Electronic Supplementary Material (ESI) for RSC Applied Polymers.


# Supplementary information

**Metal-free, hydrogen bond-rich poly(dimethyl siloxane) networks *via* Thiol Michael addition for improved electrical properties and self-healing.**

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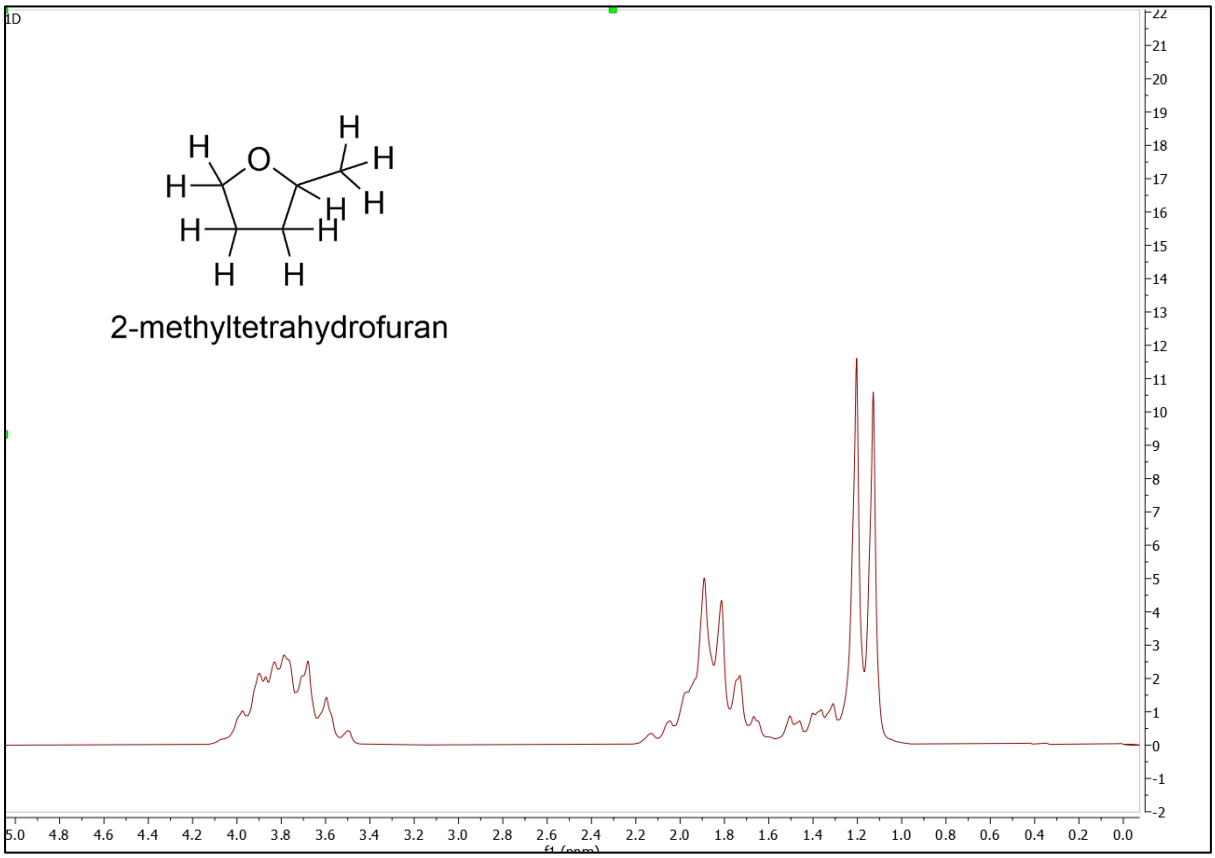



Figure S1. $^{1}$H NMR spectra of the used solvent 2-methyltetrahydrofuran (2mTHF).

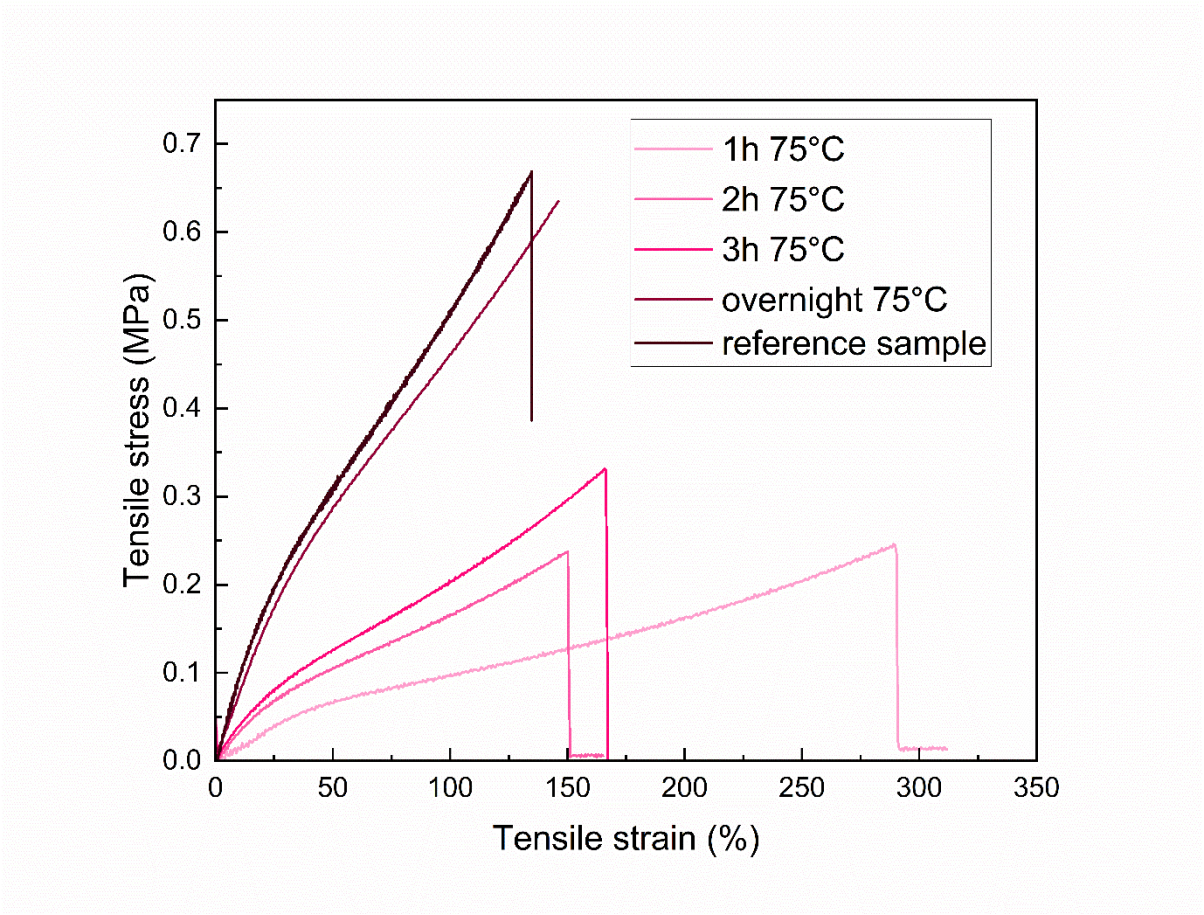



Figure S2. Illustration of the effect of post-curing: Tensile test of progressively more cross-linked MA5. After leaving the sample overnight at 75 ºC, the post-curing is complete. Post-curing deemed complete due to near-overlap with a reference sample from previous batch.

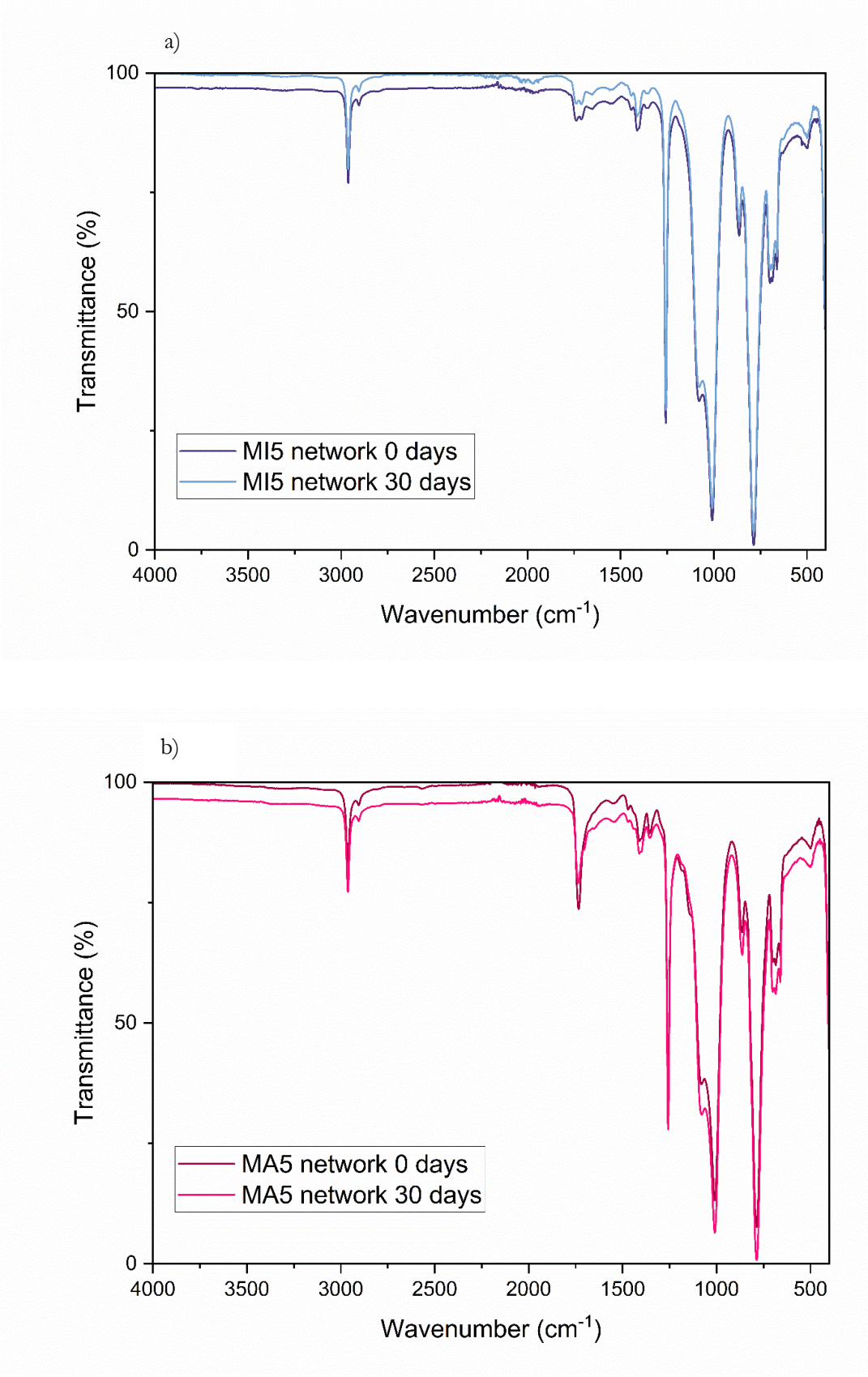
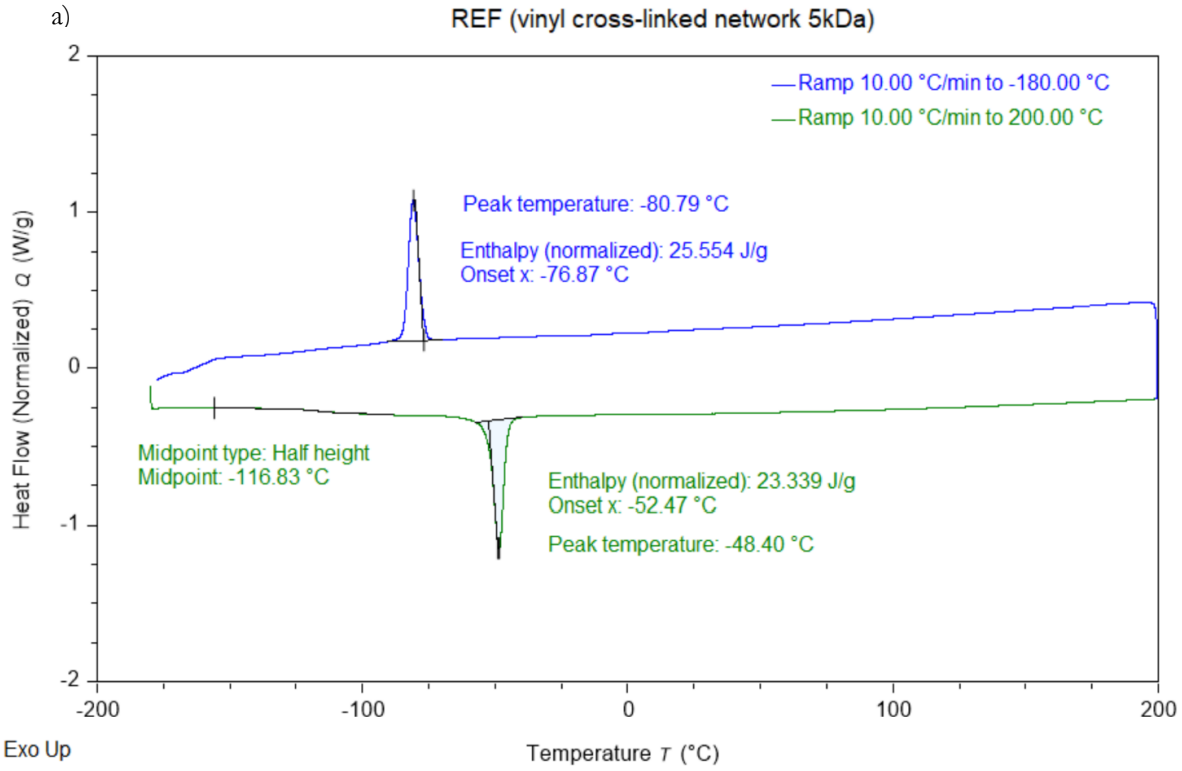
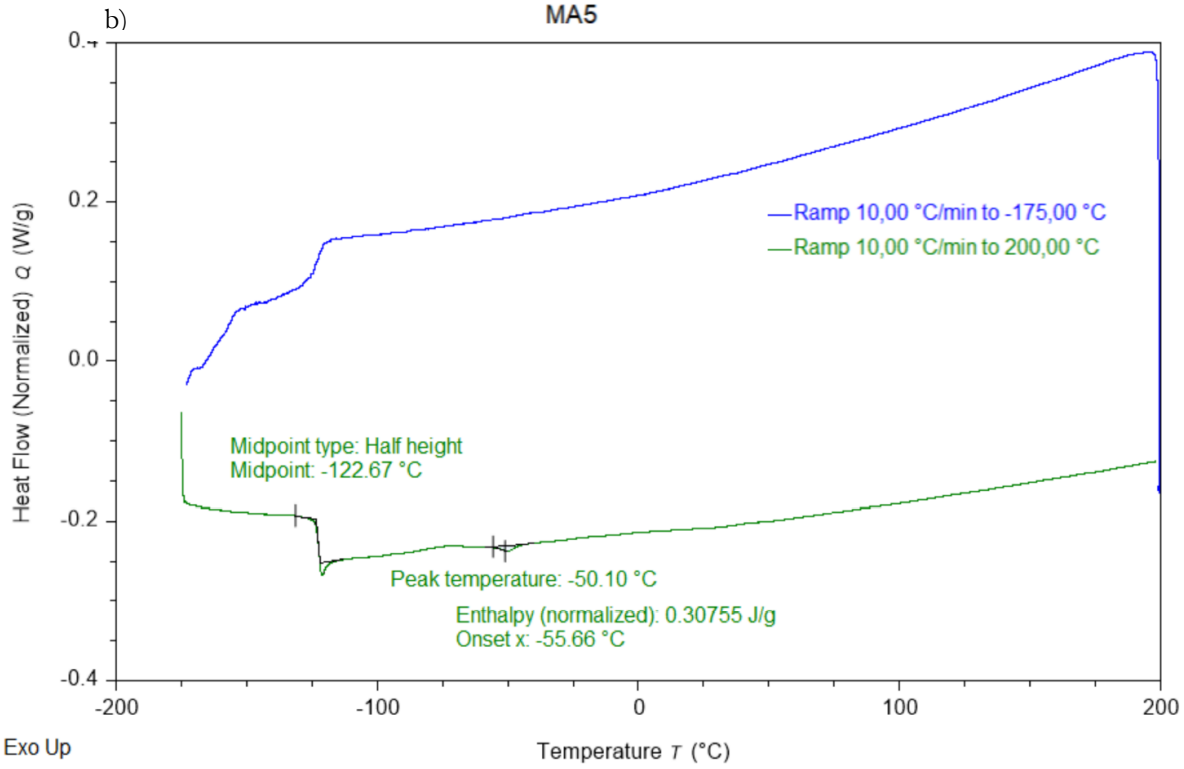



Figure S3. FTIR spectra of a) MI5 and b) MA5 cross-linked networks, immediately upon cross-linking is finished and after 30 days.

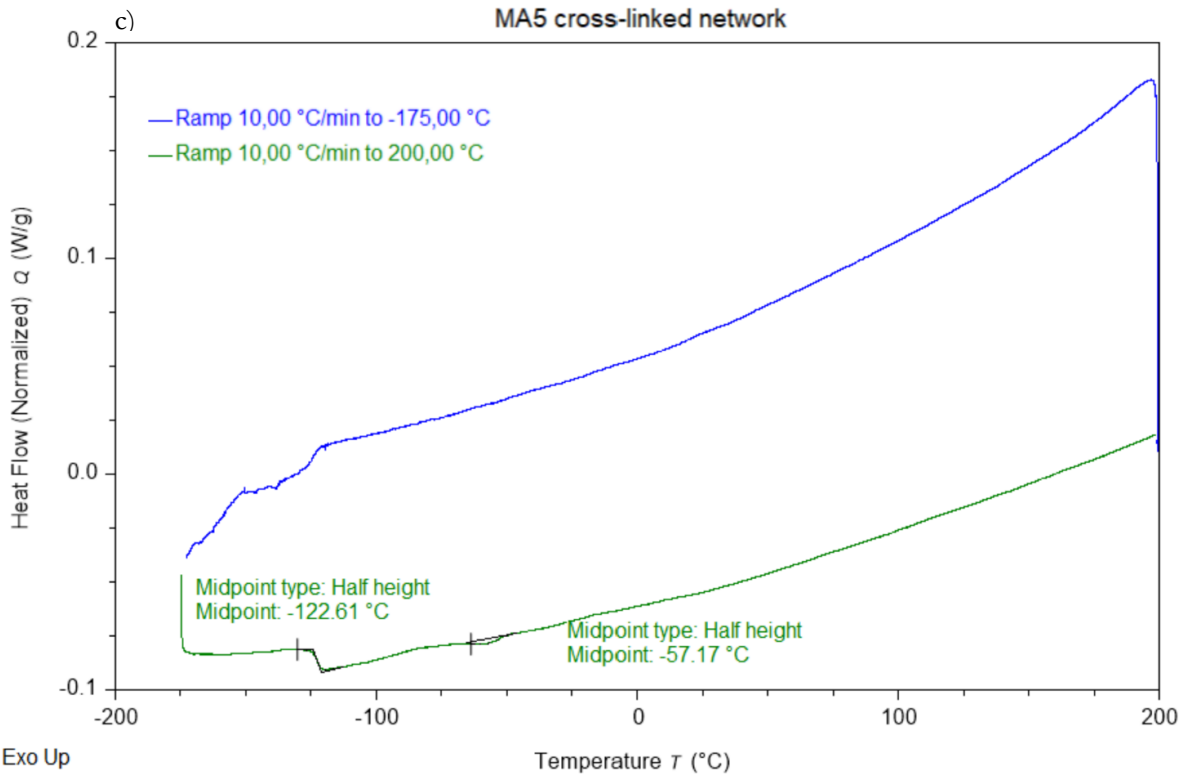
a)


REF (vinyl cross-linked network 5kDa)
Ramp 10.00 °C/min to -180.00 °C
Ramp 10.00 °C/min to 200.00 °C
Peak temperature: -80.79 °C
Enthalpy (normalized): 25.554 J/g
Onset x: -76.87 °C
Midpoint type: Half height
Midpoint: -116.83 °C
Enthalpy (normalized): 23.339 J/g
Onset x: -52.47 °C
Peak temperature: -48.40 °C
Heat Flow (Normalized) Q (W/g)
Temperature T (°C)
Exo Up

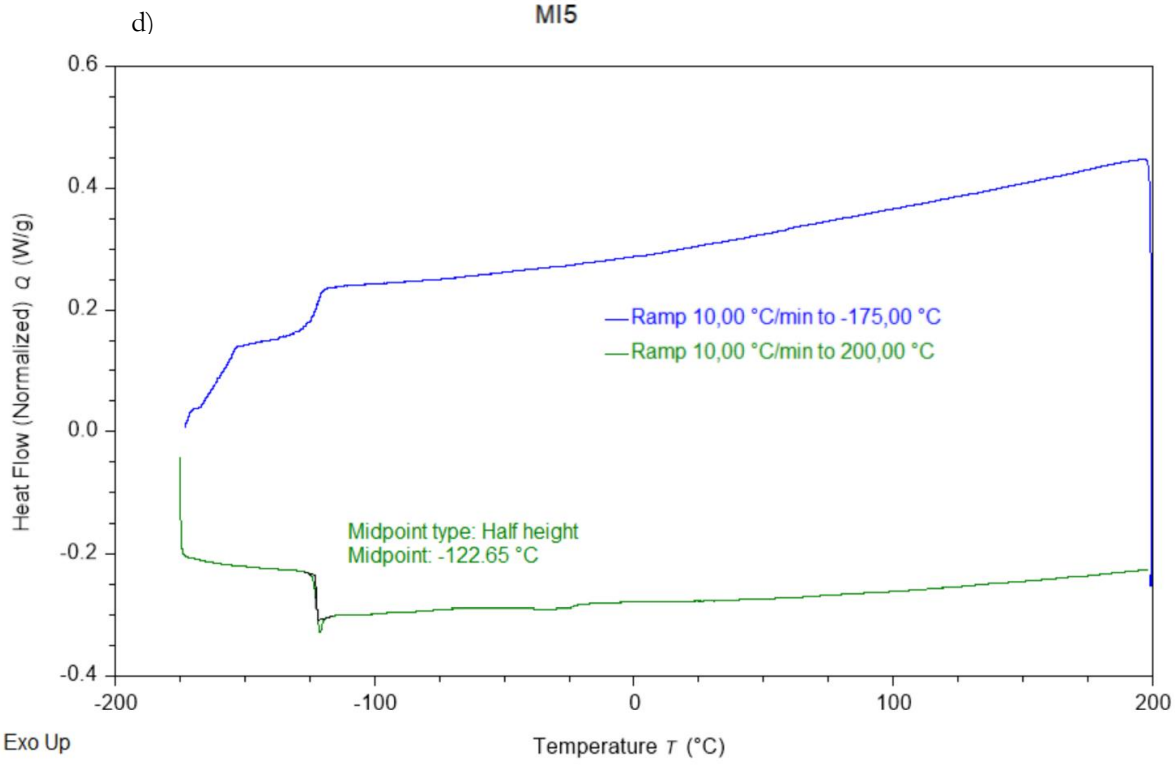
b)


MA5
Ramp 10,00 °C/min to -175,00 °C
Ramp 10,00 °C/min to 200,00 °C
Midpoint type: Half height
Midpoint: -122.67 °C
Peak temperature: -50.10 °C
Enthalpy (normalized): 0.30755 J/g
Onset x: -55.66 °C
Heat Flow (Normalized) Q (W/g)
Temperature T (°C)
Exo Up

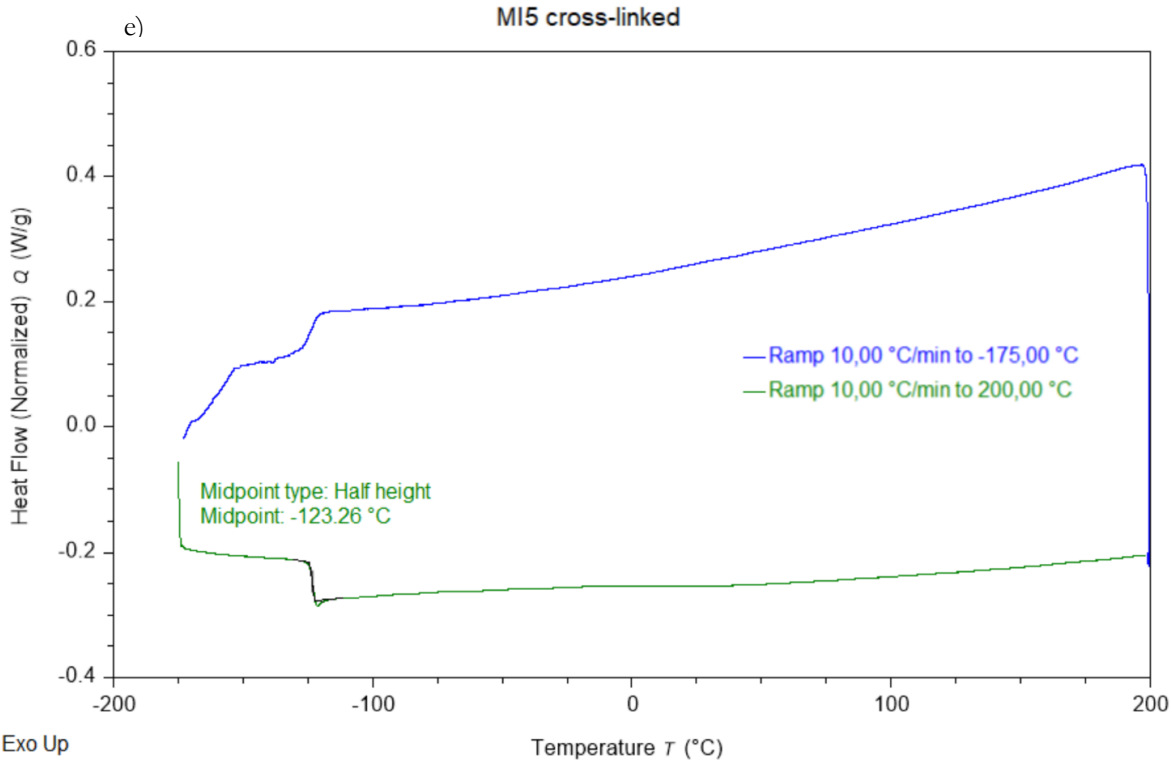
c)


MA5 cross-linked network
Ramp 10,00 °C/min to -175,00 °C
Ramp 10,00 °C/min to 200,00 °C
Midpoint type: Half height
Midpoint: -122.61 °C
Midpoint type: Half height
Midpoint: -57.17 °C
Heat Flow (Normalized) Q (W/g)
Temperature T (°C)
Exo Up
0.2
0.1
0.0
-0.1
-200
-100
0
100
200

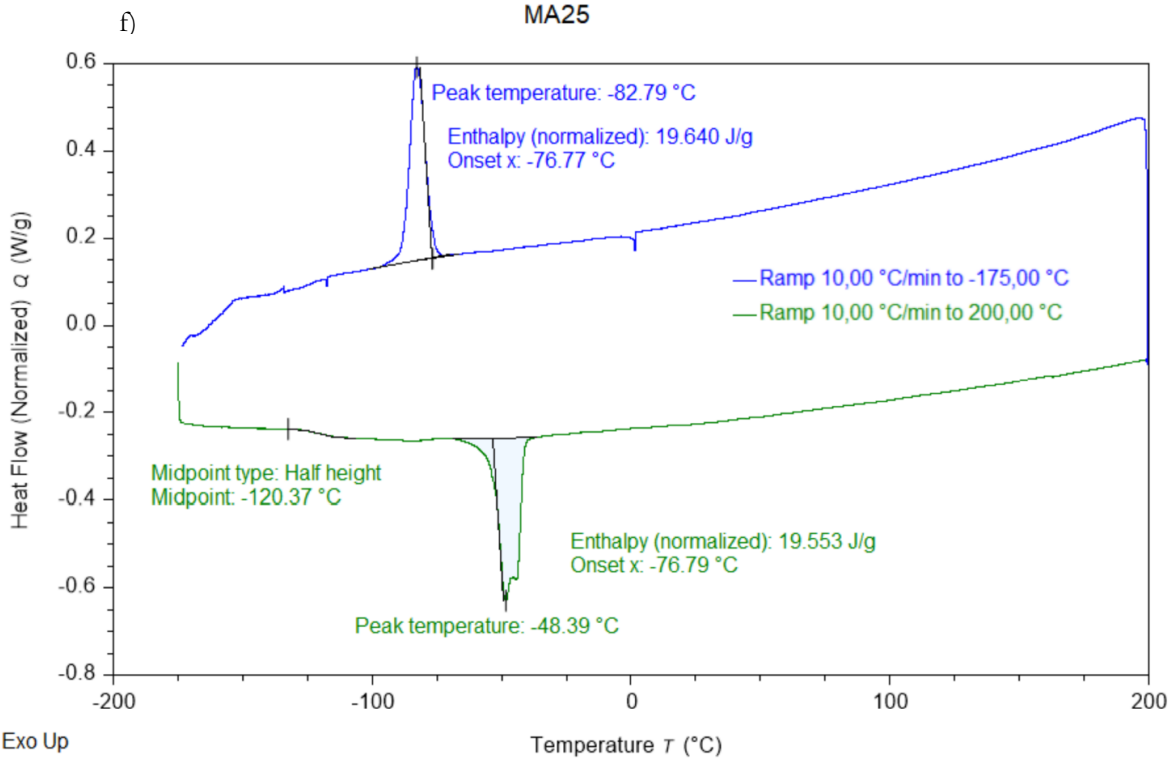
d)


MI5
Ramp 10,00 °C/min to -175,00 °C
Ramp 10,00 °C/min to 200,00 °C
Midpoint type: Half height
Midpoint: -122.65 °C
Heat Flow (Normalized) Q (W/g)
Temperature T (°C)
Exo Up
0.6
0.4
0.2
0.0
-0.2
-0.4
-200
-100
0
100
200

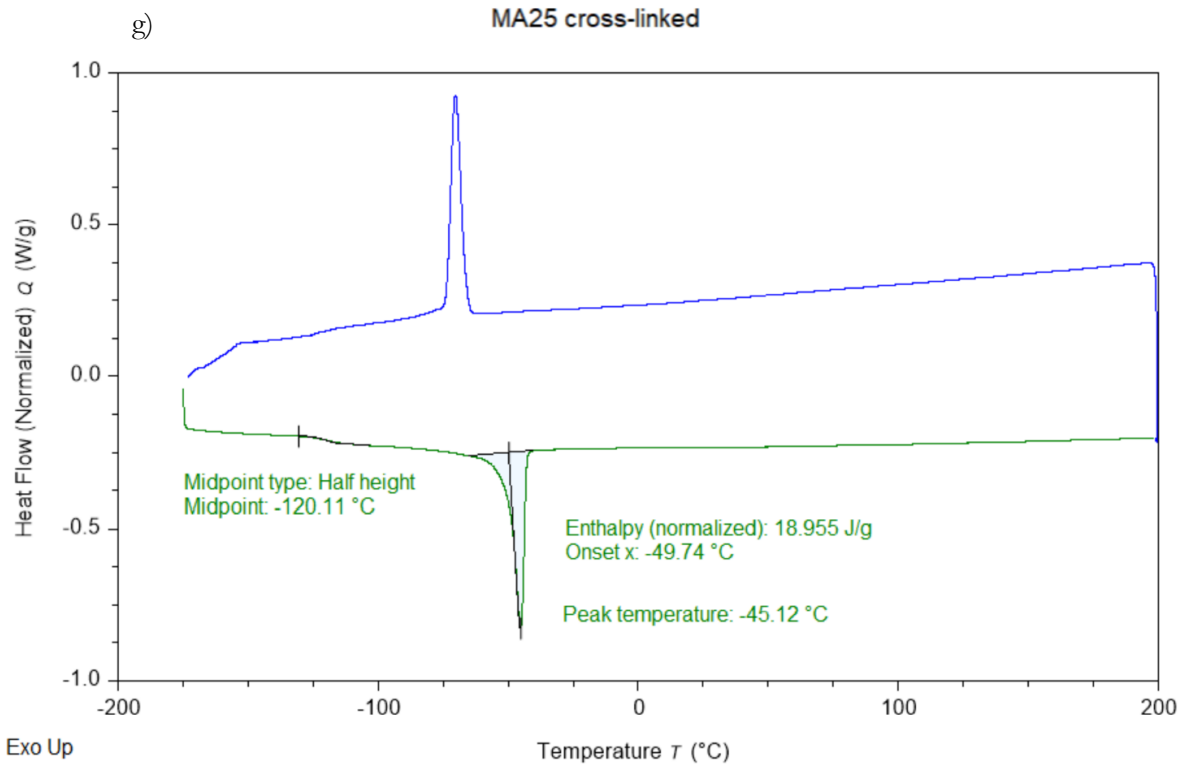
e)


MI5 cross-linked
Heat Flow (Normalized) Q (W/g)
0.6
0.4
0.2
0.0
-0.2
-0.4
-200
-100
0
100
200
Temperature T (°C)
Exo Up
Ramp 10,00 °C/min to -175,00 °C
Ramp 10,00 °C/min to 200,00 °C
Midpoint type: Half height
Midpoint: -123.26 °C

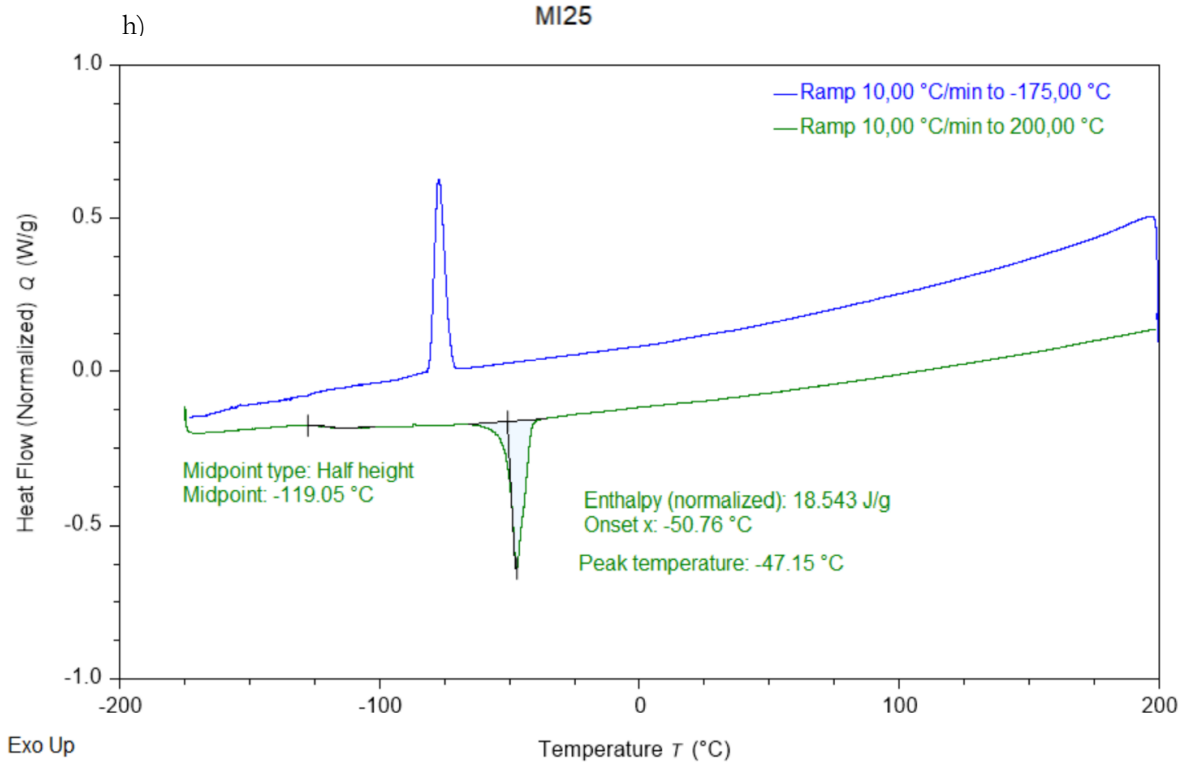
f)


MA25
Heat Flow (Normalized) Q (W/g)
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-200
-100
0
100
200
Temperature T (°C)
Exo Up
Peak temperature: -82.79 °C
Enthalpy (normalized): 19.640 J/g
Onset x: -76.77 °C
Ramp 10,00 °C/min to -175,00 °C
Ramp 10,00 °C/min to 200,00 °C
Midpoint type: Half height
Midpoint: -120.37 °C
Enthalpy (normalized): 19.553 J/g
Onset x: -76.79 °C
Peak temperature: -48.39 °C

g)


MA25 cross-linked
Heat Flow (Normalized) Q (W/g)
1.0
0.5
0.0
-0.5
-1.0
-200
-100
0
100
200
Temperature T (°C)
Exo Up
Midpoint type: Half height
Midpoint: -120.11 °C
Enthalpy (normalized): 18.955 J/g
Onset x: -49.74 °C
Peak temperature: -45.12 °C

h)


MI25
Ramp 10,00 °C/min to -175,00 °C
Ramp 10,00 °C/min to 200,00 °C
Heat Flow (Normalized) Q (W/g)
1.0
0.5
0.0
-0.5
-1.0
-200
-100
0
100
200
Temperature T (°C)
Exo Up
Midpoint type: Half height
Midpoint: -119.05 °C
Enthalpy (normalized): 18.543 J/g
Onset x: -50.76 °C
Peak temperature: -47.15 °C

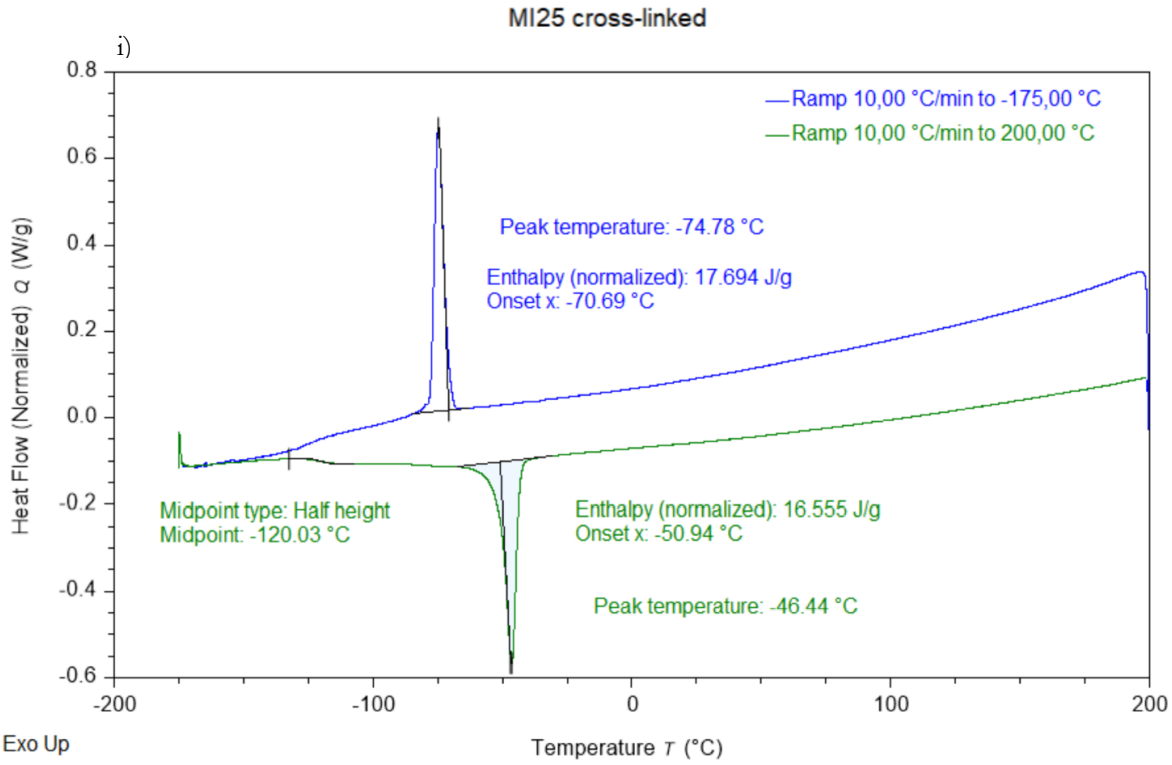



Figure S4. Differential scanning calorimetry (DSC) results from the various materials tested. Tg and Tm annotated (where present), with their characteristic temperatures and calculated enthalpies. a) A (stoich. eq.) cross-linked system with a vinyl terminated PDMS (5kDa) and 4-functional cross-linker with hydride groups. b) MA5 prepolymer. c) MA5 cross-linked network. d) MI5 prepolymer. e) MI5 cross-linked network. f) MA25 prepolymer. g) MA25 cross-linked network. h) MI25 prepolymer. i) MI25 cross-linked network.

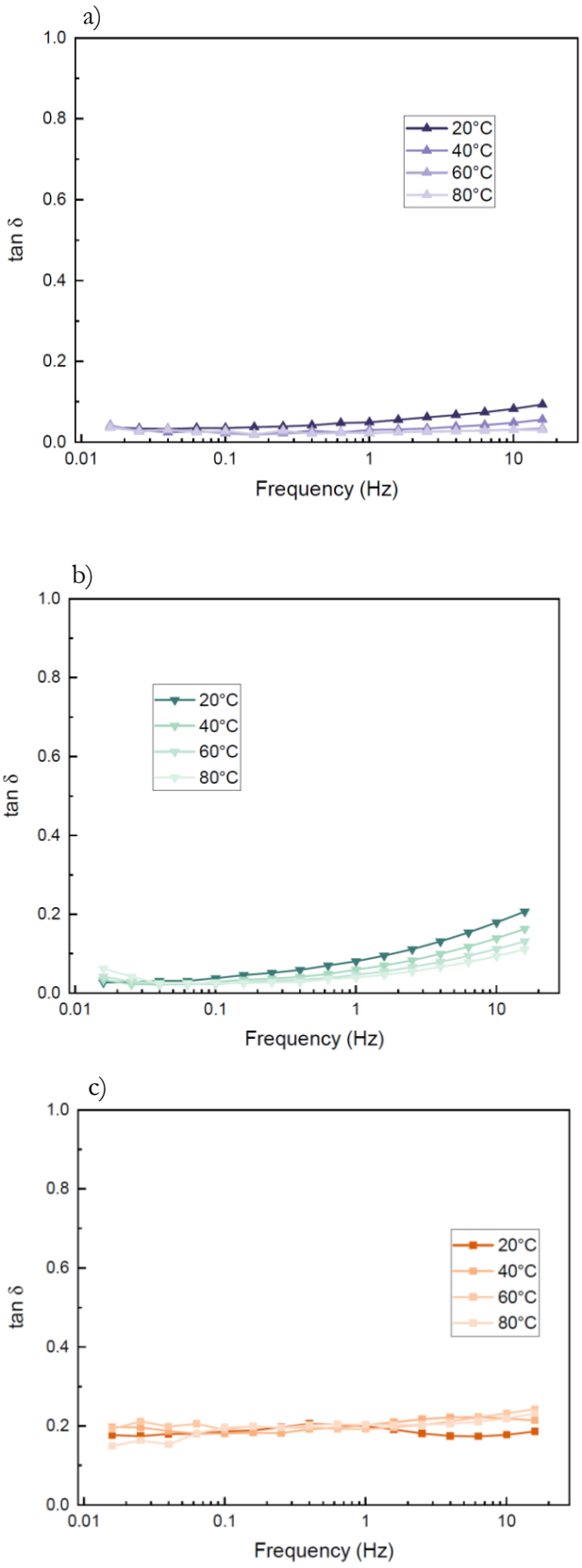



Figure S5. The rheological loss factor of a) MI5, and b) MI25 and c) MA25, respectively, at different temperatures from 20 °C to 80 °C.

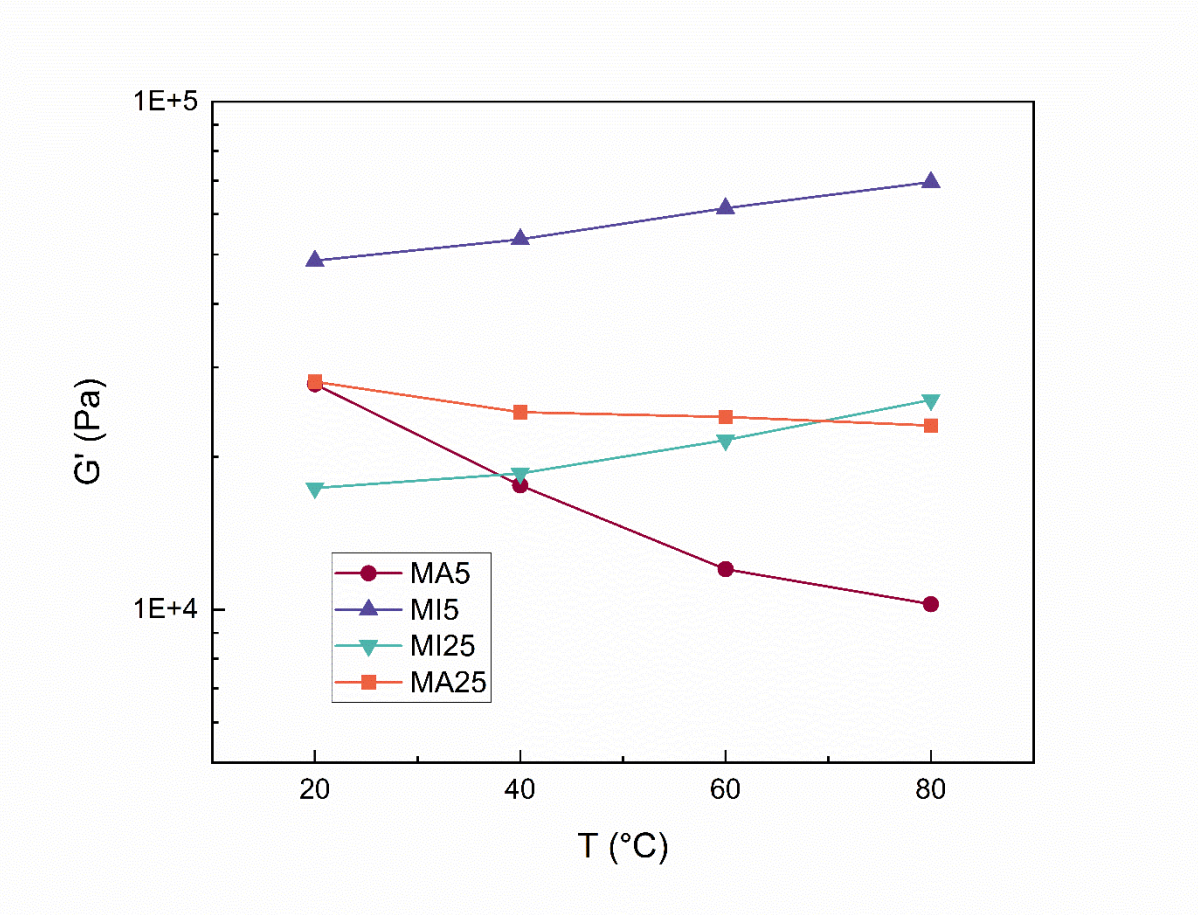



Figure S6. The storage modulus of all cross-linked samples at the investigated temperatures.

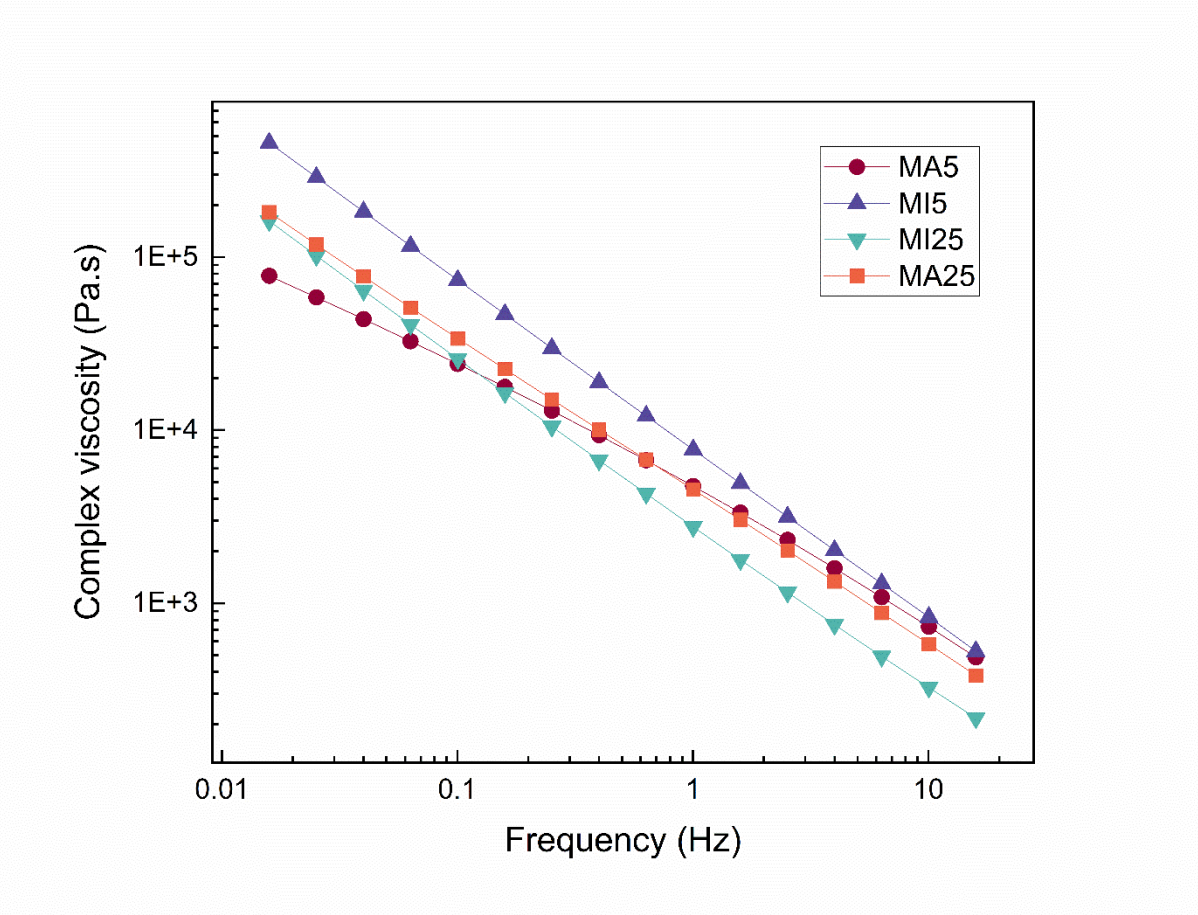



Figure S7. Complex viscosity at room temperature for all the samples.

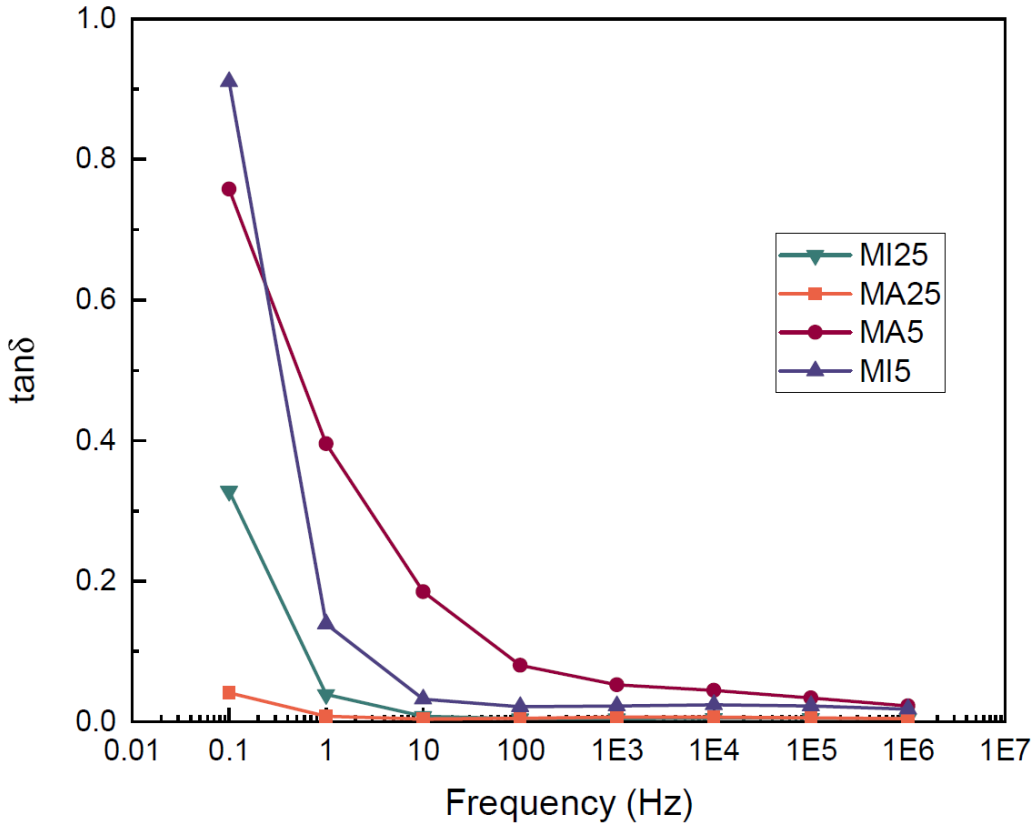
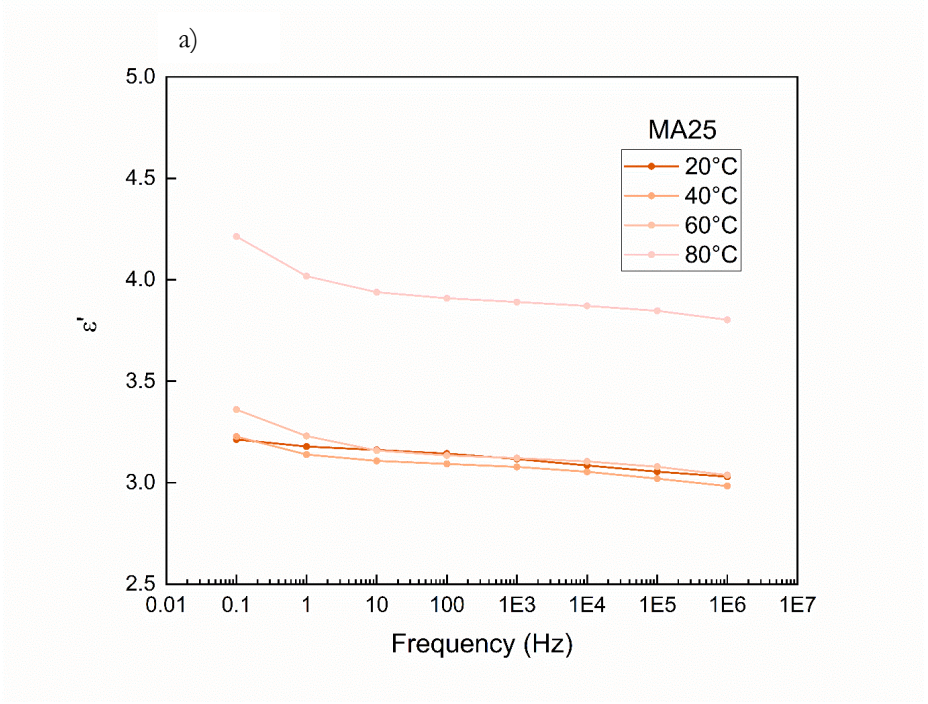



Figure S8. The dielectric loss factor of the investigated cross-linked networks at room temperature.



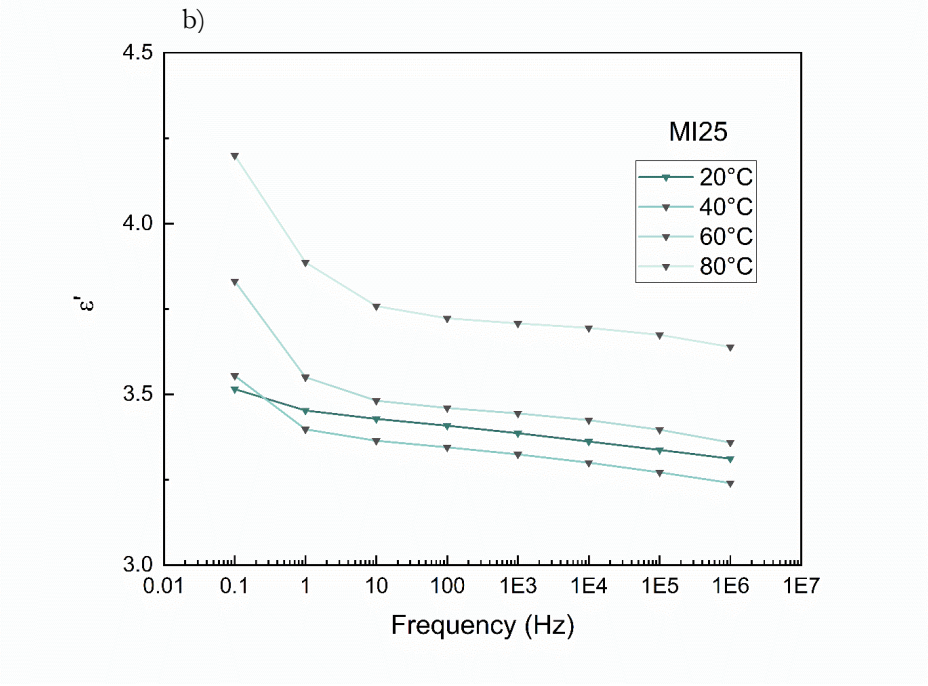




Figure S9. a) Dielectric permittivities in the investigated temperature range for MA25, b) dielectric permittivities in the investigated temperature range for MI25

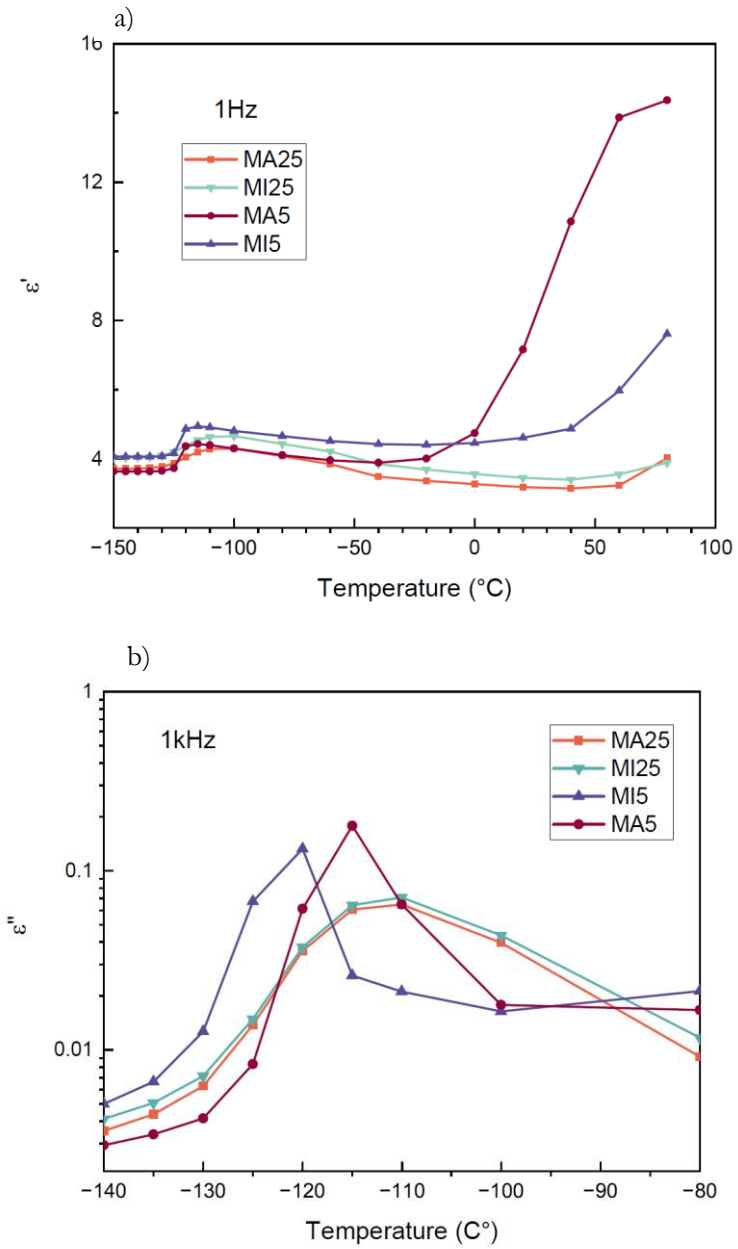



Figure S10. Temperature dependence of the dielectric properties: a) Permittivity over a temperature range (-150 – 100) ºC and b) ε" at low temperatures. The plateu value of permittivity (< 120 ºC) can be taken as the glass transition indicator through the appearance of the so-called depolarization peak in the dielectric loss curve line [1].

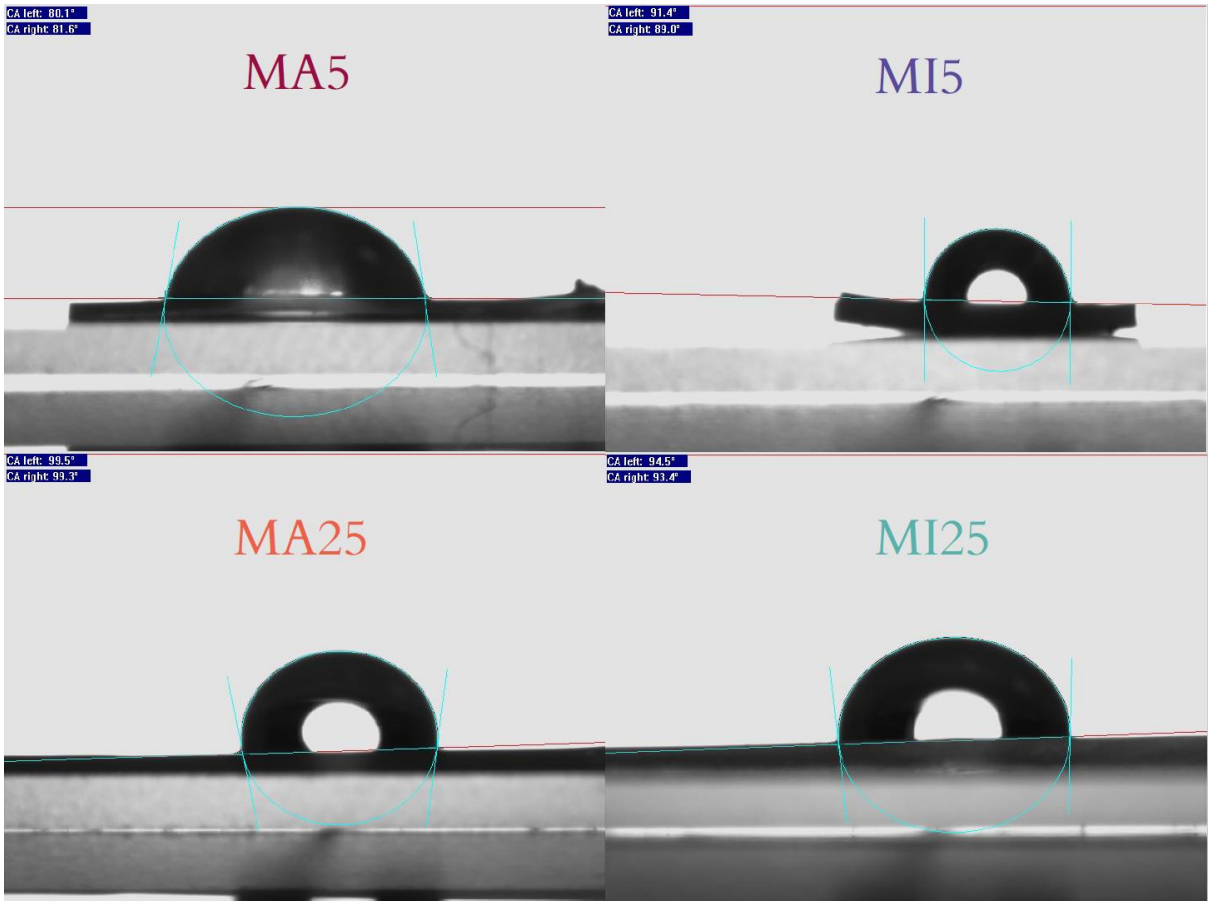



Figure S11. Contact angle measurements of all the cross-linked samples

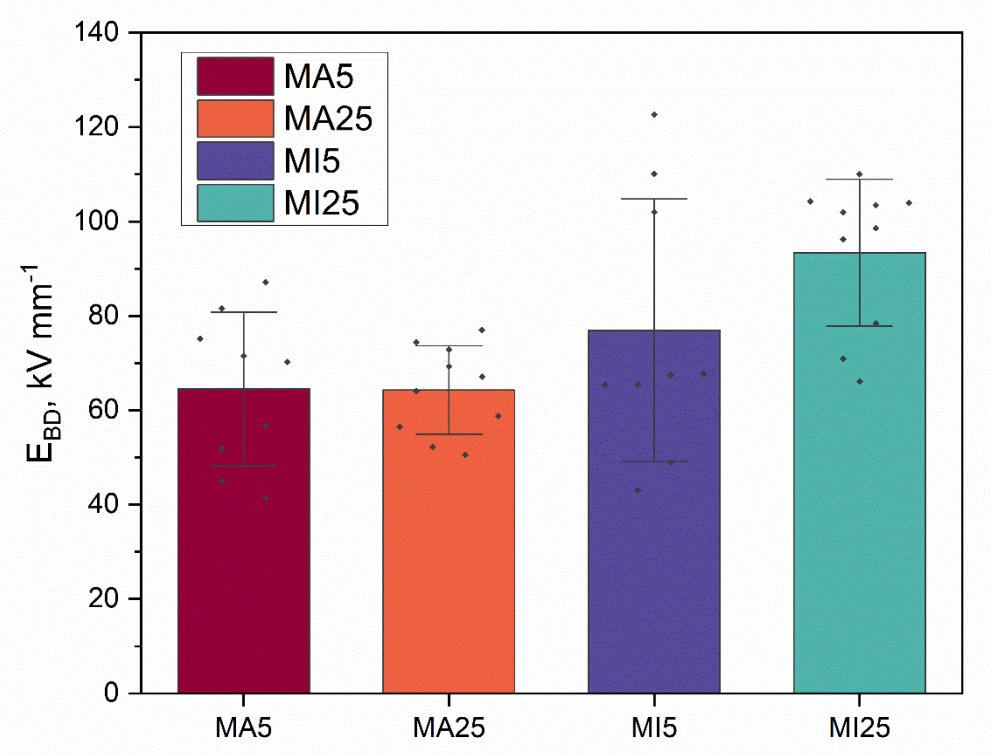



Figure S12. Electric breakdown strength of all the cross-linked samples.

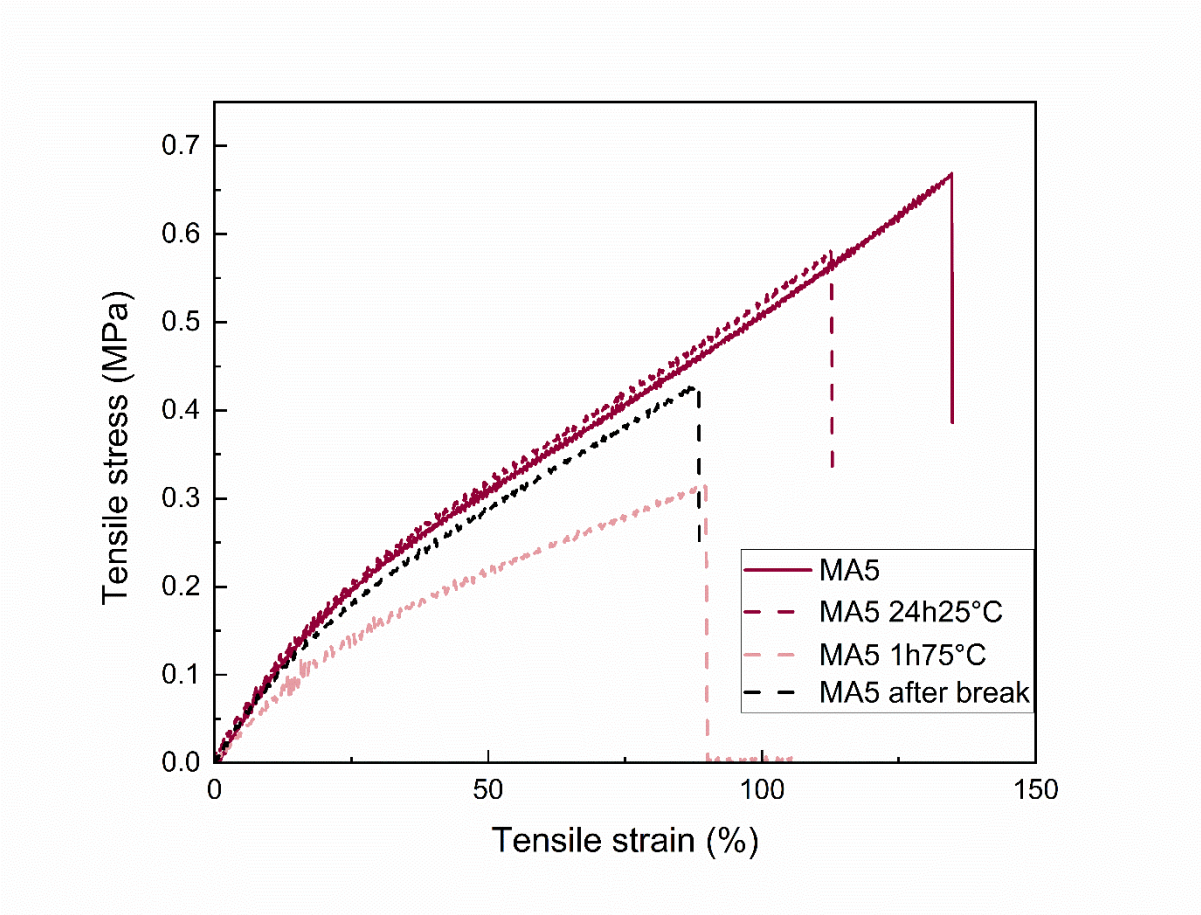



Figure S13. Tensile test of all the self-healed materials, following regular self-healing procedure (24 h at room temperature), varying the temperature and healing times (1h at 75 ºC) , and healing „after break“ (24h at room temperature, after a sample was broken by a tensile test)

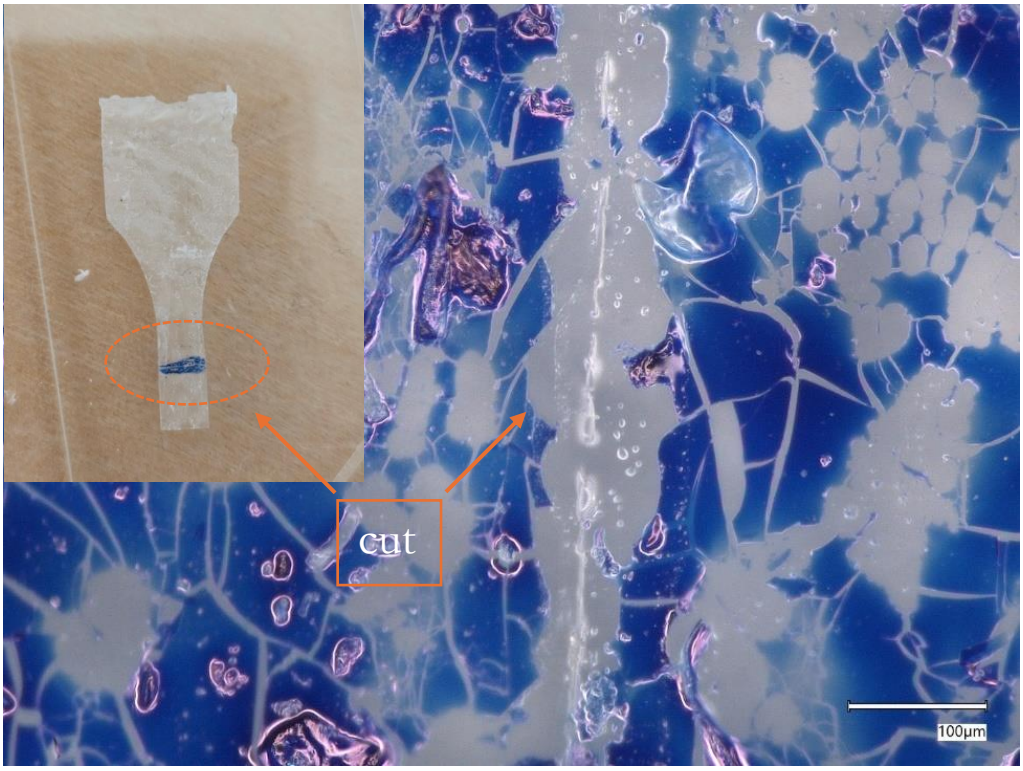



Figure S14. Optical microscopy at 400x magnification of MA5N with the imposed cut visible after self-healing for 24 h under room temperature. The blue color is marker residue.

REFERENCES:

[1] Klonos, P. A. Crystallization, Glass Transition, and Molecular Dynamics in PDMS of Low Molecular Weights: A Calorimetric and Dielectric Study. Polymer 2018, 159, 169–180. https://doi.org/10.1016/j.polymer.2018.11.028.