Supplementary Information (SI) for RSC Applied Polymers.

SUPPLEMENTARY INFORMATION

Debondable phenoxy-based structural adhesives with β-amino amides containing reversible crosslinkers

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Materials and methods

Methyl acrylate (stabilized with MEHQ, 99%), trimethyl hexamethylenediamine (2,2,4- and 2,4,4-mixture, TMHD, 99%) were purchased from TCI Chemicals Europe. 4,4'-trimethylene dipiperidine (97%, TMHD), 2-(1-piperazinyl)ethylamine (PEA), triethylenetetramine (TETA) were purchased from Sigma Aldrich. Epikote 828-LV (epoxy equivalent of approximately 185 g/equivalent) was provided by Westlake Epoxy. Ancamide 3030 curing agent (amine equivalent of 95 g/{H}) was provided by Evonik. Priamine 1074 was provided by Croda. All chemicals and solvents were used without further purification unless stated otherwise.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance Ultrashield 300 MHz spectrometer. Deuterated chloroform $CDCl_3$ was used as solvent. Chemical shifts are given in parts per million (ppm).

Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) spectra were measured using a Perkin-Elmer Spectrum1000 FTIR infrared spectrometer with a diamond ATR probe.

Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/SDTA851e instrument under air atmosphere at a heating rate of 10 $°C \cdot min^{-1}$ from 30 to 800 °C for the ramp or at 200 °C for 1 h for the isothermal measurement.

Differential scanning calorimetry (DSC) analyses were performed with a Mettler Toledo instrument 1/700 under air atmosphere at a heating rate of 10 $°C \cdot min^{-1}$ from 0 to 200 °C.

Rheology experiments were performed on an Anton Paar MCR 302. The experiments were performed in parallel plate geometry using 8 mm sample disks. Amplitude sweep experiments were performed using a frequency of 1 Hz, a constant force of 1 N, and a variable shear strain that was ramped up logarithmically from 0.01% to 10% to observe the linear viscoelastic region. Stress-relaxation experiments were performed using a constant shear strain within the linear viscoelastic region of the samples, and a constant force of 1 N. The obtained characteristic relaxation time (τ^*), using the stretched Maxwell model, was used to calculate the activation energy.

Tensile tests were performed on a Tinius-Olsen H10KT tensile tester, equipped with a 5 kN load cell, at a speed of 10 mm·min-1, and with a pre-load of 0.05 N. Flat dog bone type samples, prepared by a Ray-Ran dog bone cutter, with an effective gauge length of 13 mm, a width of 2 mm and a thickness of around 1-2 mm using ASTM standard type IV dog bones (ISO 527-2- 2B) were used for the tensile tests.

(Re)processability was investigated by cutting the material in small pieces, which were then placed into a rectangular mold for compression molding. This assembly was placed in a preheated compression press (200 °C) for 1 min under 0.5 tonnes/m^2. Then the pressure was increased to 3 tonnes/m^2 and kept constant for an additional 30 min.

Solubility tests were carried out in 40 mL of chloroform using 2 mm in diameter, 2 mm in thickness, and a weight of around 15-20 mg samples for 24 h at 25°C. The solvent was then removed, and the samples were dried under vacuum overnight at 60 °C. The soluble fraction and swelling ratio were calculated using equation **eq. S1** and equation **eq. S2**, respectively.

$$gel\,fraction\ (\%) = 1 - \frac{m_i - m_d}{m_i} \qquad \text{(eq. } \mathit{S1}\text{)}$$

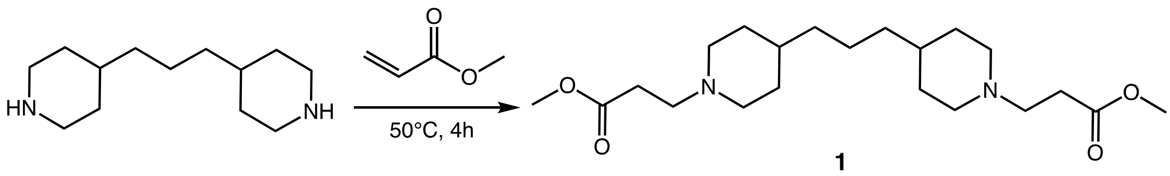
$$swelling\ ratio\ (\%) = \frac{m_s - m_i}{m_i} \qquad \text{(eq. S2)}$$

with m_i, m_s, and m_d representing the mass of initial, swollen, and dry samples, respectively.

Creep recovery experiments were performed at different temperatures (70-140 °C) using a constant normal force of 1 N. In the first 300 s, no shear stress was applied. Following this, a 2000 Pa shear stress was applied for 5000 s and a recovery period of 3600 s with no shear stress applied.

Lap-shear tests were performed on a Tinius-Olsen H10KT tensile tester, equipped with a 10 kN load cell, using ASTM D1002-05 standard test method for apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading (metal-to-metal) at the test speed of 1.3 mm·min^{-1}. Experiments were conducted at 20 – 25 °C with at least three samples for reproducible results.

Dimethyl 3,3’-(propane-1,3-diylbis(piperidine-4,1-diyl))dipropionate



Scheme S1. Synthesis of BAE 1.

In a round bottom flask, 20 g of 4,4’-trimethylene dipiperidine (1 eq) was dissolved in 20 mL of methanol, then 28 mL of methyl acrylate (3 eq) was added using a dropping funnel to the reaction mixture. The reaction was conducted at 50 °C for 24 h. Afterwards, methanol and the excess of methyl acrylate was removed under vacuum distillation and compound **1** was obtained as a transparent liquid in quantitative yield.

^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm: 3.61 (s, 6H), 2.79 (d, 4H), 2.60 (t, 4H), 2.45 (t, 4H), 1.87 (t, 4H), 1.59-1.57 (m, 4H), 1.21-1.09 (m, 12 H).

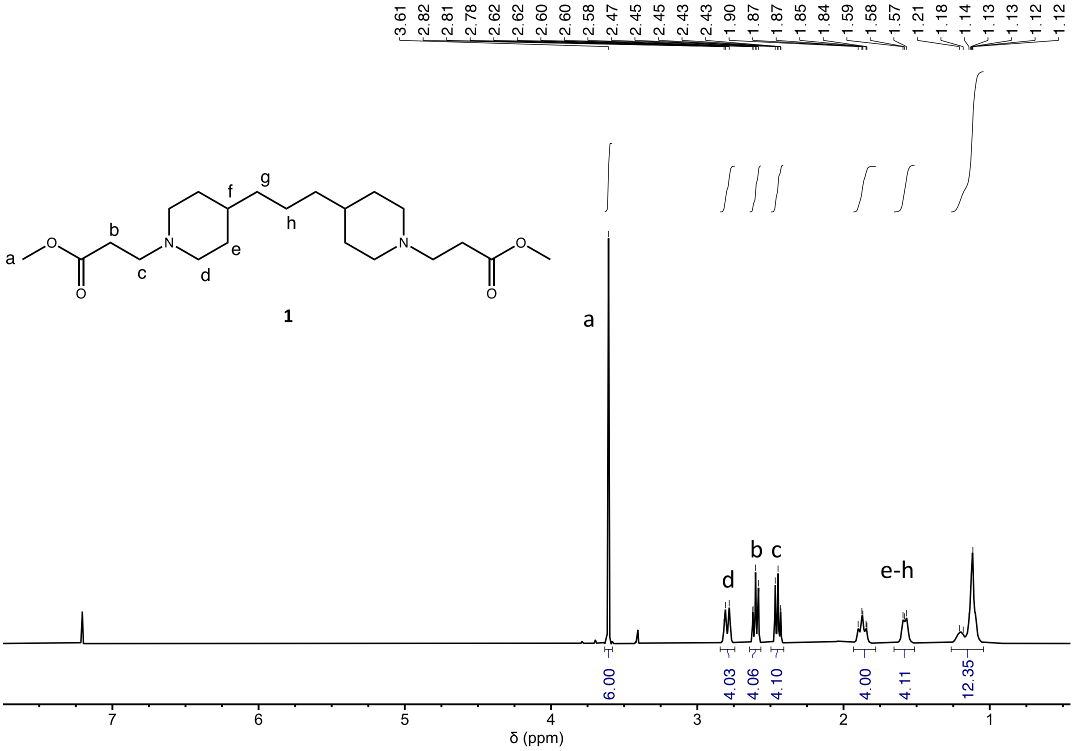


Figure S1. ^{1}H-NMR of compound 1 ($CDCl_3$, 25 °C, 300 MHz).

General procedure for curing agent

In a 20 mL propylene cup, compound **1** was mixed with the selected amines using a DAC 150.1 FVZ speed mixer (conditions of mixing: 2 min with a speed of 2500 rpm). The reaction was conducted at 120 °C for 24 h, then in a vacuum oven for an additional 16 h at 120 °C to completely remove the methanol generated from the reaction.

Table S1. Equivalent and grams used for the preparation of the crosslinkers.

	BAE 1 (eq, g)	**Priamine (eq, g)**	**TETA (eq, g)**	**TMHD (eq, g)**	**PEA (eq, g)**	**AHEW (g/mol)**
BAA-T0	1, 3	1.08, 4.64	-	-	0.12, 0,122	671.31
BAA-T5	1, 3	0.57, 2.44	0.06, 0.069	0.51, 0.633	0.06, 0.061	540.36
BAA-T10	1, 3	0.51, 2.19	0.18, 0.206	0.45, 0.558	0.06, 0.061	882.87

The amine hydrogen equivalent weight (AHEW) of BAA-T5 and BAA-T10 was calculated using Equation **eq. S3**, for BAA-T0 using Equation **eq. S4**:

$$AHEW = \frac{m_{Priamine} + m_{TETA} + m_{PEA} + m_{TMHD} + m_{BAE1}}{n_{BAE1} + n_{PEA} + 2n_{TETA}} \qquad \text{(eq. S3)}$$

$$AHEW = \frac{m_{Priamine} + m_{PEA} + m_{BAE1}}{n_{BAE1} + n_{PEA}} \qquad \text{(eq. S4)}$$

Epoxy adhesive synthesis (E-BAAT0, E-BAAT5, E-BAAT10)

The dynamic crosslinkers were reacted with Epikote 828LV (epoxy to amine ratio-1:1) in a propylene cup using a DAC 150.1 FVZ speed mixer (conditions of mixing: 2 min with a speed of 2500 rpm). The curing of the network was performed in an oven at 80 °C for 16 h, then post-cured at 100 °C for 1 h. The same procedure was followed for the preparation of the reference epoxy material using Ancamide as a commercial hardener.

Table S2. Equivalent and grams used for the preparation of epoxy networks.

	BAA-X (eq, g)	**Epikote (eq, g)**
E-BAAT0	1, 5.46	1, 1.5

E-BAAT5	1, 5.86	1, 2
E-BAAT10	1, 7.17	1, 1.5

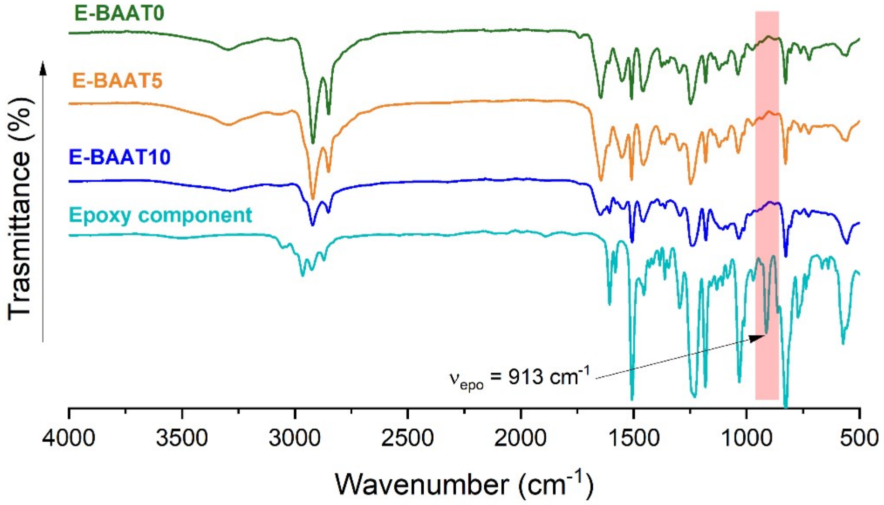


Figure S2. FTIR spectra of the dynamic epoxy networks E-BAAT0, E-BAAT5 and E-BAAT10.

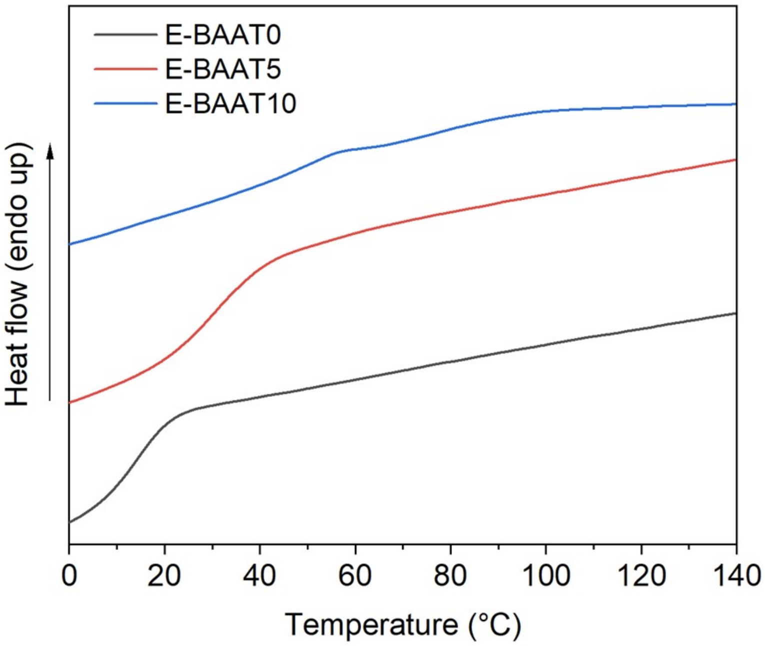


Figure S3. DSC curves performed at 10°C/min in air atmosphere of the epoxy network synthetized.

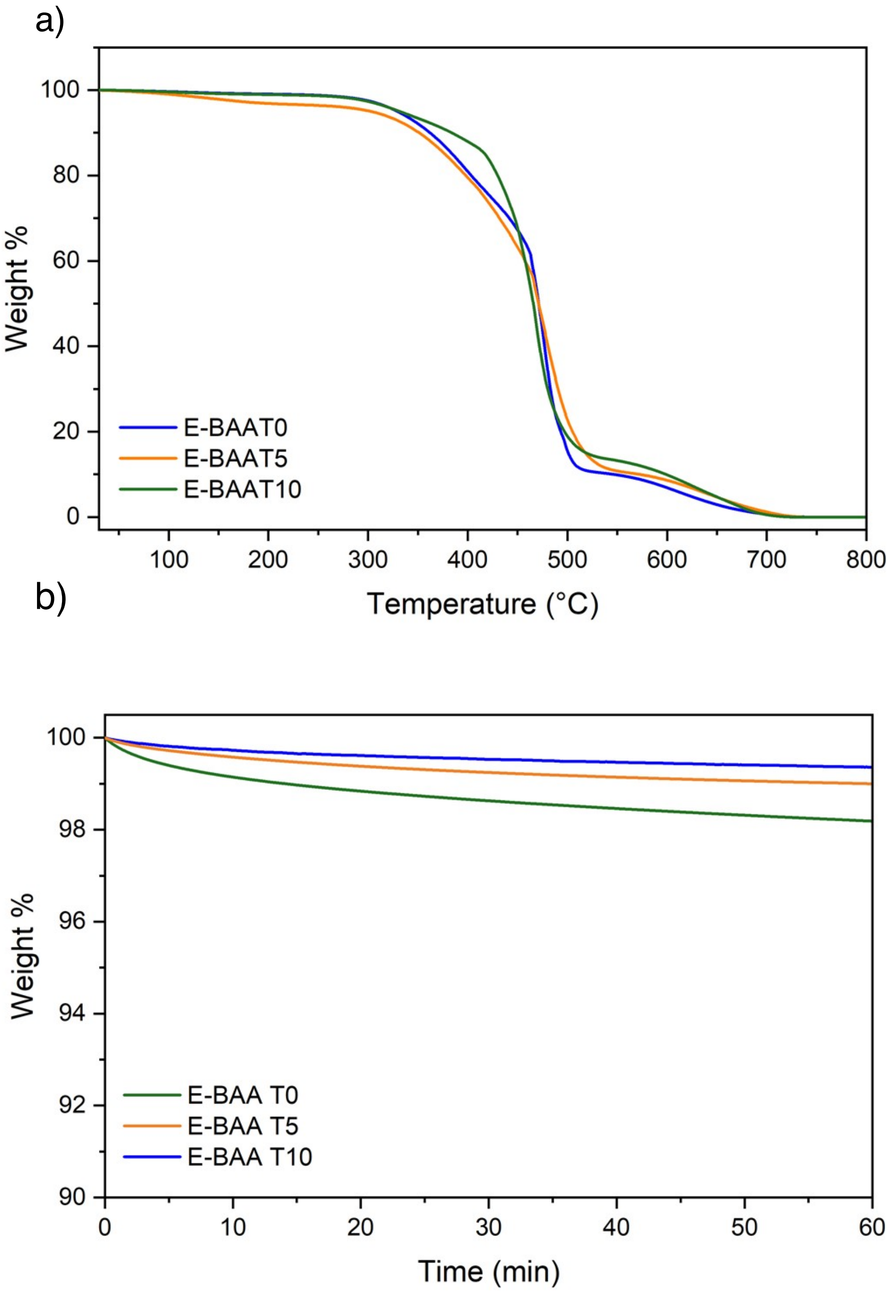


Figure S4. a) TGA performed at heating rate of 10 °C/min under air atmosphere; b) isothermal TGA curves performed at 200 °C for 1 h under air atmosphere.

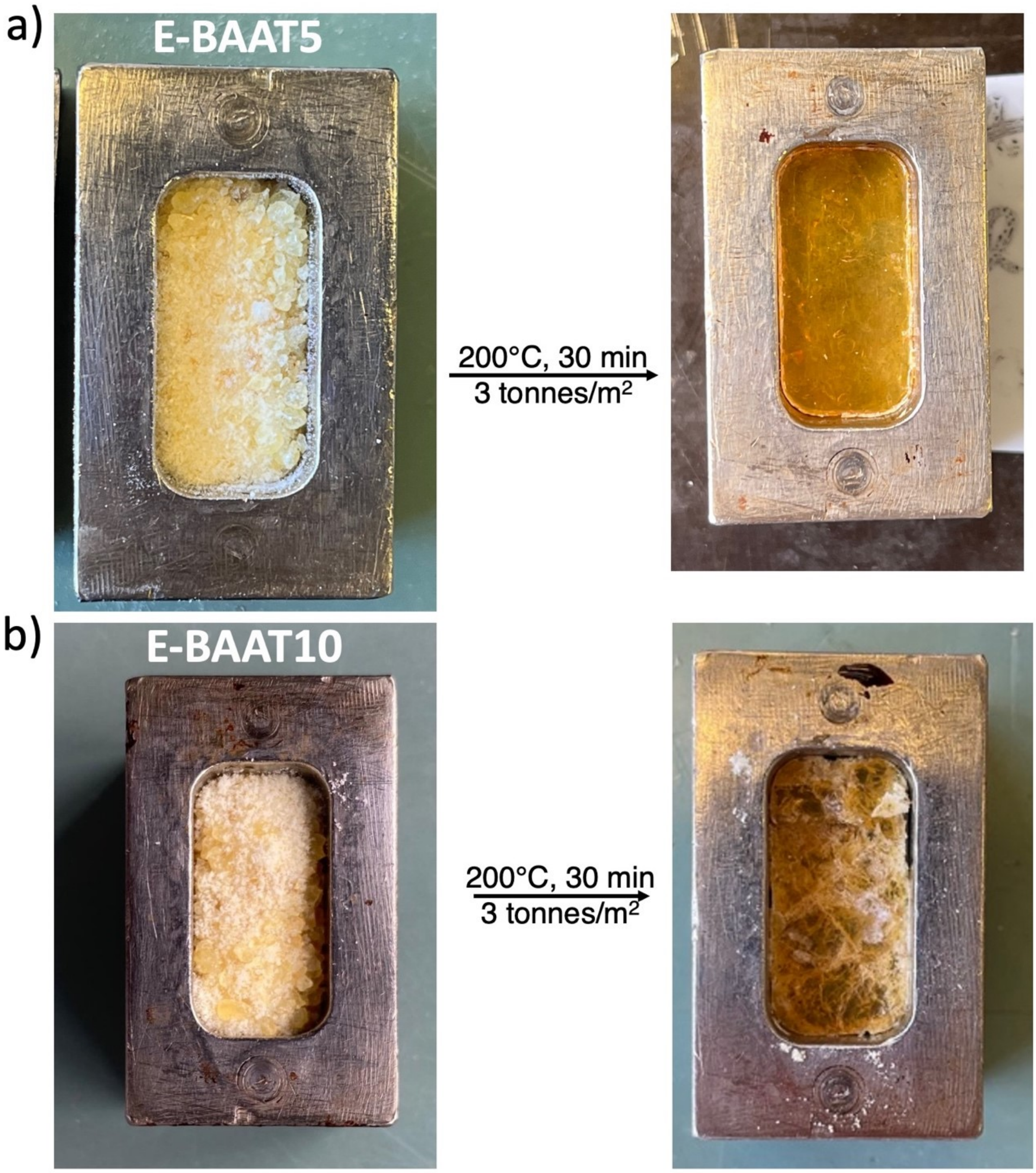


Figure S5. Picture of a) E-BAAT5 and b) E-BAAT10 before reprocessing test (left) and after the pressing at 200 °C for 30 minutes under 3 tonnes/m^2 of pressure. For E-BAAT10 only a partial healing of the initial powder is visible but not sufficient to obtain a homogenous sample.

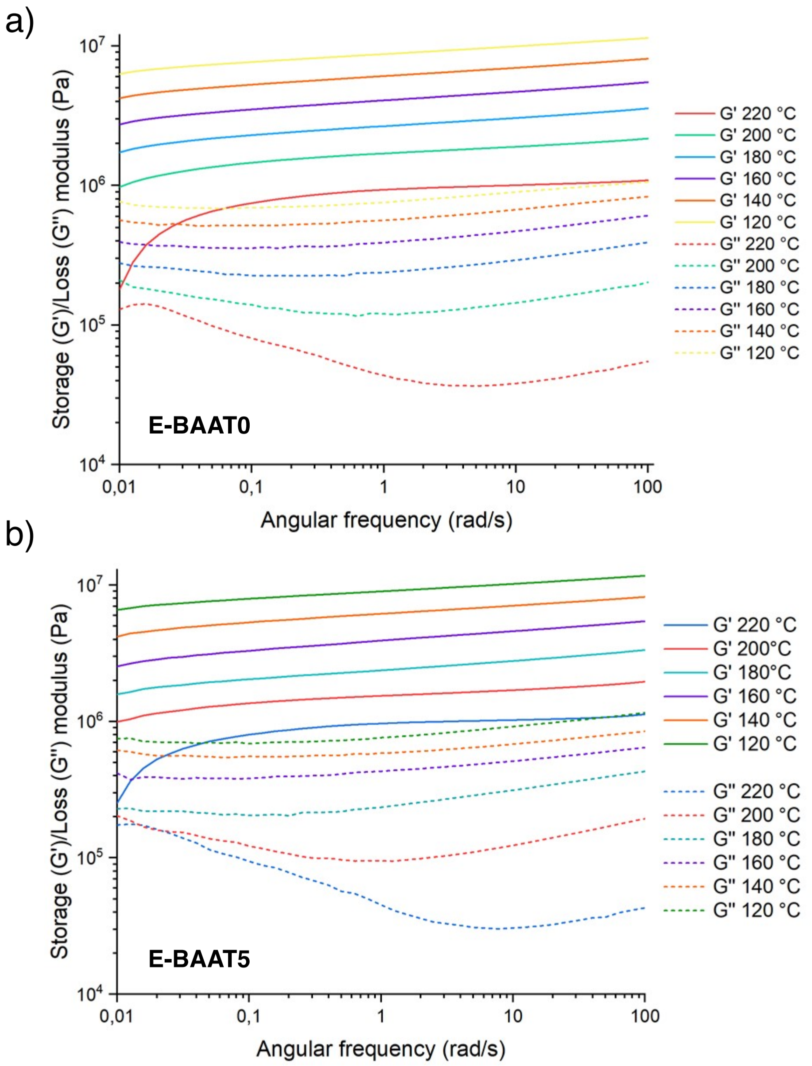


Figure S6. Frequency sweep experiment of (a) E-BAAT0 and (b) E-BAAT5 in a temperature range from 120 °C to 220 °C.

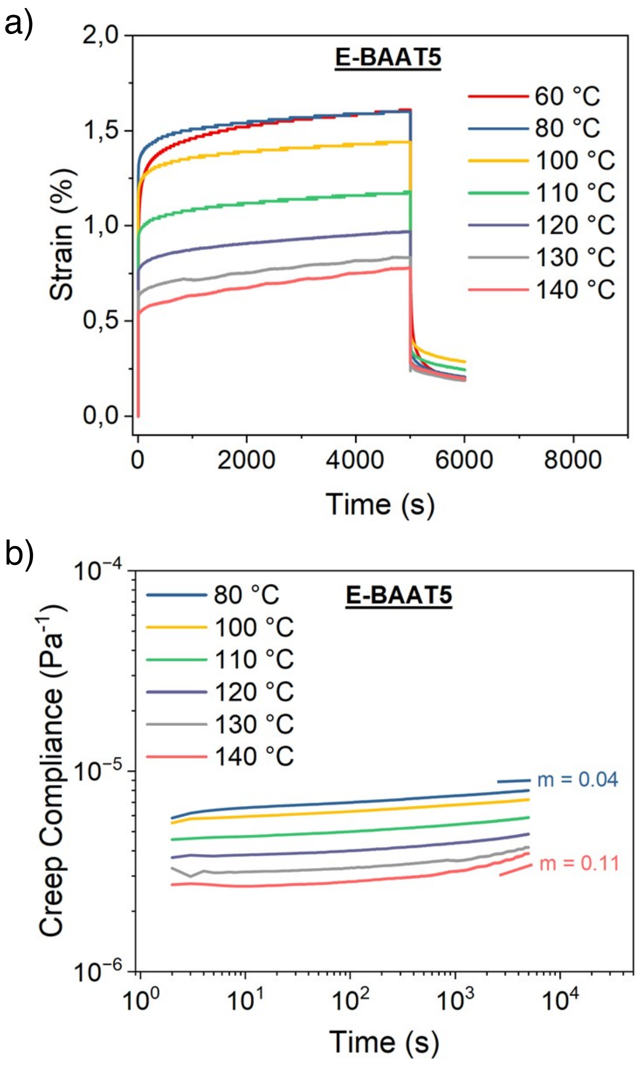


Figure S7. a) Creep recovery result of E-BAAT5; b) creep compliance *vs* time.

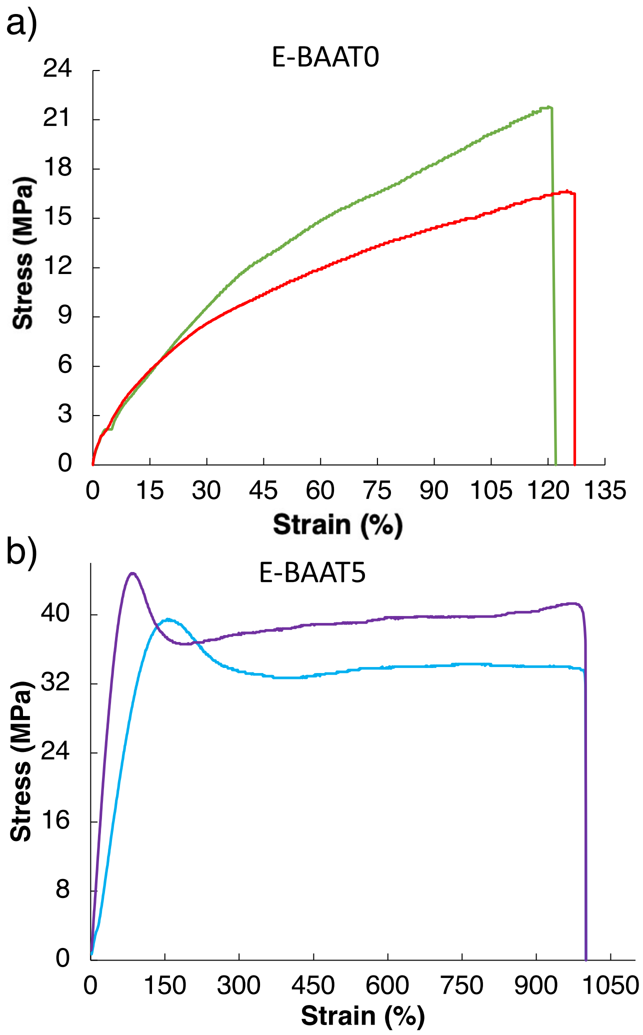


Figure S8. Tensile test performed on the dynamic networks a) E-BAAT0 and b) E-BAAT5.

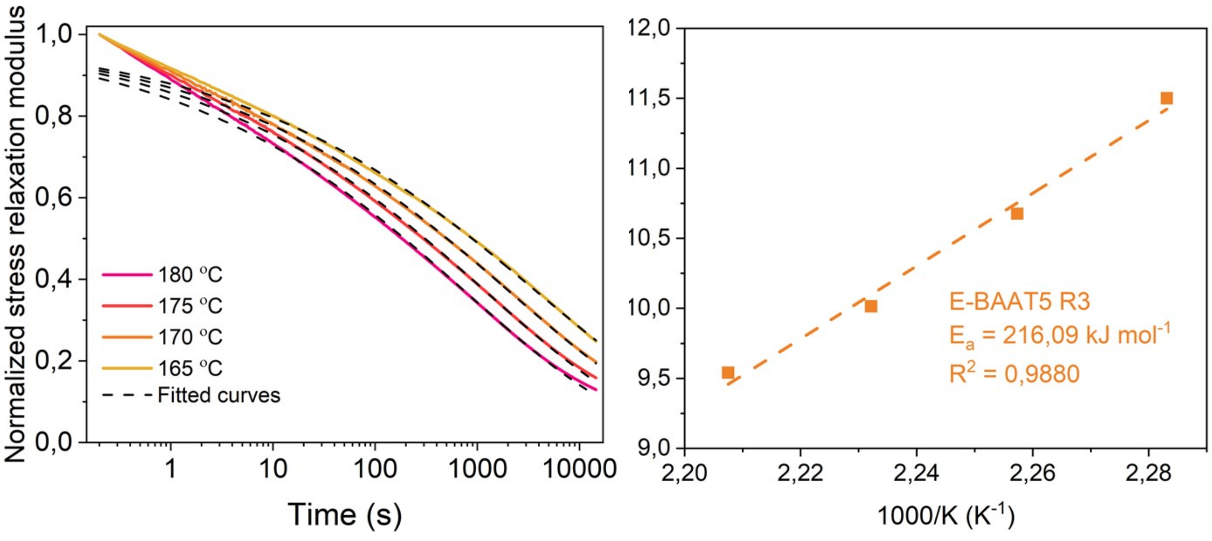


Figure S9. Stress relaxation curves (left) and Arrhenius plot (right) on E-BAAT5 after the third reprocessing cycle (R3).

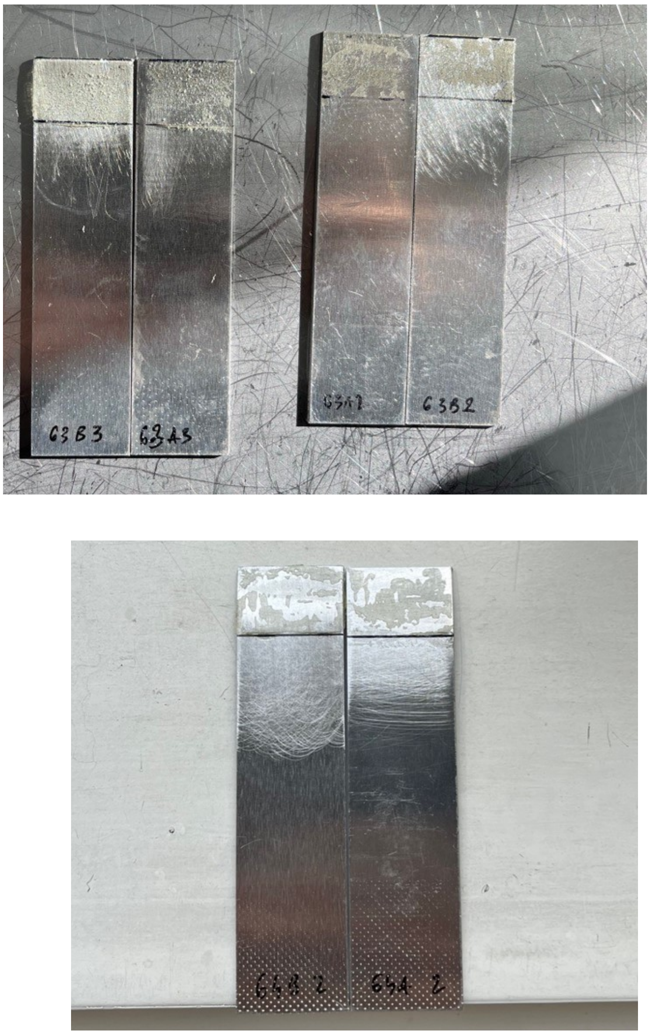


Figure S10. Pictures of E-BAAT0 (left) and E-BAAT5 (right) aluminum specimens after lap shear tests.

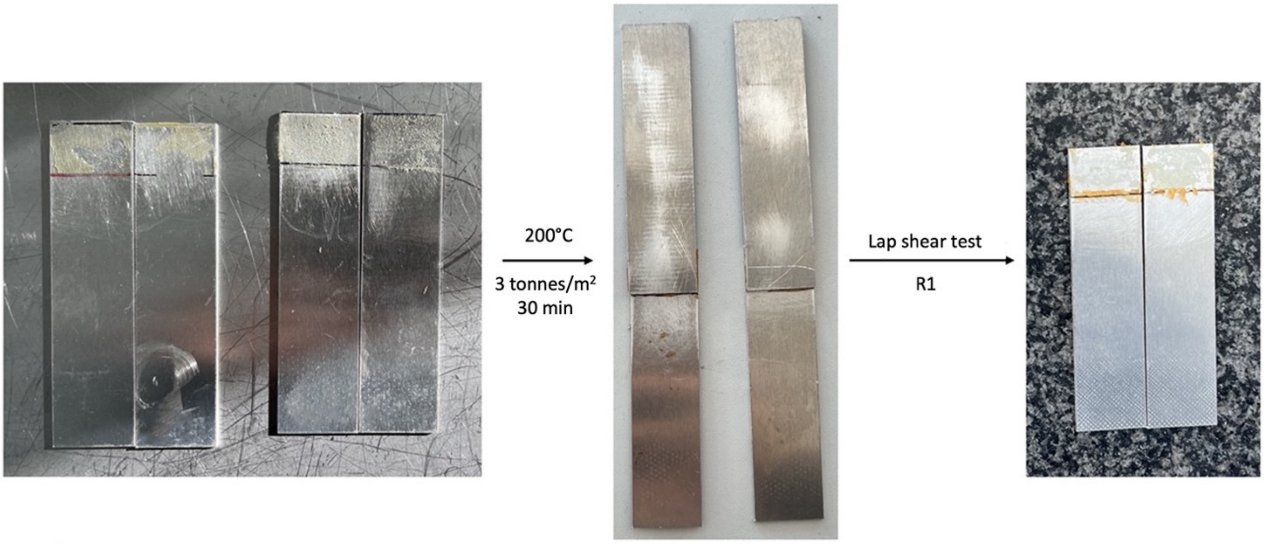


Figure S11. Pictures of broken specimens after lap shear test (left) of the dynamic epoxy materials. They were pressed together (middle) at 200 °C for 30 minutes under 3 tonnes/m^2 of pressure and tested again until failure (right).