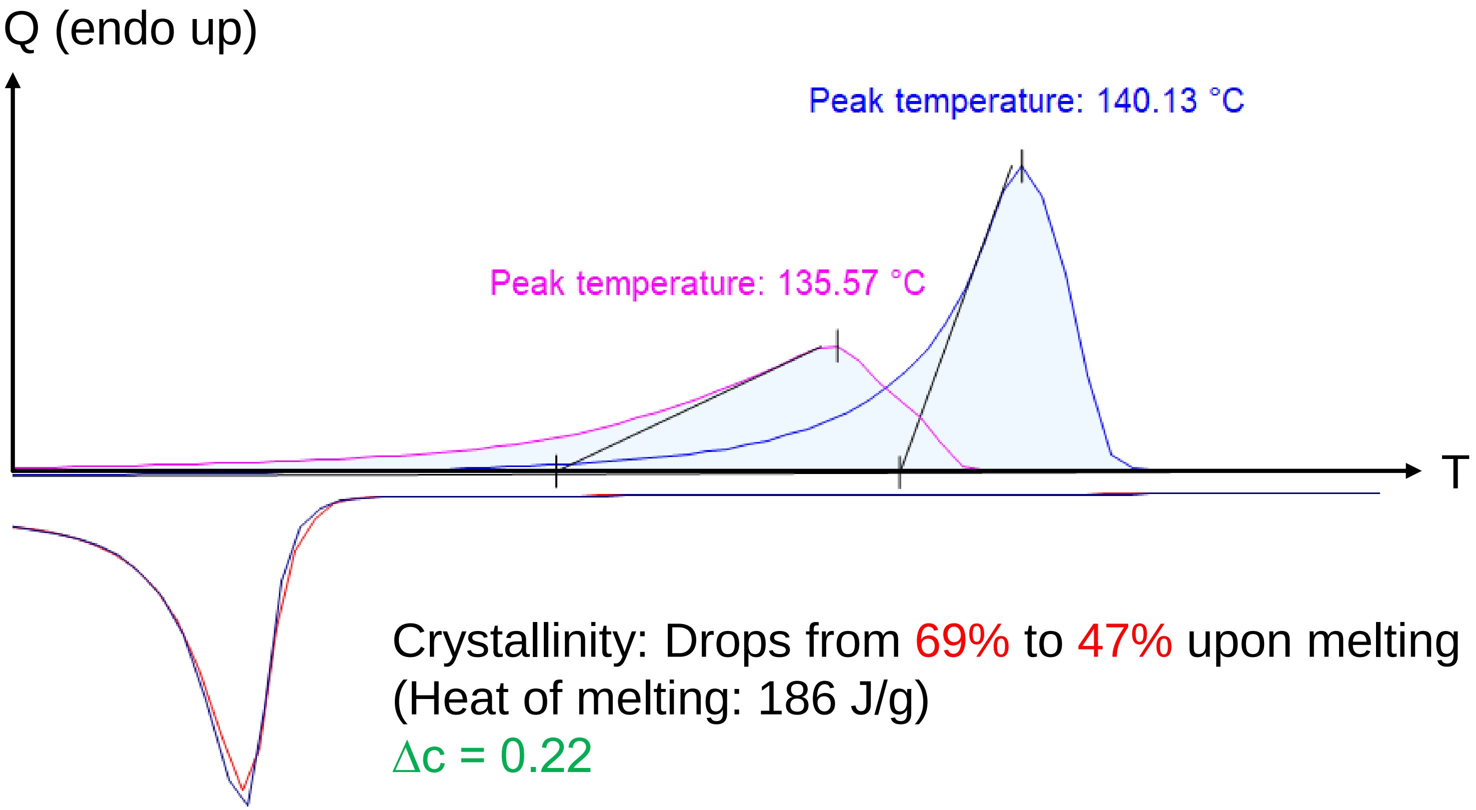


- Materials
  - UHMWPE particles:
    - Mitsui Mipelon PM-200
    - Particle size ~10 microns
    - Melting point: 140°C
  - High Tg epoxy
    - To be synthesized

High T_g epoxy composite

Shrinkage of epoxy: About 1% over 200K

- DSC of the UHMWPE powder



Crystallinity: Drops from 69% to 47% upon melting
(Heat of melting: 186 J/g)
$\Delta c = 0.22$

Calculations

- $p_c = 1.004$ g/cm3
- $p_a = 0.853$ g/cm3
- $\Delta c = 0.22$

$$\left(\left(\frac{p_c}{p_a}-1\right)\Delta c+1\right)^{\frac{1}{3}} = 1.0128$$

→ 1.28% linear expansion (melting)

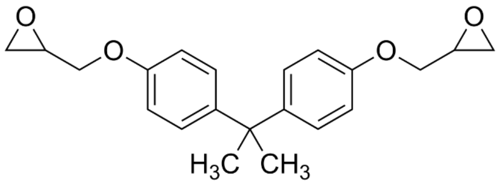
- $\alpha_{PE} = 108 \cdot 10^{-6}\ K^{-1}$
- $\Delta T = 200K$

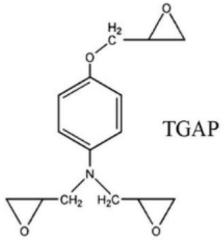
→ 2.16% linear thermal expansion over 200K

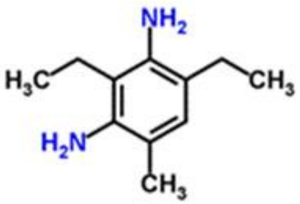
High T_g epoxy composite

- Composition from reference paper

DGEBA	100 pHr
TGAP	20 pHr
DETDA	34 pHr

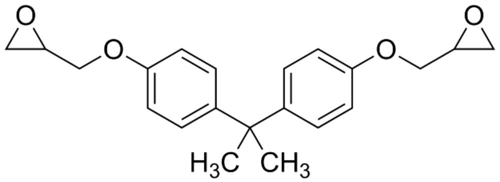


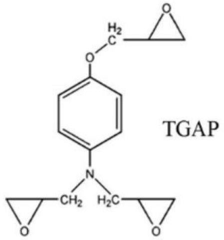


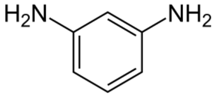


  - Miscible at 40°C, curing cycle: 100°C 60 min, 150°C 90 min., 177°C 120 min.
  - Tg: 200°C

- Materials I have in the lab
  - DGEBA
  - TGAP
  - m-phenylenediamine





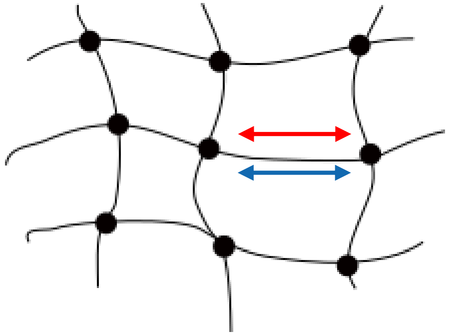


Melts at 64-66°C

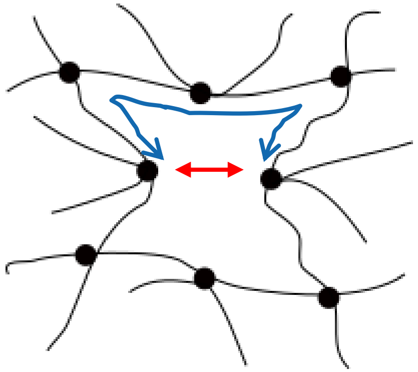
References
Jin-Woo et al., J. Appl. Polym. Sci., 2012, DOI: 10.1002/app.38040

High KIc epoxy

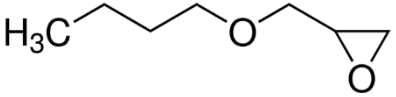
- Important research findings
  - The **toughness** increases with increasing **topological distance between crosslinks**



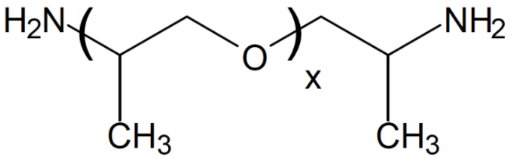
Euclidean distance
Topological distance



  - Approach: Reactive diluents, RESD, long-chain monomers such as Jeffamine



Reaction in presence of solvent,
Then drying

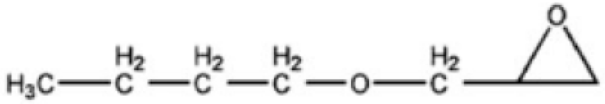


x ≈ 6.1

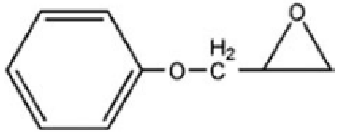
References
RESD; network topology: Sharifi et al., J. Mater. Chem., 2014, DOI: 10.1039/c4ta03051f
Reactive diluents: Jin-Woo et al., J. Appl. Polym. Sci., 2012, DOI: 10.1002/app.38040

Idea for a epoxy with high fracture toughness

- Start from a known high Tg resin: DGEBA, TGAP and DETDA
  - Change network structure with reactive diluents, e.g. butylglycidylether, BGE
  - Increases toughness of network



BGE



PGE

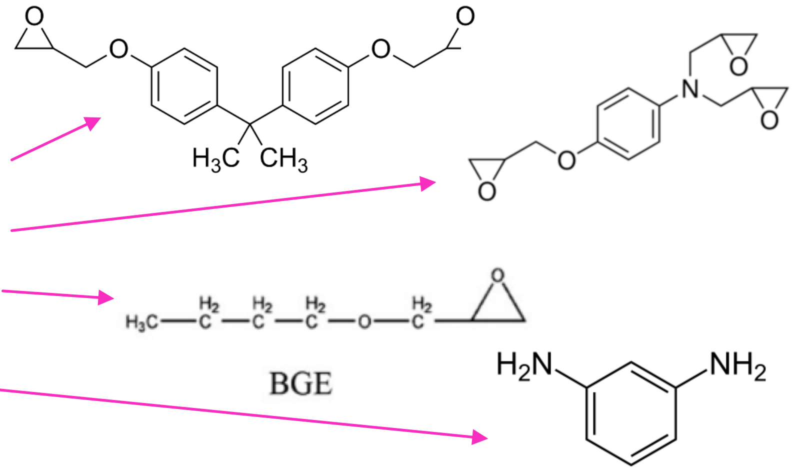
Lowers Tg

Does not affect Tg much

First result

- Materials:

Araldite MY750	DGEBA, ~5.3 equiv/kg	100 pHr
TGAP:	Tri-glycidyl p-aminophenol	20 pHr
BGE:	Butyl glycidyl ether	10 pHr
MPD:	M-phenylene diamine	22 pHr



- Procedure
  - Degassing at 75°C 10 min 10 mbar
  - Curing: 100°C 60 min, 150°C 90 min, 177°C 120 min
- Samples feel tough, testing to be done

Wrinkles on samples, from PTFE foil,
PTFE foil only wrinkled where sample was

→ Order thicker PTFE foil (this was 170g/m2)
→ Which kind available at PSI?