Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information

Dicarboxylic acid-epoxy vitrimers: Influence of off-stoichiometric acid content on cure reactions and thermo-mechanical properties

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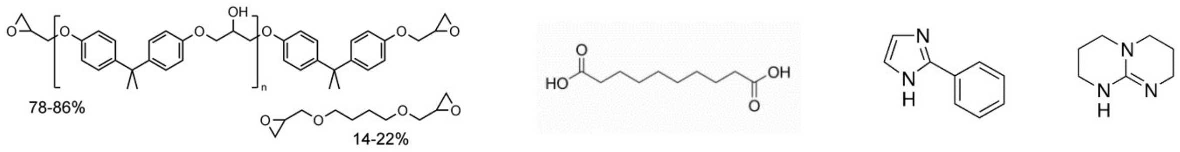
Contents :

1 Manufacture of vitrimer networks – mixing, mould casting, degassing and curing

Scheme S1: Reactants used in the study



Diepoxide monomer (LY564) Sebacic acid 2-PI TBD

Sebacic acid and TBD were added to the epoxy as received, and mixed for 24 h at 50°C until obtaining a white homogeneous mixture. The final mixture was then placed into an open mould, degassed under vacuum for 2h at 90°C to ensure removal of air inadvertently added during mixing. Samples were then cured at 145°C for 8h (ramp 1.7°C/min from room temperature to 145°C), a post-cure was then completed at 160°C for 8h.

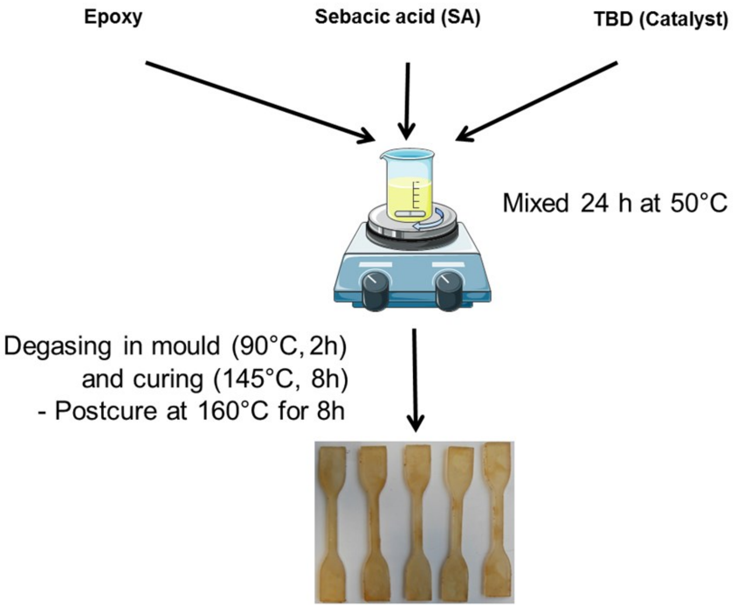


Fig. S1 Schematic of fabrication method used to produce vitrimer samples

2 IR analysis method

2.1 Data collection

Data were collected using a Bruker Tensor 37 spectrometer equipped with a Specac GoldenGate thermalized ATR stage. Components of reactive mixtures were weighed and mixed together at room temperature in a mortar before placing a drop of the mixture on the golden gate cell preheated to 125°C. Spectra were then recorded at regular 2 min intervals (resp. 1 min. intervals with 2-PI). CO_2/water vapour correction and noise reduction were applied through the Opus software. Data were then analysed using integration tools in the Opus 3D module.
Fig S2 shows a typical collection of spectra (one hour curing of 100H5CAT at 125°C), obtained in the 2000-600 cm^{-1} range. Identification of signals in the 1600-1800 cm^{-1} range is shown in Figure S3. Area ranges for integration of signals of interest are shown in Figure S4.

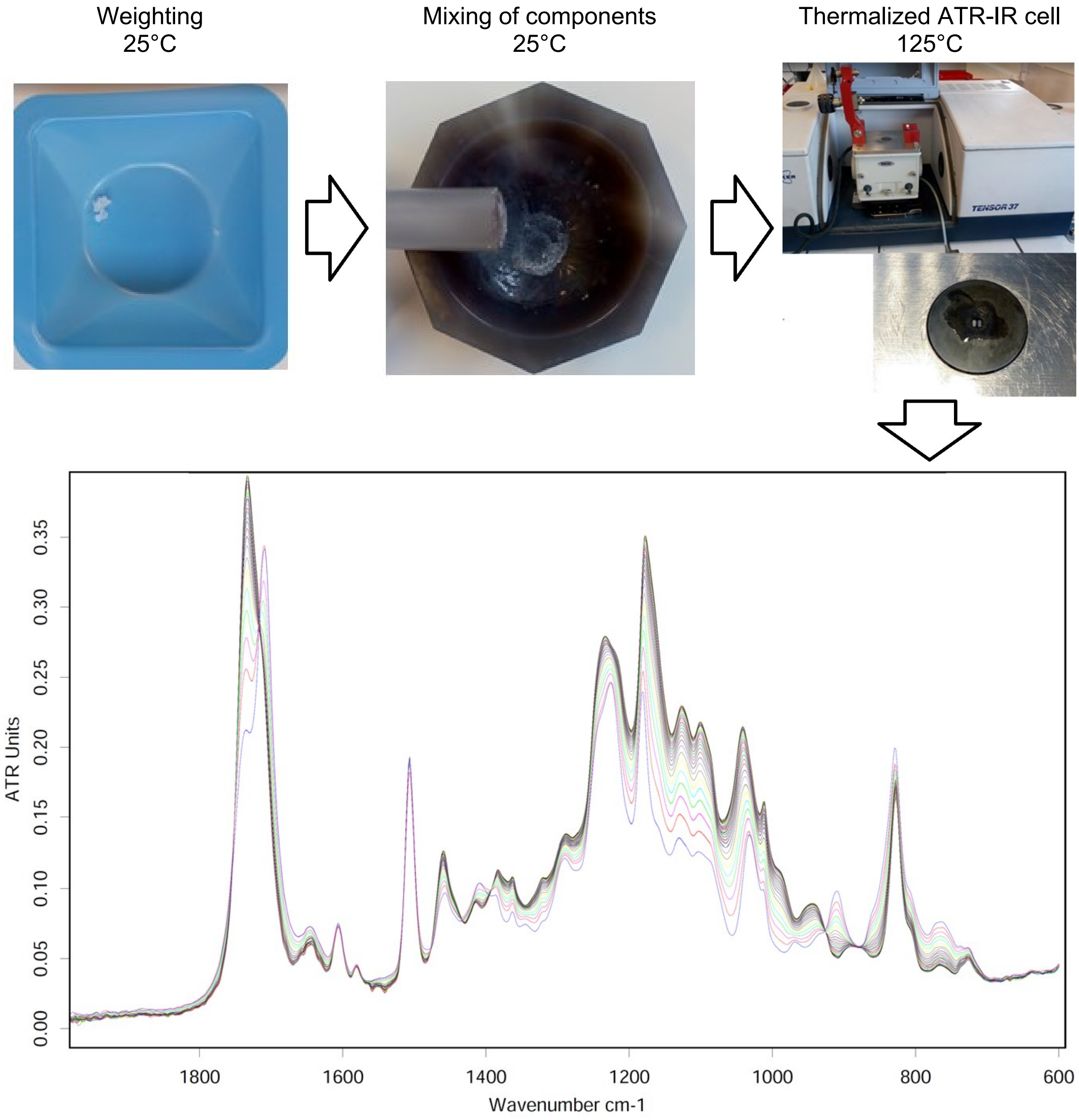


Fig. S2 Schematic of ATR-IR curing experiment to record species evolution over time.

2.2 *Carbonyl peaks assignment*

In Figure S2, major changes are observed in the 1600-1800 cm^{-1} region during curing. The signal detected at 1706 cm^{-1} is attributed to the C=O stretching of H-bonded dimerized carboxylic acid groups. Another signal, detected at 1735 cm^{-1} is attributable to the C=O stretching of the ester. However, for all investigated formulations, a signal at 1735 cm^{-1} was already present before starting the cure cycle while no ester was yet present. Spectra of sebacic acid recorded in varions liquid environments and concentrations (Fig S3) lead to the conclusion that the C=O stretching signal of solvated COOH groups (forming an H-bond to surrounding ether groups) overlaps the signal of ester at 1735 cm^{-1}.

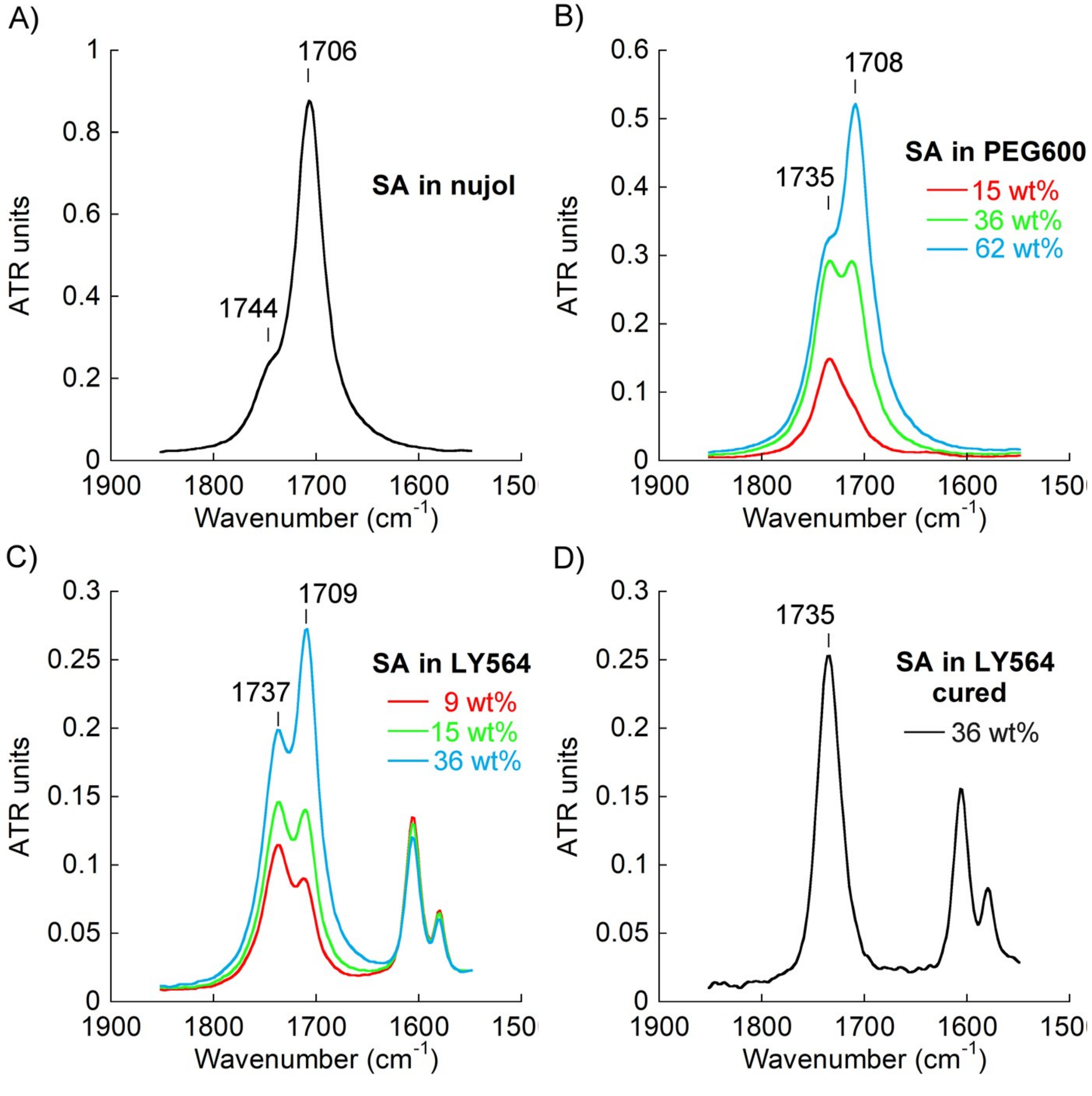


Fig. S3 Identification of C=O stretching signals. A) Sebacic acid in the molten state at 145°C in paraffin oil. The signal at 1706 cm^{-1} is the regular signal of dimerized H-bonded COOH groups, B) Sebacic acid at different concentrations in PEG600 used as a solvent. The signal at 1735 cm^{-1} is due to COOH groups interacting through H-bonds with the ether groups of the solvent. C) Sebacic acid at different concentrations in epoxy resin; the same signals are present. The ether groups of uncured epoxy resin interact with dissolved COOH groups. D) Sebacic acid in epoxy resin after full curing. The C=O stretching signal of the ester is detected at 1735 cm^{-1}.

2.3 *Integration of signals*

Integration of ATR signals was used for monitoring of curing reactions. The method of integration is illustrated in Figure S4. The result of integration (either positive or negative) as a function of time is plotted without any post treatment or normalization in Figures 2 and 3.

Esters: Monitoring was performed by integration of the C=O stretching peak (1735 cm^{-1}) over the 1748–1724 cm^{-1} interval.

Carboxylic acids: Monitoring was performed by integration of the C=O stretching peak (1705 cm^{-1}) over the 1718–1703 cm^{-1} interval.

Epoxides: Monitoring was performed by integration of the asym. epoxy ring deformation[1] (914 cm^{-1}) over the 921–904 cm^{-1} interval.

Ethers : According to literature,[2] the following signals are expected for the ether:
Characteristic C–O stretching signals:
- Aliphatic ether functions: several signals in the 1140-1100 cm^{-1} range.

Interfering C–O stretching signals:
- Aryl-alkyl ether functions: two signals around 1250 cm^{-1} and 1040 cm^{-1}.
- Primary and secondary alcohol functions: two signals around 1065 cm^{-1} and 1100 cm^{-1}.
- Ester functions: several signals in the 1280-1160 cm^{-1} range.

In order to extract a specific signal of ethers formed by the anionic polymerization of the epoxy with minimum interference with other functions present, the ether signature was isolated by integration of the ATR trace between 1150 and 1120 cm^{-1}. Baseline for integration was taken by connecting the maximums of the neighboring peaks (1182 cm^{-1} and 1033 cm^{-1}) which showed little change during the reaction.

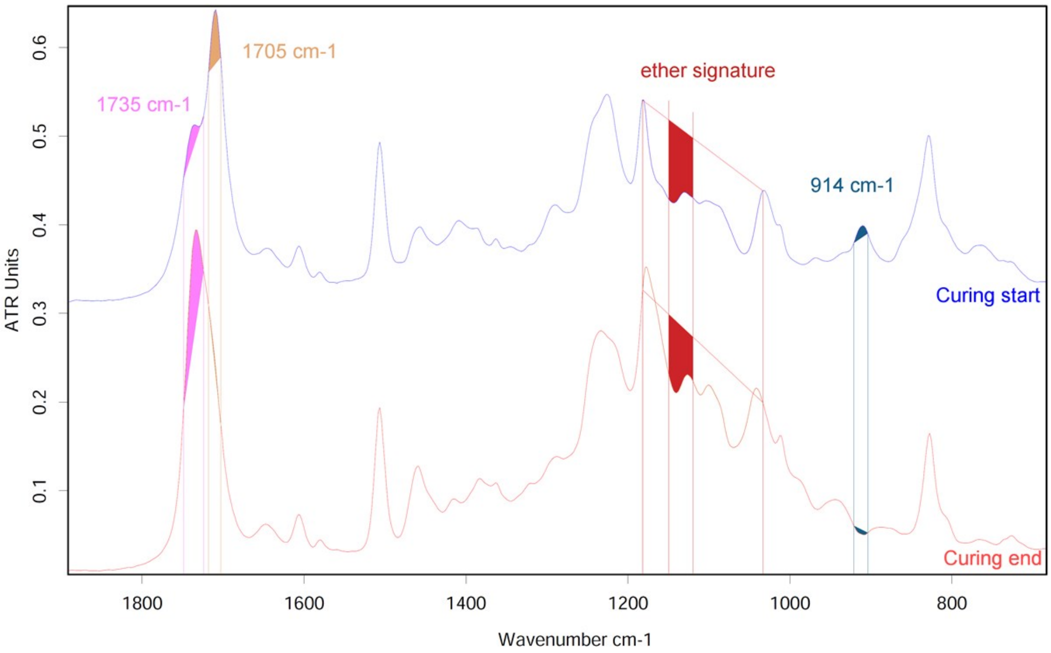


Fig S4 Typical integration zone for epoxy peak at the beginning (blue curve) and at the end (red curve) of cure process for sample 100H 5CAT

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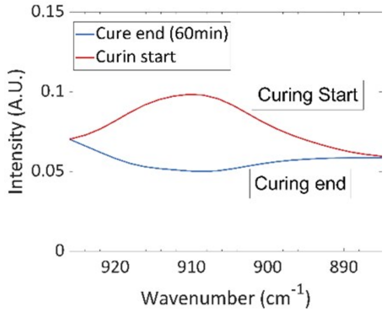
[1] Interpreting Infrared, Raman, and Nuclear Magnetic Resonance Spectra, Vol. 2, Chapter 1 - Epoxides and Ethers, Richard Allen Nyquist ed., Academic Press, 2001, Pages 1-26.

[2] Spectrochimie Moléculaire, Bruno Wojtkowiak, Martial Chabanel, Chapter 6 - Composés à fonction oxygénée. Technique et Documentation, Paris 1977, Page 213.

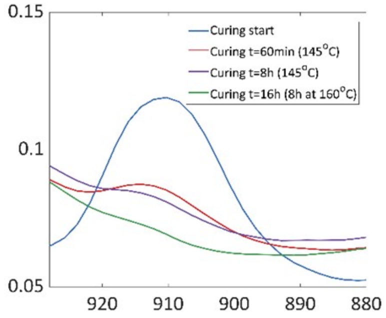
2.4 *Complementary FTIR data*

To ensure that all epoxy groups were consumed at the end of the curing cycle, a postcure was applied to all samples. Figure S5a shows that epoxy groups of 100H samples are virtually exhausted after the cure cycle of 60 min at 145°C. Samples 50H and 30H (Fig S5b and S5c respectively) were still containing some epoxy after 60 min at 145°C. Therefore, the reaction was carried out for 8 h at 145°C and then 160°C for 8 h for all samples. The figure shows small remaining absorption at 914 cm^{-1} did not change for several hours at 160°C indicating that the eventual small fraction of remaining epoxy groups is no longer reactive (probably due to reduced mobility after crosslinking).

a)



b)



c)

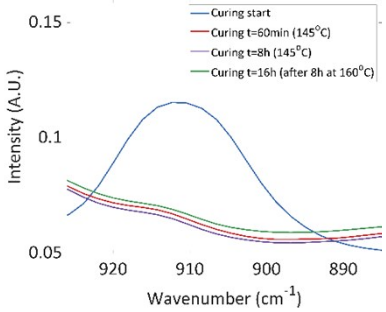


Fig.S5a Evolution of epoxy peak during curing of sample 100H 5CAT: beginning (red) and after 60 min (blue) at 145°C

Fig. S3b Evolution of epoxy peak during curing of sample 50H 5CAT: beginning (blue), after 60 min (red) after 8h at 145°C (purple), and 8h at 160°C (green)

Fig. S5c Evolution of epoxy peak during curing of sample 30H 5CAT: beginning (blue), after 60 min (red) after 8h at 145°C (purple), and 8h at 160°C (green)

3 Dynamic mechanical analysis – onset value of T_g from storage moduli curves

The values of T_α taken at maximum value of the tan delta curves are given in Table S1. The data are fitted using the Fox-Flory equation:

$$\frac{1}{T_\alpha} = \frac{\phi_1}{T_{\alpha 1}} + \frac{\phi_2}{T_{\alpha 2}}$$

where ϕ_1, ϕ_2 are the volume fractions of polymer 1 and polymer 2 and $T_{\alpha 1}$, $T_{\alpha 2}$ their respective glass transition temperatures. The results are presented in Fig. S6; ϕ_1 and ϕ_2 are approximated respectively by the weight fractions of excess epoxy and the weight fraction of stoichiometric epoxy + acid monomers in the composition. $T_{\alpha 2}$ and $T_{\alpha 1}$ are taken as adjustable parameters and represent respectively the glass transitions of epoxy homopolymer and that of a 1:1 adduct of epoxy + sebacic acid. The trace of the fitting curve is shown in Fig. S6. Best fit was achieved with $T_{\alpha 1}$ = 39°C, $T_{\alpha 2}$ = 160°C. The latter value is close to the one commonly reported for the epoxy homopolymer[3,4]

Table S1 Glass transition temperatures for different ratios taken from the tan delta curves

	Samples					
	100H5CAT	**75H5CAT**	**60H5CAT**	**50H5CAT**	**30H5CAT**	**30H10CAT**
T_α (°C)	40	50	69	80	100	101

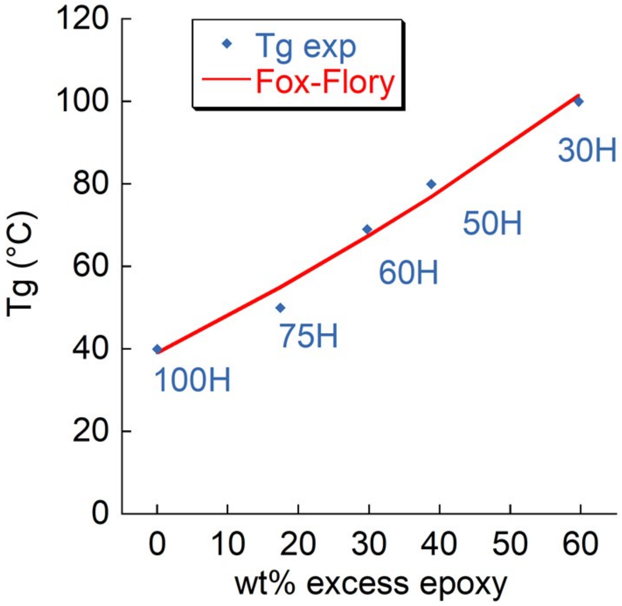


Fig. S6 Evolution of the glass transition as a function of composition (diamonds) and trace of the fit using the Fox-Flory equation (red solid line)

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[3] Heise, M. S., Martin, G. C. (1989). *Macromolecules* 22, 99–104

[4] Ooi, S. K., Cook, W. D., Simon, G. P., Such, C. H. (2000) *Polymer* 41, 3639–3649)

4 Mechanical results

Mechanical properties of vitrimers at different ratios is reported in Table S2.

Table S2 Tensile properties for different ratios of vitrimer

	Samples					
	100H 5CAT	**75H 5CAT**	**60H5CAT**	**50H5CAT**	**30H5CAT**	**30H10CAT**
Young modulus (MPa)	0.471 ± 0.14	1.63 ± 21	886 ± 8	2300 ± 200	2100 ± 300	2300 ± 100
Breaking strain (%)	328.1 ± 19	143.6 ± 36.6	6.4 ± 0.9	7.2 ± 0.1	13.42 ± 0.1	12.7 ± 0.1
Ultimate tensile strength (MPa)	0.83 ± 0.02	11.2 ± 1.5	18.46 ± 4	43.2 ± 4.2	47.1 ± 1	39.8 ± 0.9

5 Stress relaxation results

Fig. S7 shows the results of stress relaxation experiments for each ratio. For compounds 100H5CAT and 75H5CAT, the solid red lines indicate the results of fitting by a monoexponential decay. The values of relaxation time thereby determined are plotted in Arrhenius axes in Fig 9, initial value of the shear relaxation modulus G_0 for these two samples are reported in table S3.

Table S3 Relaxation modulus (initial value)

Samples	**100°C**	**120°C**	**140°C**	**160°C**	**180°C**	**220°C**
100H 5CAT G_0 (MPa)	0.57	0.63	0.69	0.55	0.58	
75H 5CAT G_0 (MPa)		4.40	5.05		5.80	5.30

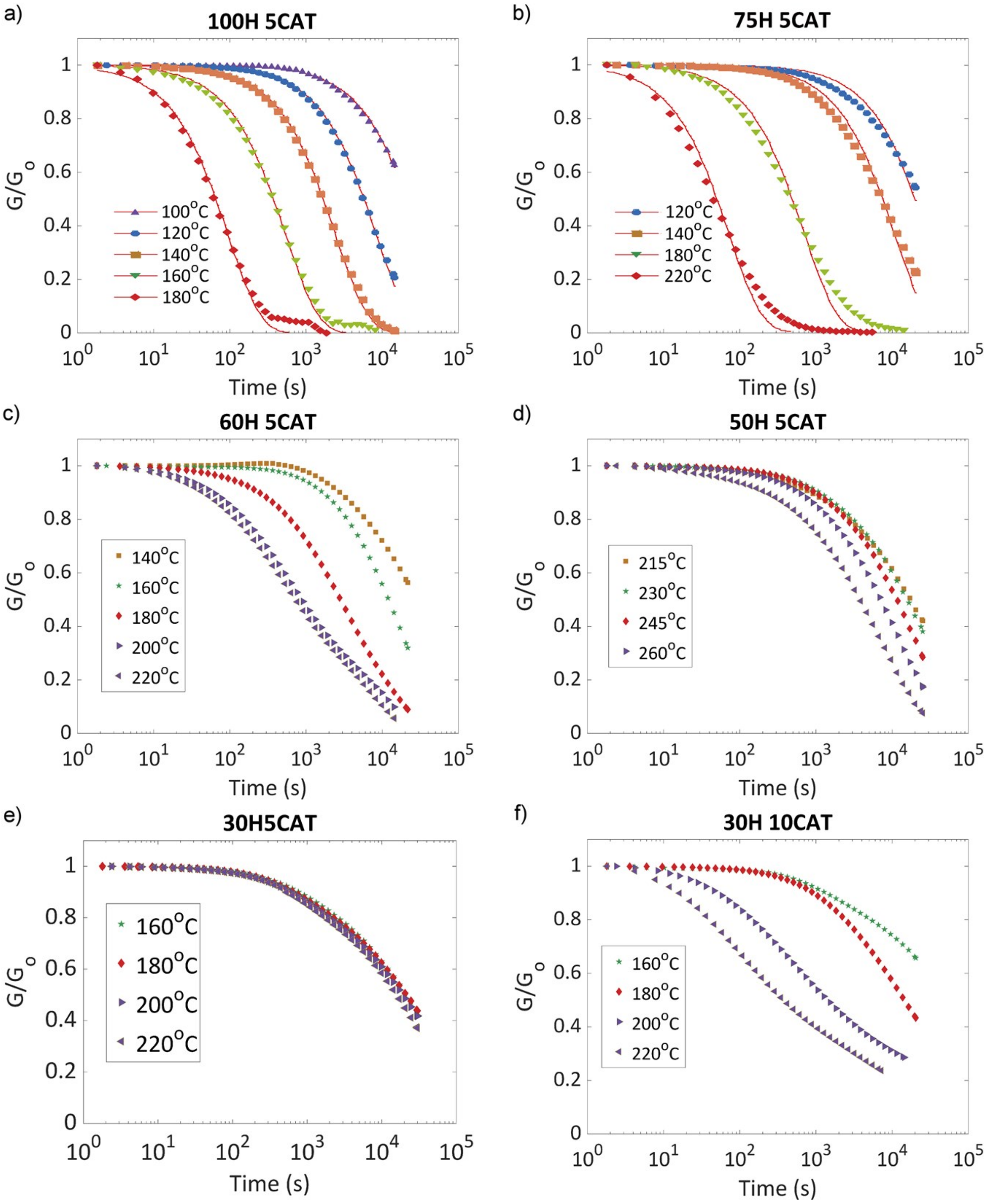

Fig. S7 Stress relaxation results obtained by DMA in shear geometry: a) 100H 5CAT, b) 75H 5 CAT c) 60H5CAT, d) 50H5CAT, e) 30H5CAT, and d) 30H10CAT

6 Creep results for all samples

Fig. S shows the results of creep experiments for each ratio. The value of applied stress is indicated. Compound 100H 5CAT and compound 75H 5CAT flow under application of stress whereas other compounds only show very limited values of creep.

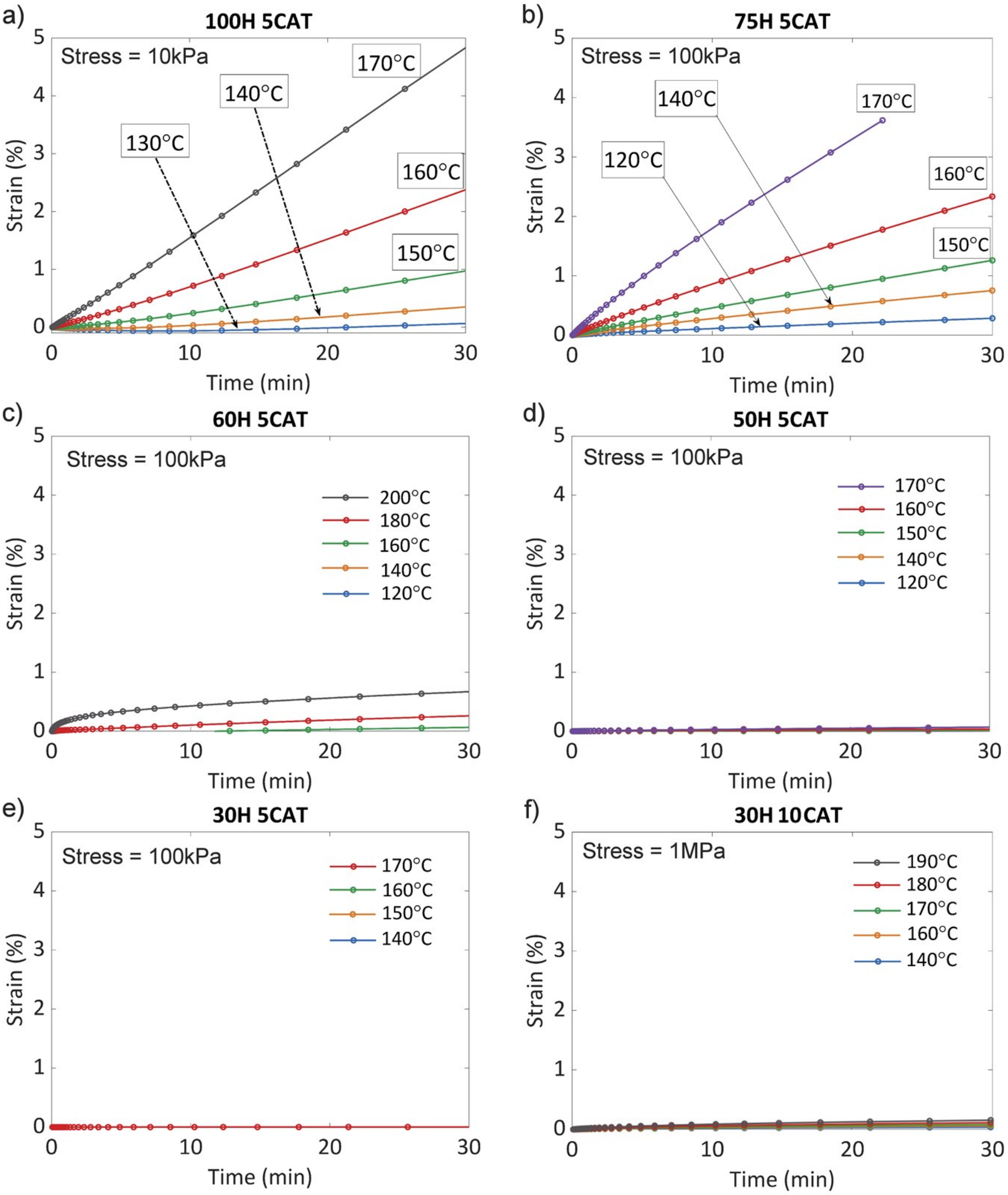

Fig. S8 Creep results for all samples