Molecular mobility in model heterogeneous cross-linked epoxy networks

C. Franzon[1,*] A. Roggero[1], J.F.Gérard[1]

[1] *IMP, UMR 5223 CNRS - Université Claude Bernard Lyon1, INSA Lyon, Université Jean Monnet, F-69621 Villeurbanne, France*

- Auteur correspondant : carolina.franzon@insa-lyon.fr

49èmes Journées d'Etudes des Polymères (JEPOs 2022)

Du 2 au 7 octobre 2022
À Bussang (Vosges)

Epoxy networks are an important class of thermoset polymers

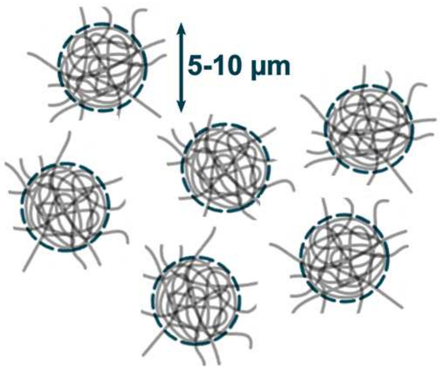
- Drawback for their use as structural materials: **Brittleness**
- **Network structure** is believed to play a crucial role in the **ultimate mechanical properties** of polymers, such as **fracture toughness**

> A clear understanding of how **network structure** is correlated with thermosets' **ultimate mechanical properties** is yet to be achieved to enable the **design of polymer materials** with functionalities tailored to specific industrial applications

Objective of the project:

➡ **To analyze the molecular mobility in polymer systems presenting an increasing degree of heterogeneity.**

Strategy



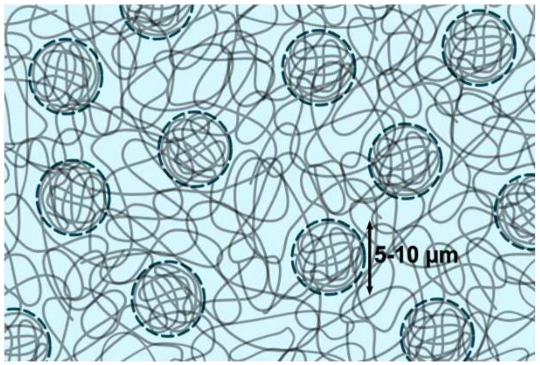
Crosslinked **E**poxy **M**icrogels (**CEM**s)

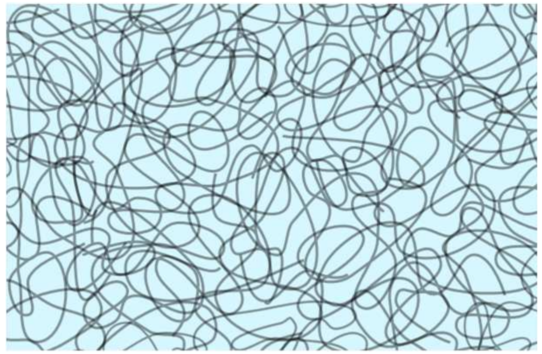
Epoxy-amine chemistry

Commercial epoxy resin | Amine hardener

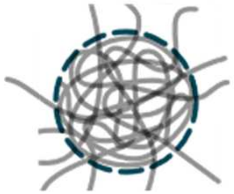
Precipitation polymerization | Bulk polymerization

Heterogeneous system





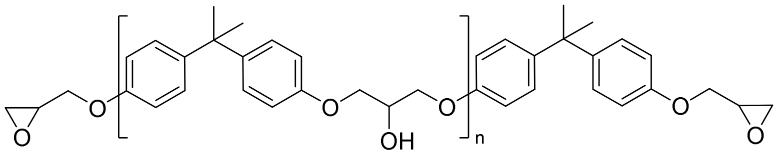
Epoxy matrix



CEMs synthesis

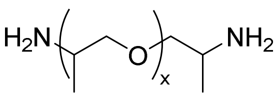
The Crosslinked Epoxy Microgels (CEMs) were synthesized by precipitation polymerization[1]

- **Monomers:**



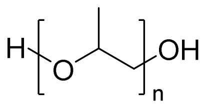
DGEBA
(EEW = 183 –192 g/eq, n ~ 0.12)

+

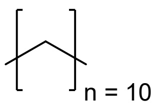


Jeffamine
(D230, x~2.5)

- **Solvent:**



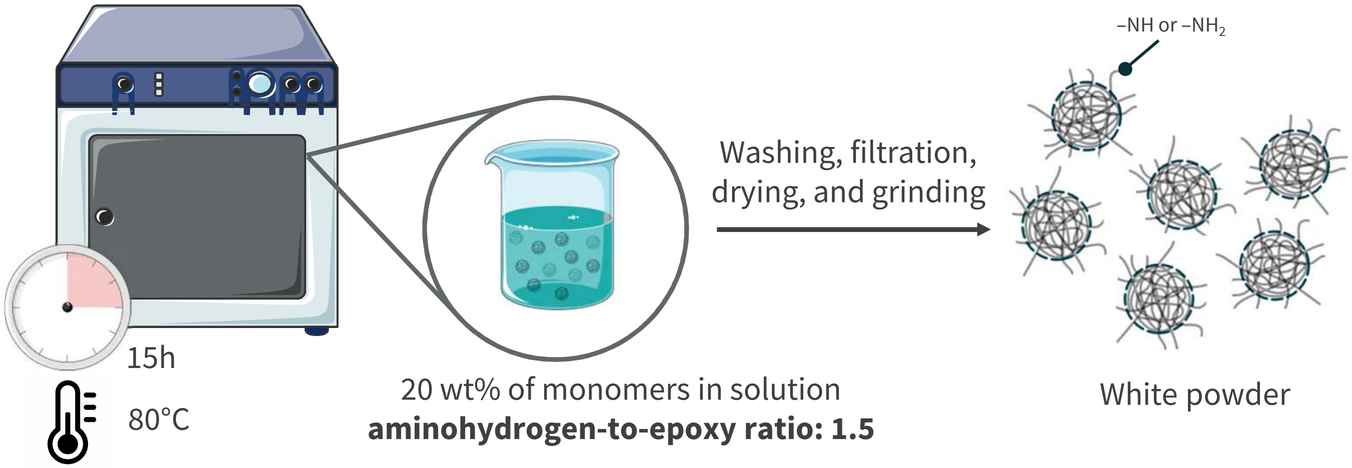
9:1
(wt)



Poly(propylene glycol)
Mn ~1,000

Dodecane

- **Precipitation polymerization protocol:**



- **Characterization:**

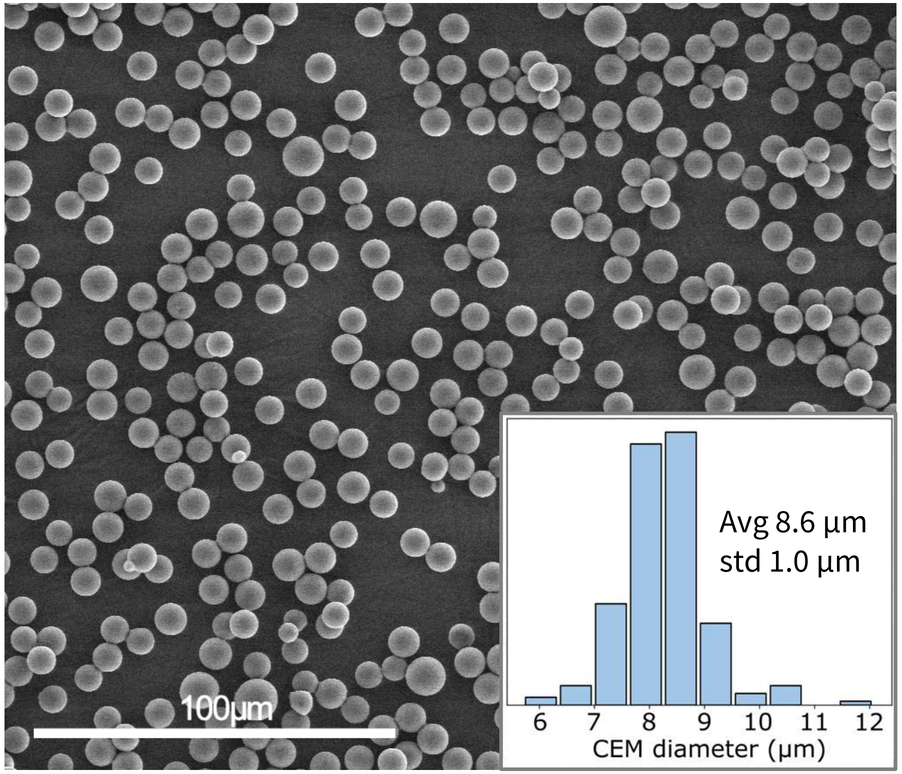
- DSC
- TGA
- IR
- SEM
- Helium pycnometry

Optimized to obtain **narrow size distribution**

1. M.L. Michon, INSA Lyon PhD, 2014.

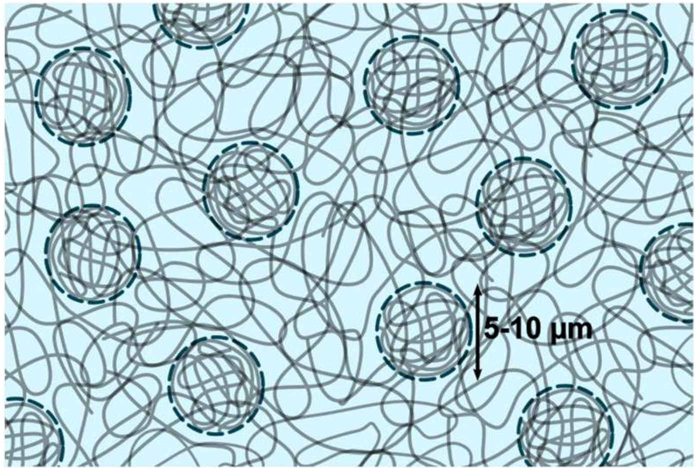
CEMs obtained have narrow size distribution

SEM micrographs of model CEMs:



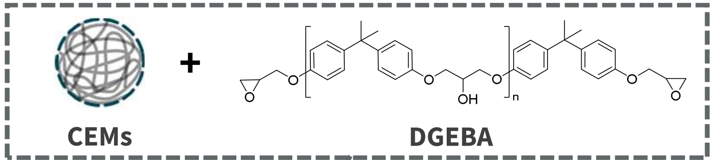
- **TGA** Solvent removal during whashing protocol was confirmed
- **IR** The presence of remaining primary and secondary amine functional groups was confirmed
- **Pycnometry** Average density of CEMs : 1.18 g/cm^3
- **DSC** T_g 1st run: 67 °C
  T_g 2nd run: 70°C

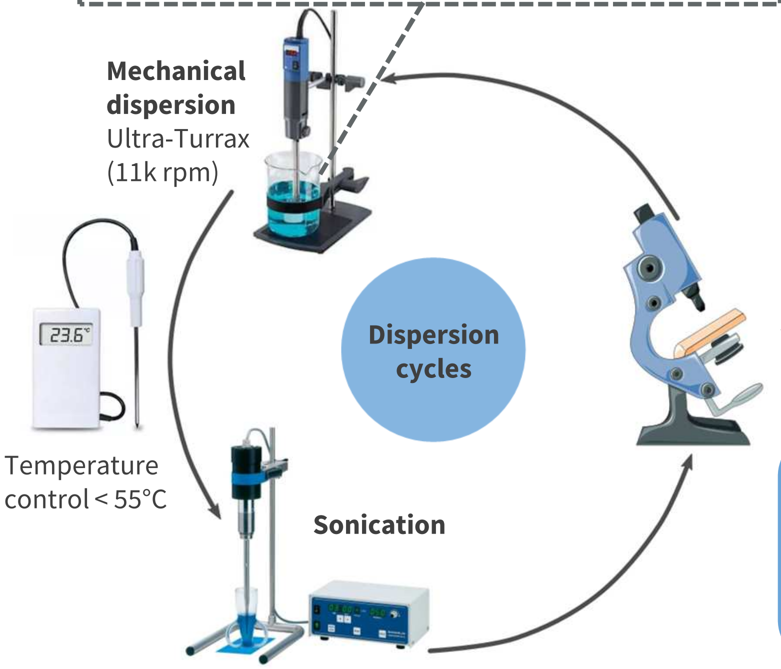
Obtention of the heterogeneous system



The CEMs were dispersed in DGEBA and cured using D230 as hardener

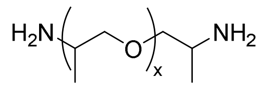
1 Masterbatch (MB) preparation:





Dispersion control with optical microscopy

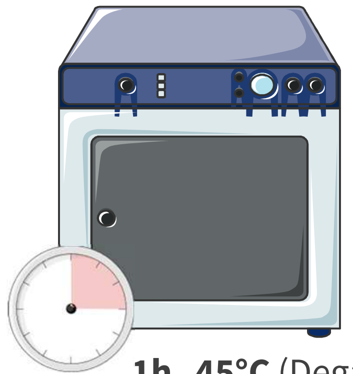
2 MB dilution in DGEBA followed by hardener addition

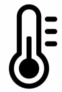


Jeffamine
(D230, x~2.5)

Homogeneization using Vacuum speedmixer
30min
800 – 2000 rpm
30 mbar

3 Curing in vacuum oven



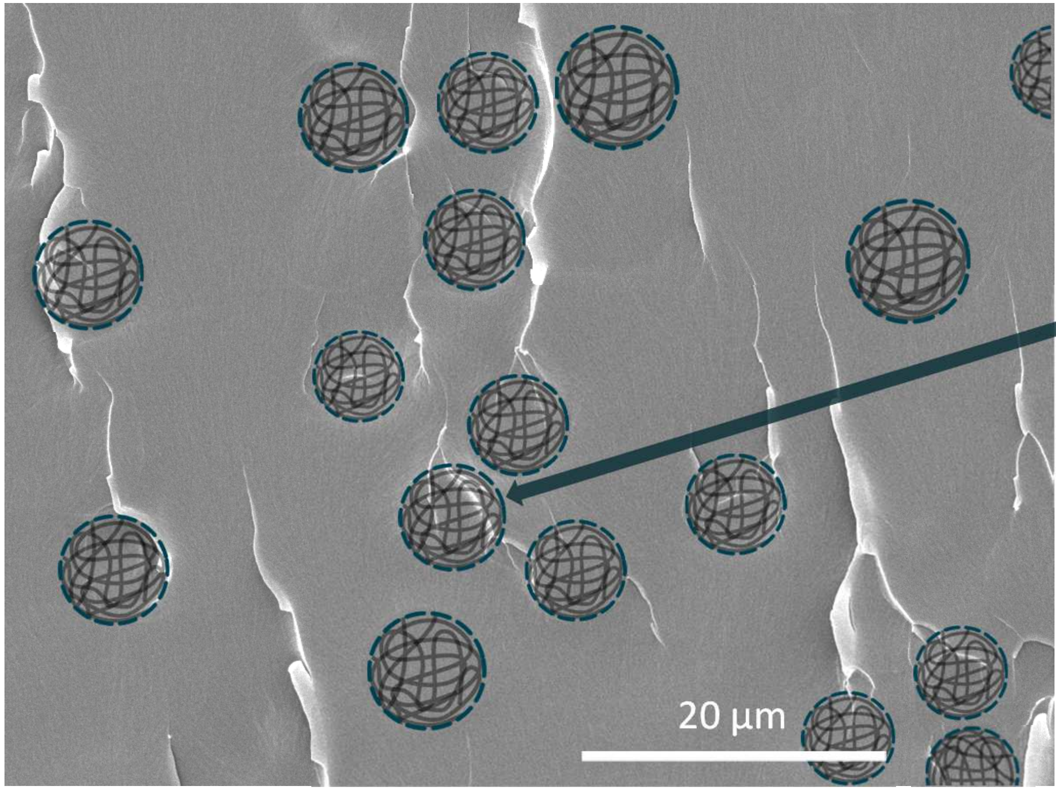


1h 45°C (Degassing step)
2h 80°C[1]
3h 125°C
1h 200°C

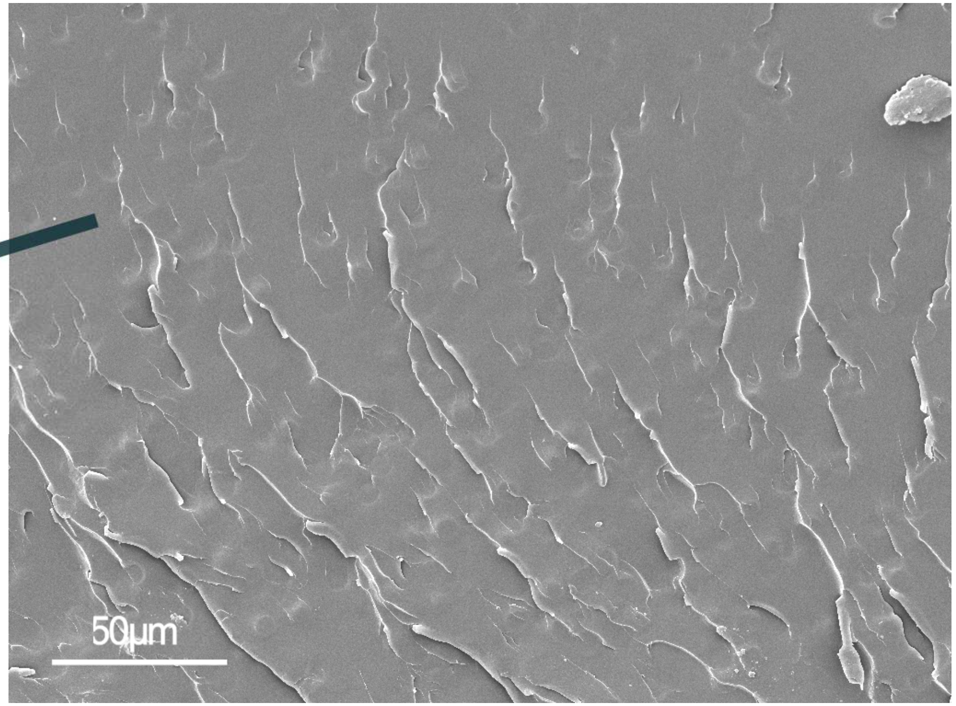
The networks were obtained as **thin films (~500µm)** with **homogeneous thickness**; the **reference matrix film** (DGEBA/Diamine, a/e = 1) was synthesized using the same curing protocol.

1. Nguyen, T. K. L., Livi, S., Soares, B. G., Pruvost, S., Duchet-Rumeau, J., & Gérard, J. F. (2016). Ionic liquids: A new route for the design of epoxy networks. ACS Sustainable Chemistry & Engineering

SEM micrographs of cryogenic fracture surface of fully cured networks

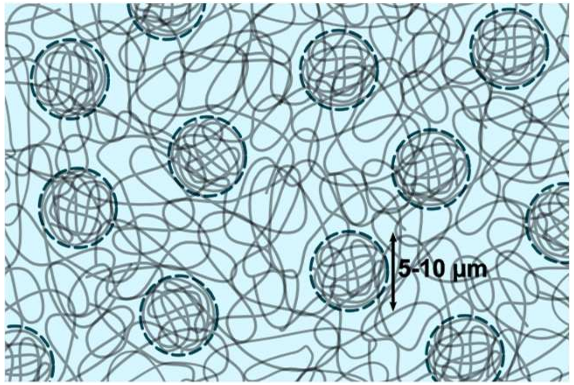


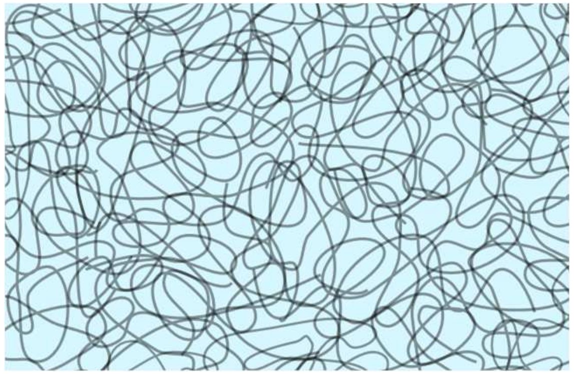
Heterogeneous network (20wt% of CEMs)



- **Strong adhesion** suggests that **CEMs** could be **covalently bonded** to the matrix.

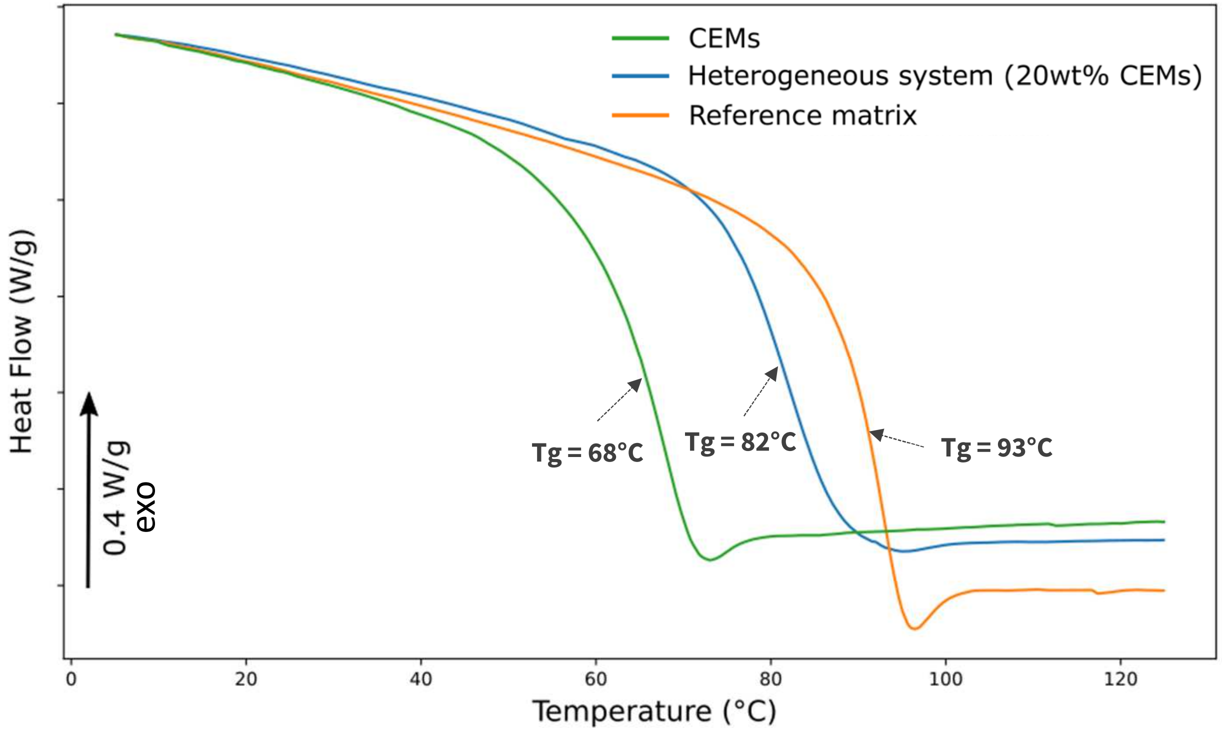
Analysis of molecular mobility of the heterogeneous system compared to reference matrix





DSC of the heterogeneous system compared to reference film and CEMs

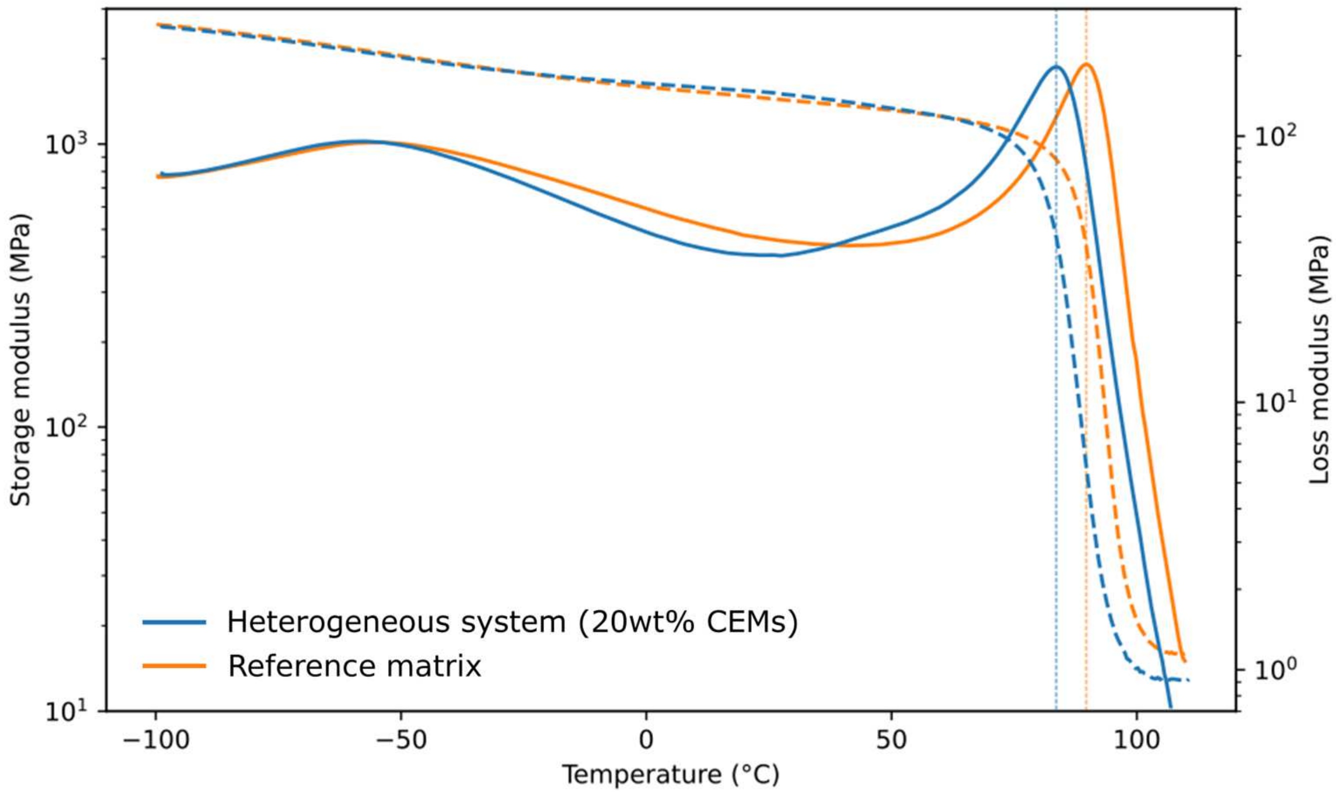
2nd heating scan at 10 K/min



- Only **one single glass transition temperature** is observed for the heterogeneous system, behaving like a **homogeneous system** despite the **heterogeneity in SEM analysis**

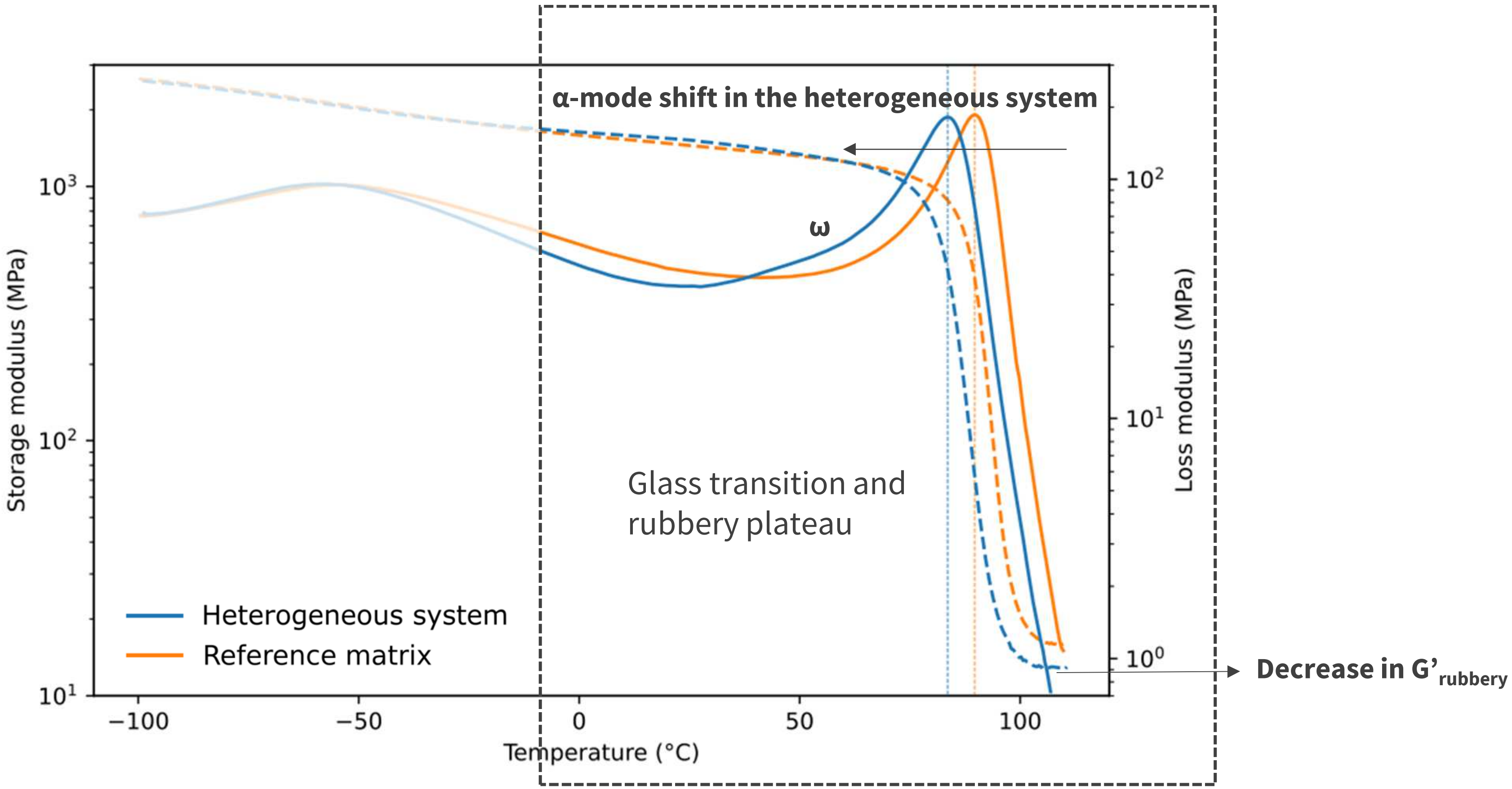
DMA characterization of the heterogeneous system and reference matrix

- DMA storage and loss modulus curves obtained by **retangular torsion mode** at **1 Hz**, **3 K/min** and **0.05% strain** (2nd heating ramp)



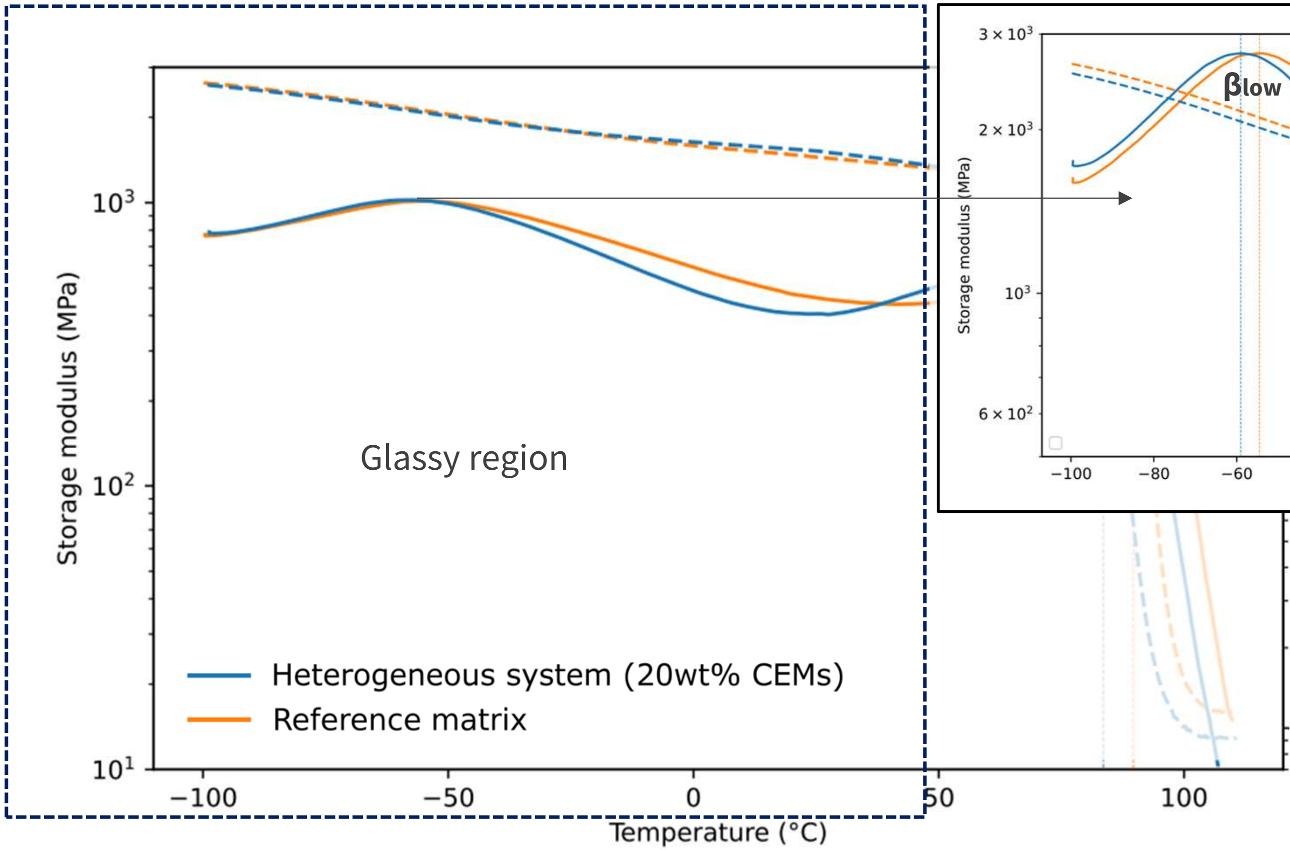
DMA characterization of the heterogeneous system and reference matrix

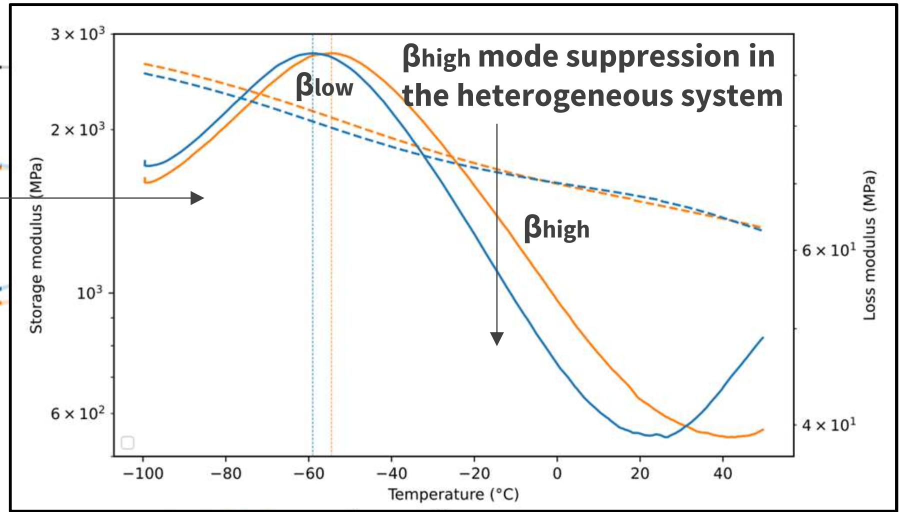
- DMA storage and loss modulus curves obtained by **retangular torsion mode** at **1 Hz**, **3 K/min** and **0.05% strain** (2nd heating ramp)



DMA characterization of the heterogeneous system and reference matrix

- DMA storage and loss modulus curves obtained by **retangular torsion mode** at **1 Hz**, **3 K/min** and **0.05% strain** (2nd heating ramp)

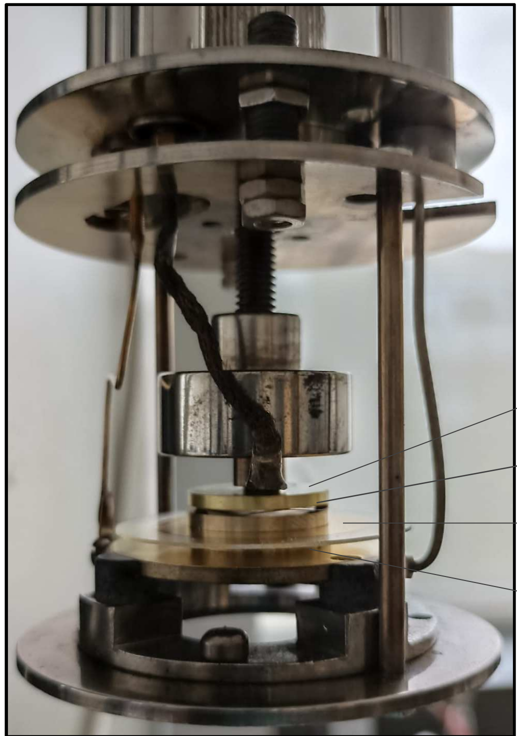




- Broad and **bimodal β relaxation** (characteristic of some epoxy-amine systems[1,2])

1. Won, Y. G. et all. (1990). Internal antiplasticization in copolymer and terpolymer networks based on diepoxides, diamines and monoamines. Polymer, 31(9), 1787-1792.
2. Ramsdale-Capper, R . et all. (2018). Internal antiplasticisation in highly crosslinked amine cured multifunctional epoxy resins. Polymer, 146, 321-330.

Broadband dielectric spectroscopy (BDS) measurements



Upper electrode

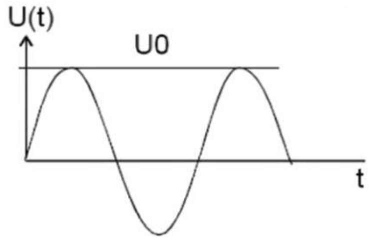
Spring

Gold plated sample

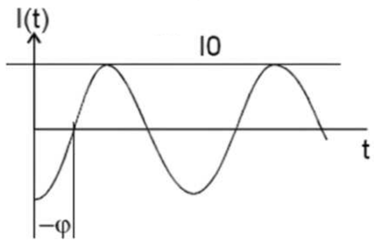
Lower electrode

Analysis parameters:
T range: -150 to 150 °C (5°C step)
f range: 10^6 to $4*10^{-2}$ Hz

- AC voltage applied



- Measured current



Complex impedance

$$Z^*(\omega) = \frac{U^*(\omega)}{I^*(\omega)}$$

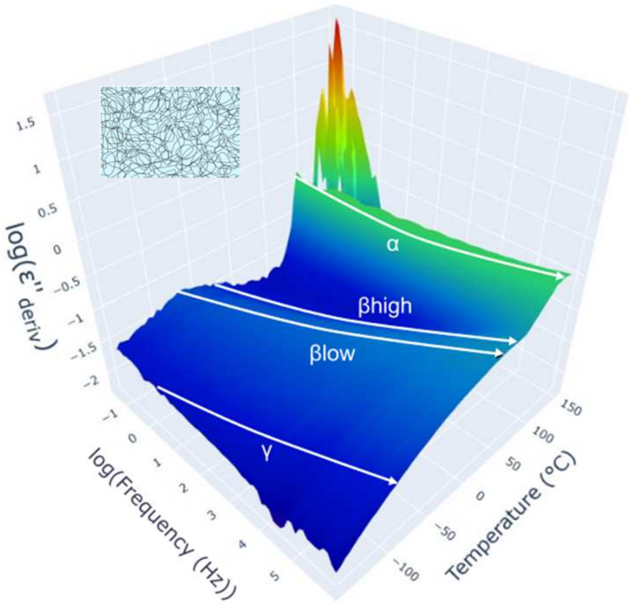
↓

Complex permittivity

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \frac{1}{i\omega C_0 Z^*}$$

Where: $C_0 = \frac{\varepsilon_0 A}{l}$ → A: Gold electrode surface; l: Sample tickness

Dielectric relaxation map of the reference sample

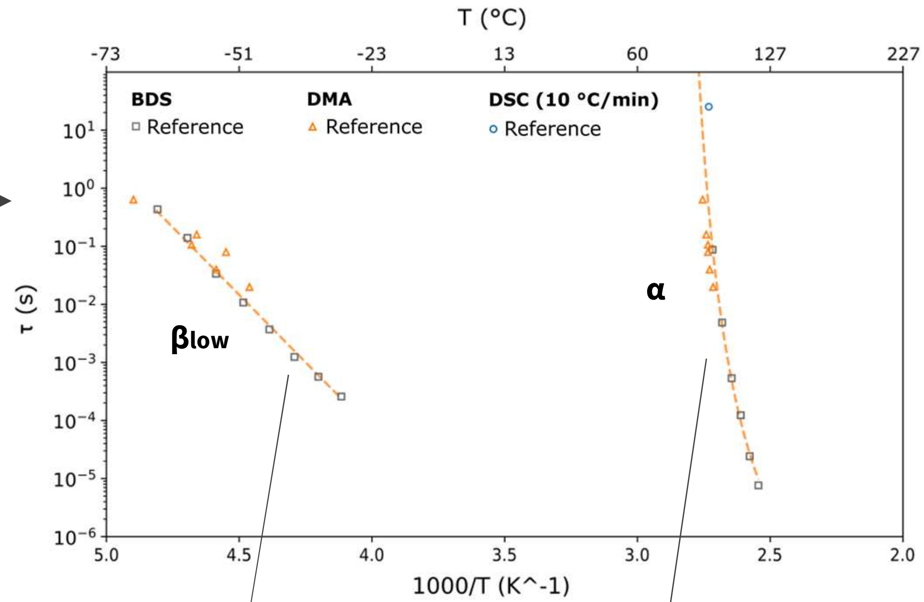


Fitted using Havriliak-Negami equation

$$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{\left(1 + (i\omega\tau_{H-N})^{\alpha_{H-N}}\right)^{\beta_{H-N}}}$$

- DSC equivalent frequency was determined using[1]:

$$f_{eq} = \frac{q}{2\pi a \delta T}$$

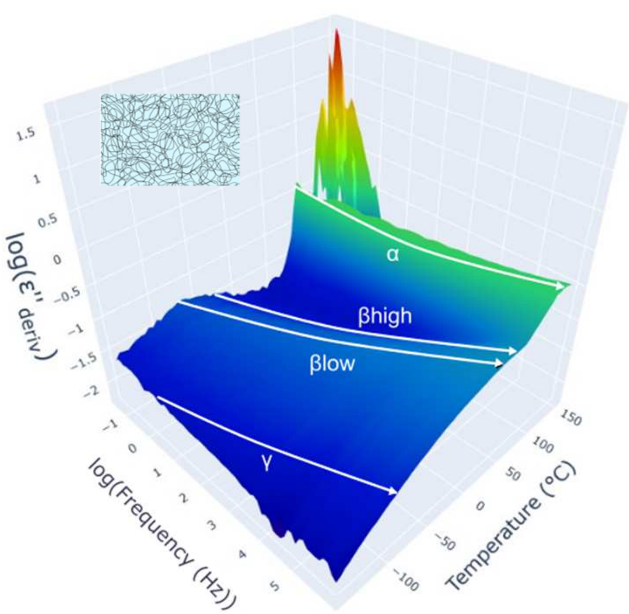


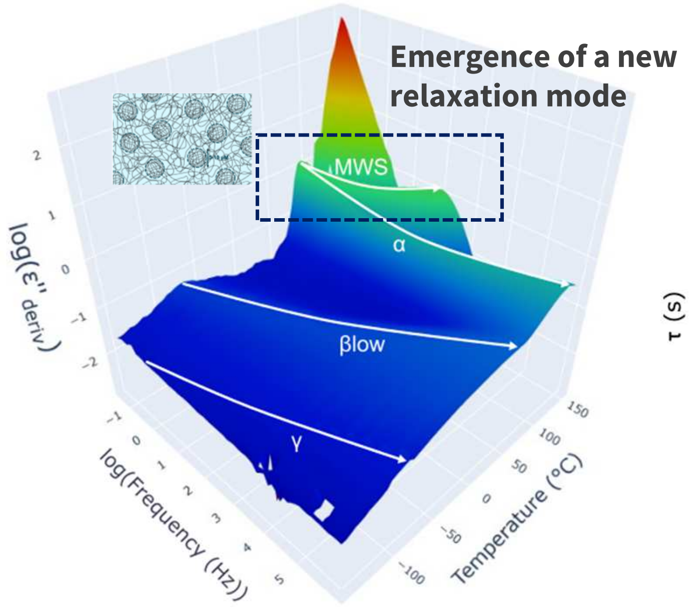
Arrhenius behavior of β-relaxation	Vogel-Fulcher-Tammann behavior of α-relaxation
$\tau^{Arr}(T) = \tau_0 e^{\frac{E_a}{RT}}$	$\tau^{VFT}(T) = \tau_0 e^{\frac{1}{\alpha_f (T - T_\infty)}}$

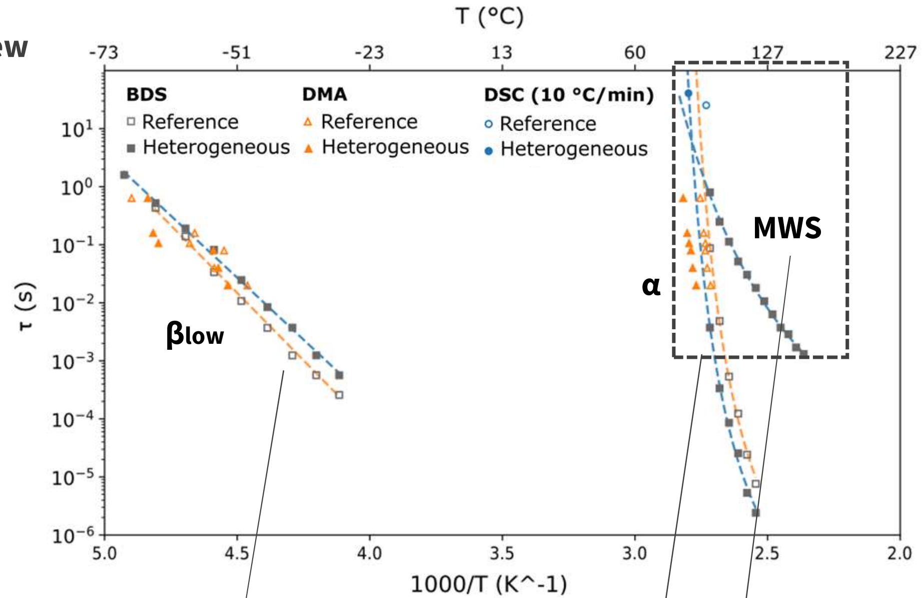
- Good agreement between DSC, DMA, and BDS data.

1. Donth, E.-J. Relaxation and Thermodynamics in Polymers: Glass Transition; Akademie Verlag: Berlin,1994.

Dielectric relaxation map of the heterogeneous network sample







Arrhenius behavior of β-relaxation

Vogel-Fulcher-Tammann behavior of α-relaxation

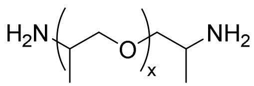
- The additional relaxation mode appears only in BDS measurement, thus **no mechanical response** of the responsible entities;
- Could be ascribed to macrodipoles formed by **interfacial polarization** or Maxwell–Wagner–Sillars **(MWS)**

⇓

Result of conductivity heterogeneity in the network

Isofrequency comparison between DMA and BDS measurements

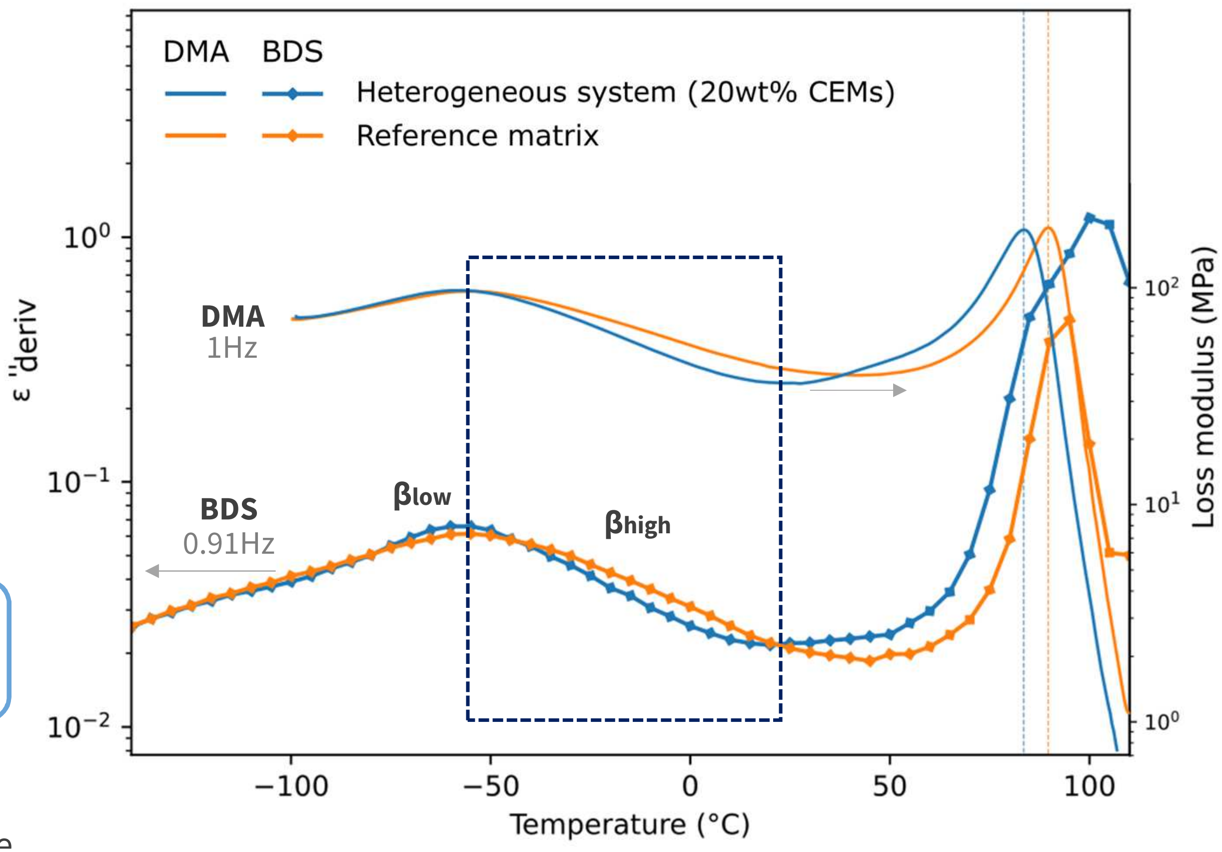
- β-relaxation ascribed to the **localized mobility** of **hydroxyether units** and/or **phenyl ring flips**
- βhigh was associated with **phenyl ring flips** in the **hardener parts** of the network[1]



No phenylene rings in the hardener

- βhigh supression is **commonly observed** in systems containing structure modification leading to a **lower network crosslink density**[2]

Would CEMs' addition to the network result in lower average cross-linking density of the material?



➡ **Complementary analysis** to understand the origin of this **restriction in molecular mobility** needs to be done.

1.Ramsdale-Capper, R., & Foreman, J. P. (2018). Internal antiplasticisation in highly crosslinked amine cured multifunctional epoxy resins. Polymer, 146, 321-330.
2. Won, Y. G., Galy, J., Gérard, J. F., Pascault, J. P., Bellenger, V., & Verdu, J. (1990). Internal antiplasticization in copolymer and terpolymer networks based on diepoxides, diamines and monoamines. Polymer, 31(9), 1787-1792.

Conclusion and perspectives

Conclusions

- The obtained results show an impact of the presence of CEMs on both the α and β modes of the epoxy matrix;
- The single T_g suggests **homogeneous-like behavior** of the heterogeneous system;
- Meanwhile, **interfacial polarization** observed in BDS measurement suggests **phase heterogeneity** in the heterogeneous system, aligned with SEM observation;
- **β high mode suppression** in the heterogeneous system seems to be **due to CEMs'** presence in the matrix. The mechanism generating this **mobility restriction** needs to be elucidated.

Perspectives

- Finalize **the interpretation of the relaxation modes** in the reference and heterogeneous networks;
- Replicate the study using **different hardeners in the matrix** (e.g. D400 and D2000) to change crosslink density and thus the **contrast between matrix and CEMS**;
- Vary **the fraction of dispersed CEMs** to study the influence of the **heterogeneity degree** on molecular mobility;
- **Network topology** visualization using **AFM**;
- Study the **networks' fracture behavior** (e.g. determine fracture toughness or solvent crack behavior);

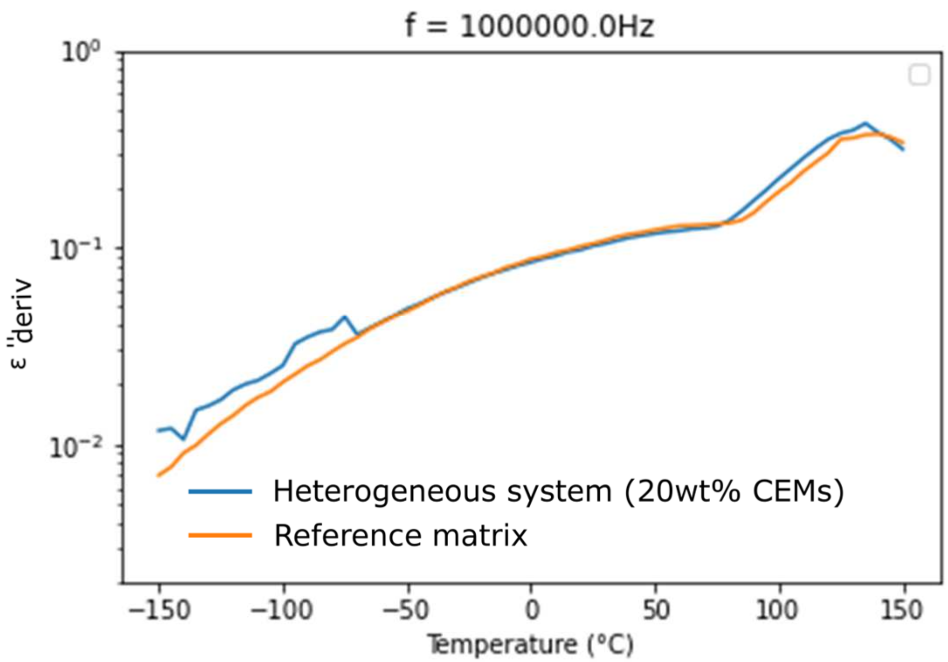
Thank you for your attention

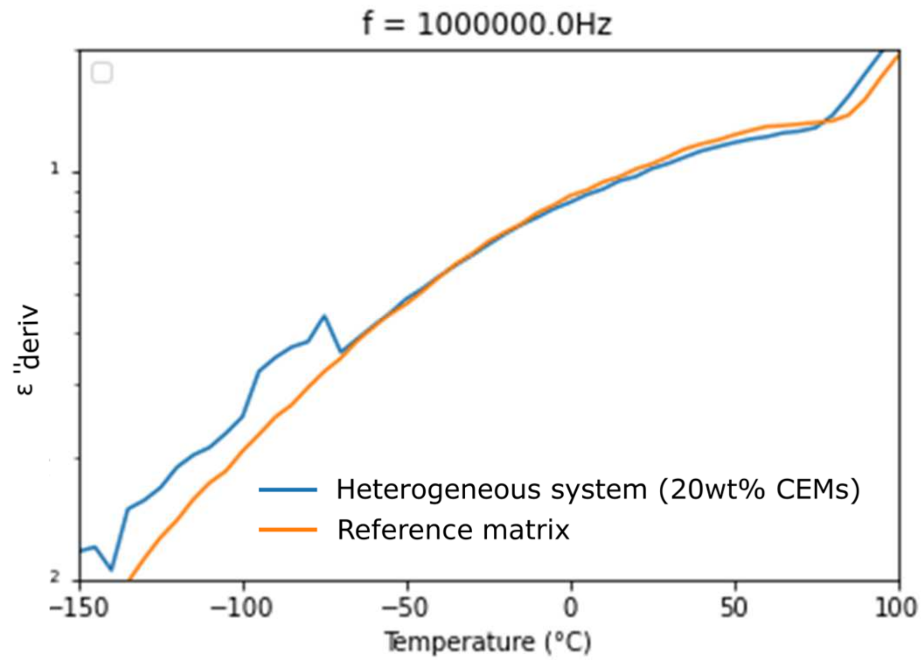
Annexes

Other perspectives

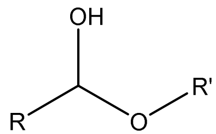
- Characterize the films by **IR/NIR**, **solvent swelling**, and **pycnometry** to gain more information about the crosslink density;
- Follow the **network build-up** of reference and heterogeneous system by **IR and DSC** to gain information on CEMs' influence on **curing kinetics**
- **Solid NMR** to gain more information about chemical environment of the entities

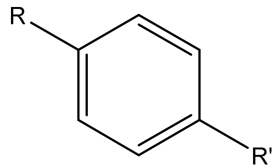
Beta relaxation mode shift with increasing frequency

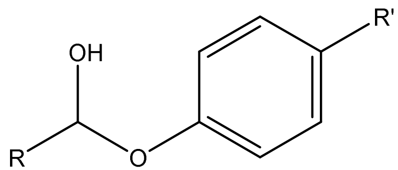


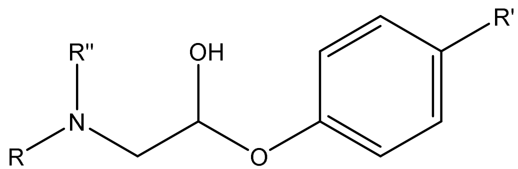


- **hydroxyether** units and/or **phenyl ring** flips







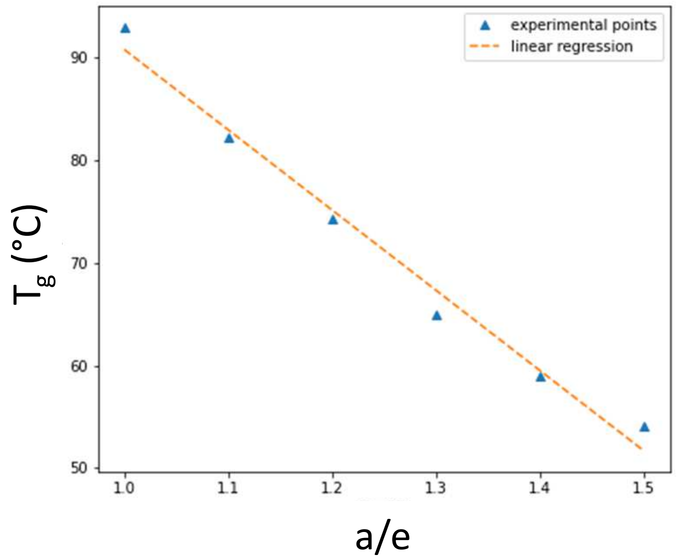


- **Eps deriv definition**

$$\varepsilon''_{\mathrm{der}} = -\frac{\pi}{2}\frac{\partial \varepsilon'(\omega)}{\partial \ln \omega} \approx \varepsilon''_{\mathrm{rel}}$$

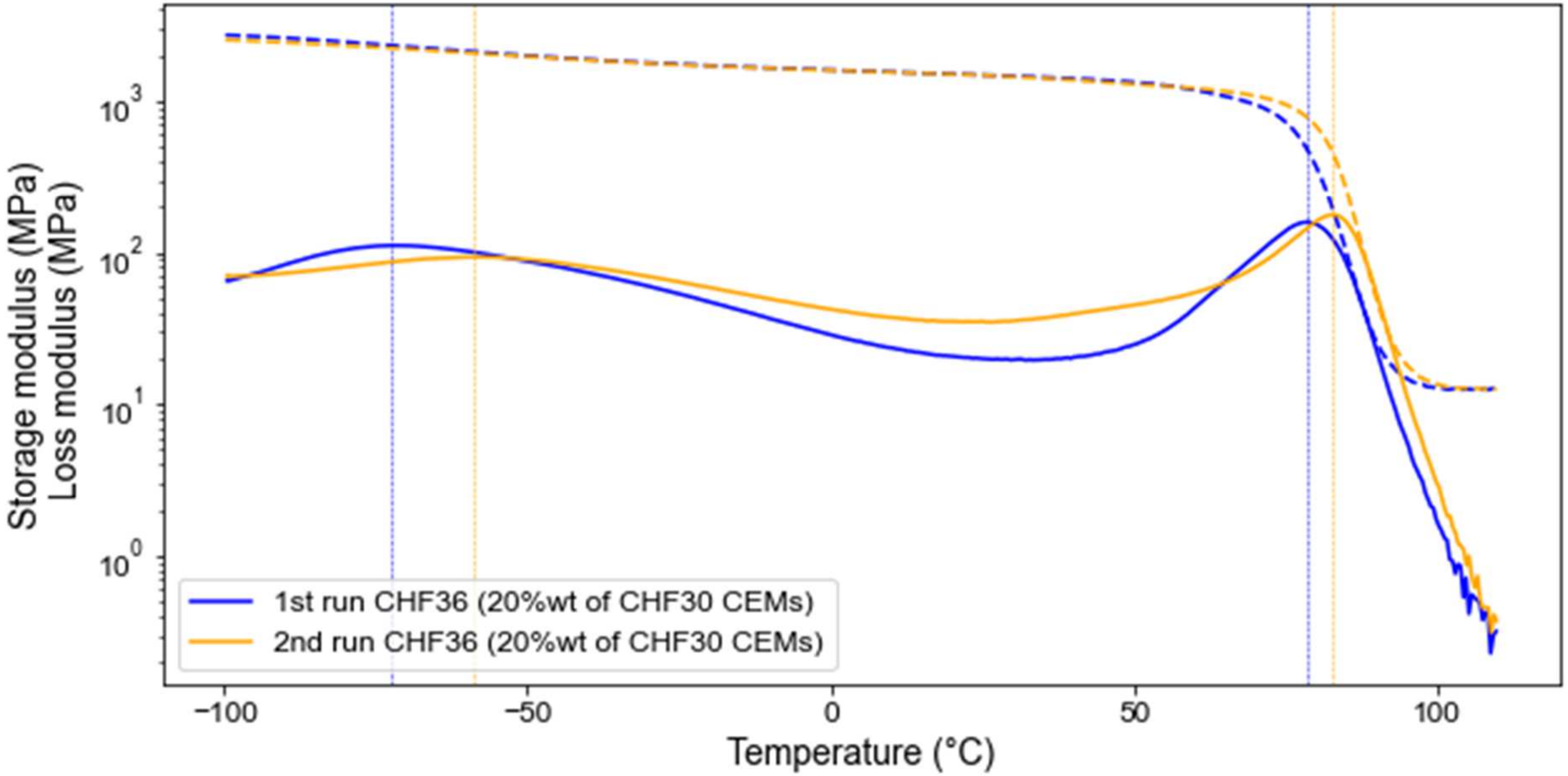
- “conduction-free” imaginary part, ε′′deriv (that is not entirely true because **ionic conductivity** and **electrode polarization** also contribute to ε’,

CEMs' final aminohydrogen-to-epoxy ratio estimate

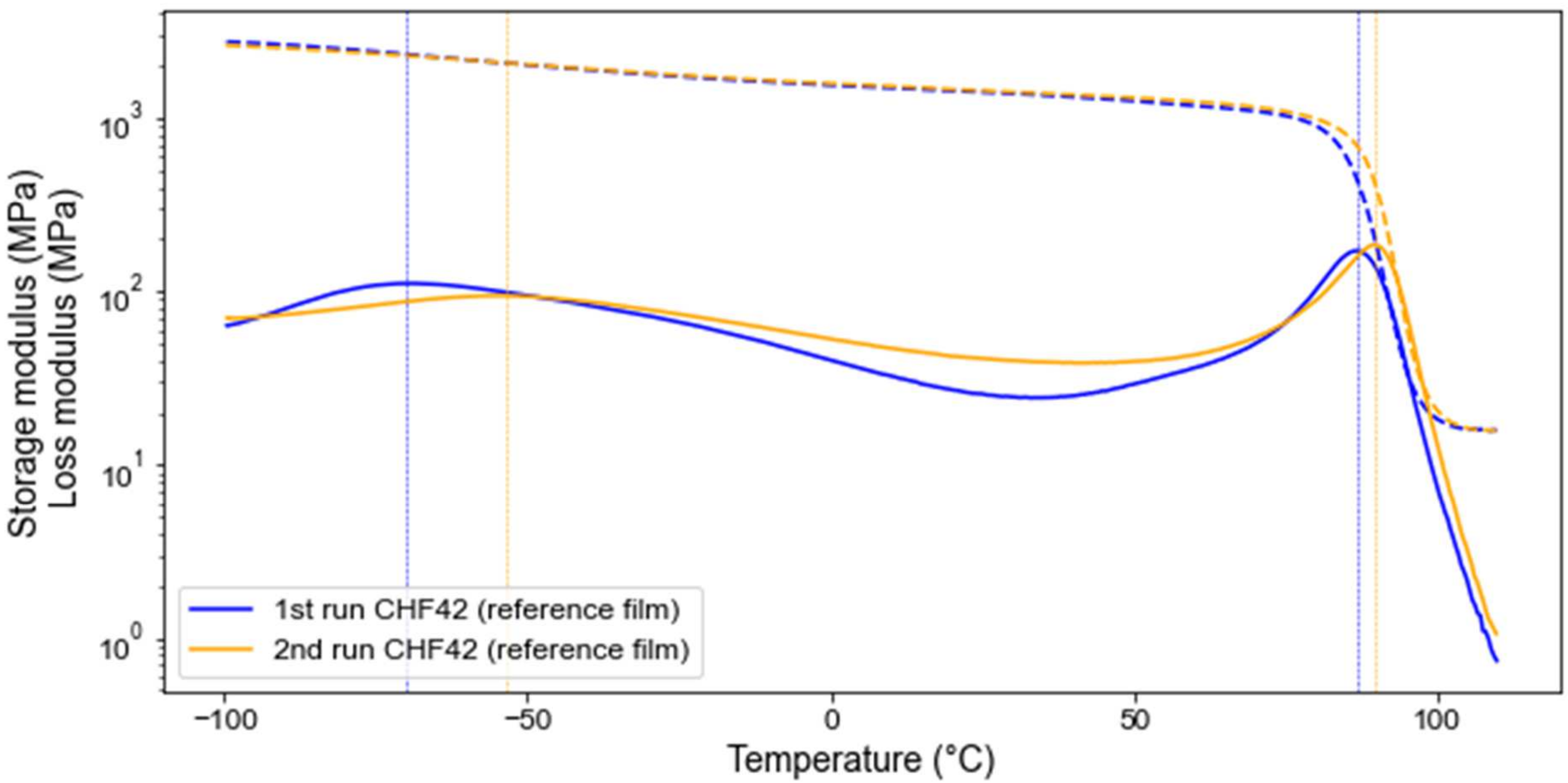


- Equivalent stochiometric ratio of microgels calculated from T_g

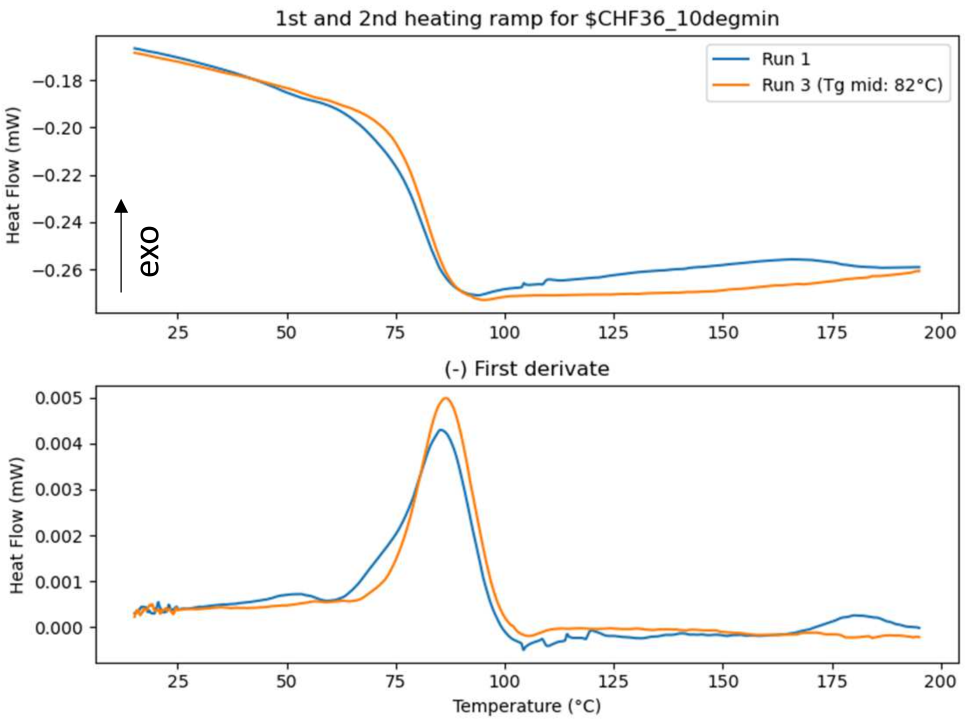
DMA first and second run: Heterogeneous system film

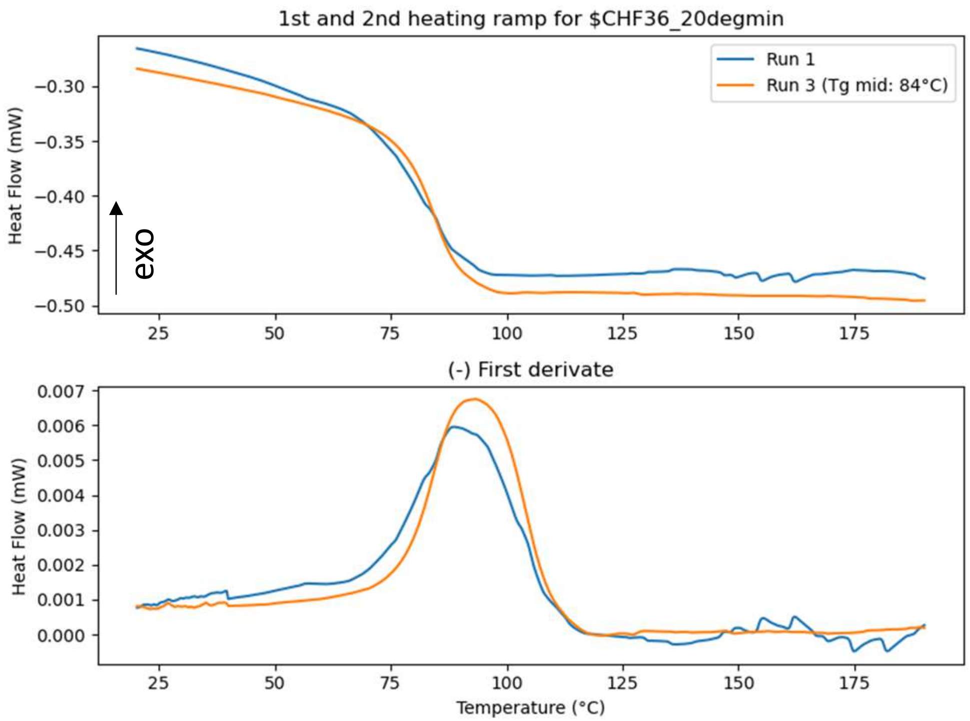


DMA first and second run: Reference film



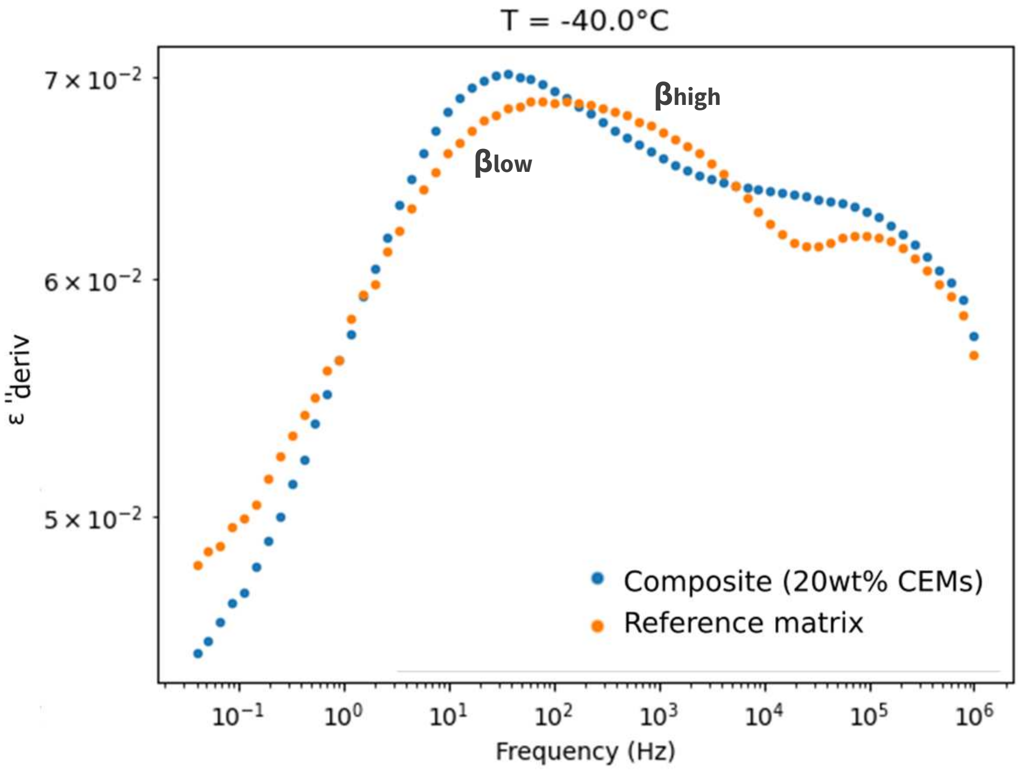
DSC heterogeneous system (20wt% CEMs): 10 and 20 K/min



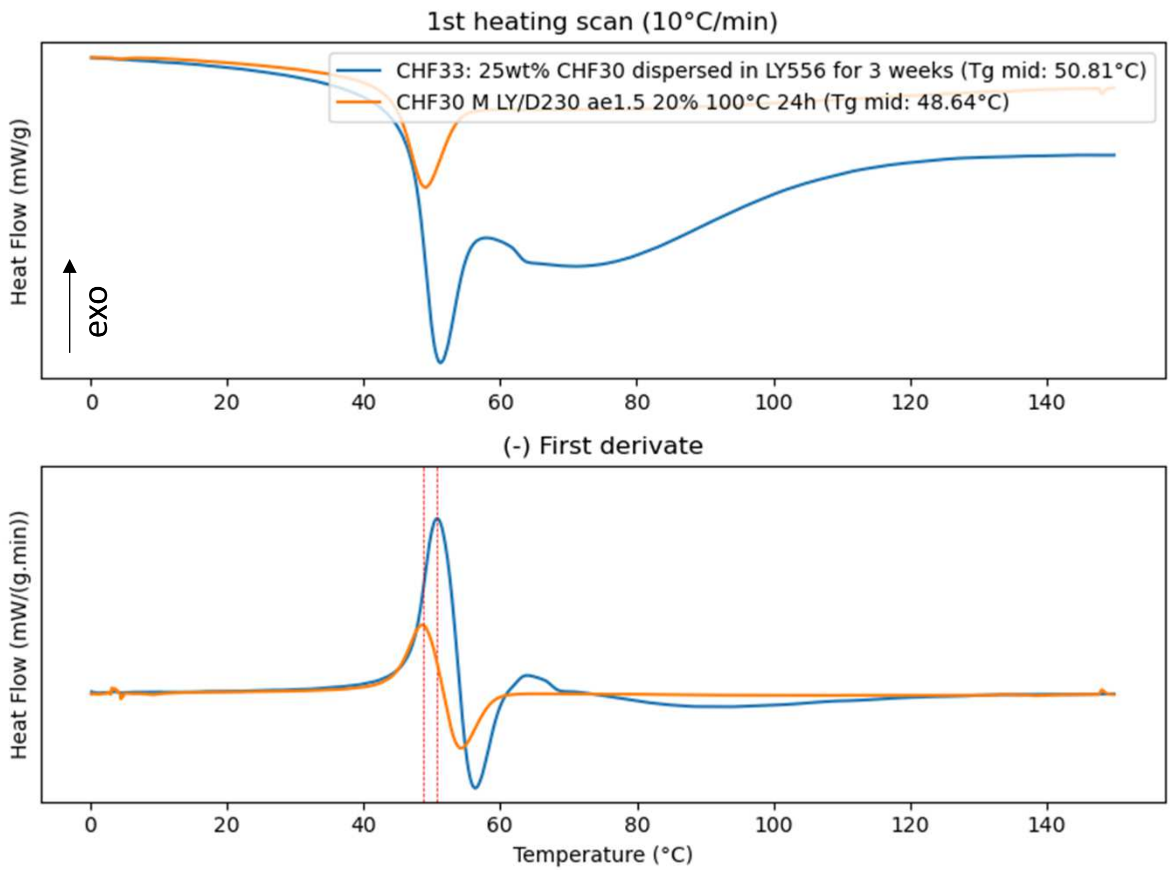


- Single T_g observed despite of the heating rate.

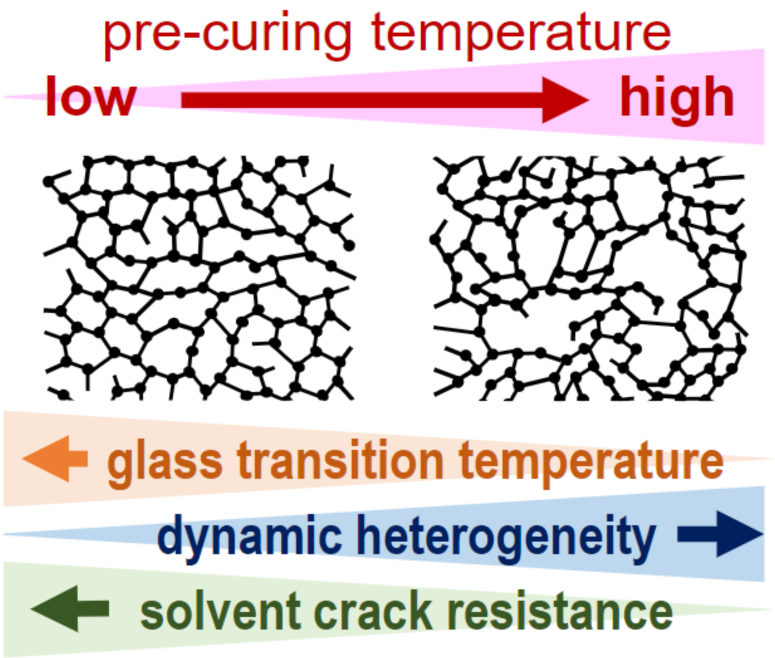
Isotherm comparison between DMA and BDS measurements

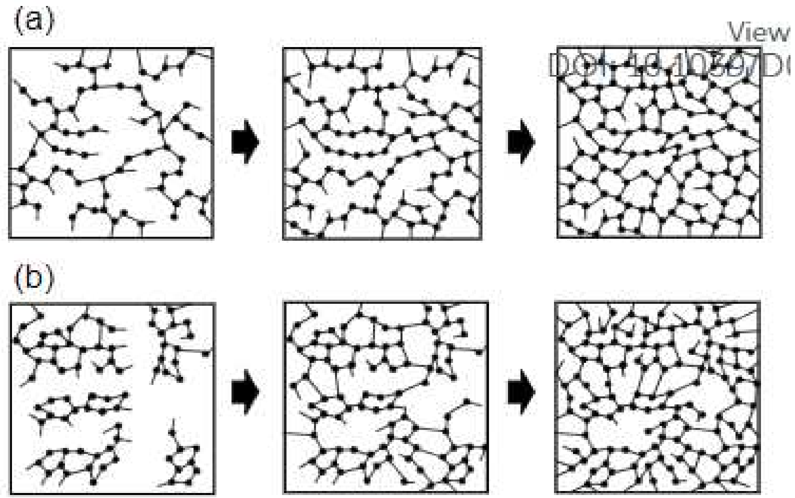


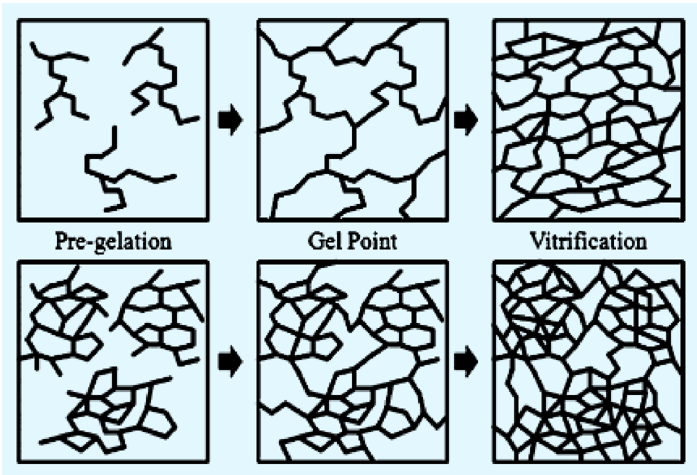
DMA characterization of reference and heterogeneous system systems



- CEMs T_g remains the same when embedded in DGEBA for 3 weeks, indicating no significant diffusion of the resin into CEMs core at masterbatch storage conditions







1. Aoki, M., Shundo, A., Yamamoto, S., & Tanaka, K. (2020). Effect of a heterogeneous network on glass transition dynamics and solvent crack behavior of epoxy resins. Soft Matter, 16(32), 7470-7478.
2. Sahagun, C. M., & Morgan, S. E. (2012). Thermal control of nanostructure and molecular network development in epoxy-amine thermosets. ACS applied materials & interfaces, 4(2), 564-572.