Supporting information

Sustainable Design of Vanillin-Based Vitrimers Using Vinylogous Urethane Chemistry

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1. Experimental

1.1 Materials

2-Methoxyhydroquinone (98%), benzyltriethylammonium chloride (99%), (±)-epichlorohydrin (99%), tris(2-aminoethyl)amine (96%) and 1,2-epoxy-3-phenoxypropane (99%) were purchased from Sigma-Aldrich. Ammonia 25% was purchased from VWR International. 1,4-Bis(hydroxymethyl)cyclohexane bis-acetoacetate (CDM-AA) was kindly supplied by AGFA NV. The experimental procedure for CDM-AA synthesis has been reported.[1] All reactants were used as received.

1.2 Synthesis of the diglycidyl ether of methoxyhydroquinone (DGE-MHQ)

The synthesis of the DGE-MHQ monomer was adapted from Fache et al.[2,3] and Aouf et al.[4] In a 1L round-bottom flask, 2-methoxyhydroquinone (1 eq., 30 g, 214.1 mmol) was charged, together with epichlorohydrin (30 eq., 503.6 mL, 594.2 mmol) and benzyltriethylammonium chloride (0,10 eq., 4.88 g, 21.4 mmol) and heated for 5 h at 80 °C. Next, the excess of epichlorohydrin was removed by rotary evaporation. The reaction mixture was heated to 40 °C and an aqueous solution of NaOH (20 g in 100 mL) and benzyltriethylammonium chloride (0,10 eq., 4.88 g, 21.4 mmol) was added. This mixture was reacted for 3 h. Water (100 mL) was added and the aqueous phase was extracted with 3 x 250 mL ethyl acetate. The organic phase was washed with 150 mL brine, dried over $MgSO_4$ and vacuum concentrated. No further purification was required. A brown solid was obtained. Yield of DGE-MHQ 91%, 49 g. Purity of DGE-MHQ (LC-MS, 214 nm, m/z, ES+, $[M + NH_4]^+ = 270.3$, $C_{13}H_{16}O_5$) 92%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.67 (m, 2H), 2.82 (m, 2H), 3.29 (m, 2H), 3.76 (m, 2H), 3.81 (s, 3H), 4.22 (m, 2H), 6.43 (dd, 1H), 6.63 (d, 1H), 6.88 (d, 1H).

1.3 Synthesis of dihydroxyamino propane of methoxyhydroquinone (DHAP-MHQ)

The synthesis was adapted from Mora et al.[5] In a pressure tube, DGE-MHQ (1 eq., 7 g, 27.8 mmol) was charged together with an aqueous 25% ammonia solution (60 eq., 126 mL, 1.67 mol) and ethanol (25.5 mL, 0.2 v/v ratio). The pressure tube was immersed in an oil bath at 85°C and the reaction mixture was reacted for 1h30. Afterwards, the reaction mixture was cooled down to room temperature. Both ethanol and ammonia were removed by rotary evaporation. Finally the product was freeze dried to remove any trace of water. A brown viscous solid was obtained. Yield of DHAP-MHQ: 99%, 7.85 g. Purity of DHAP-MHQ (LC-MS, 214 nm, m/z, ES+, $[M+H]^+ = 287.2$, $C_{13}H_{22}N_2O_5$): 92%. ^{1}H NMR (300 MHz, D_2O, δ): 2.59-2.75 (m, 4H), 3.67 (s, 3H), 3.74-3.80 (m, 6H), 6.37 (dd, 1H), 6.53 (d, 1H), 6.78 (d, 1H).

1.4 Synthesis of octyl vinylogous urethane (VU) **(1)**

The synthesis was adopted from Denissen et al.[6] and proceeds as follows. Ethyl acetoacetate (1.0 eq.) and octylamine (1.1 eq.) were mixed in bulk and heated for 2 h at 90 °C while purging with N_2 to remove H_2O. The excess of amine was removed by passing the mixture over a short silica plug using ethyl acetate as eluent. Yield of octyl VU: 85%; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.55 (s, 1H, *NH*), 4.42 (s, 1H), 4.07 (t, 2H), 3.17 (q, 2H), 1.91 (s, 3H), 1.56 (m, 2H), 1.27 (m, 13H), 0.88 (m, 3H).

1.5 Synthesis of 1-amino-3-phenoxypropan-2-ol (APP) **(2)**

In a pressure tube, 1,2-epoxy-3-phenoxypropane (7 g, 46.61 mmol) was charged together with an aqueous 25% ammonia solution (106 mL, 1.40 mol) and water-soluble tetrahydrofuran (21 mL, 0.2 v/v ratio). The pressure tube was immersed in an oil bath at 85°C and the mixture was reacted for 1h30. After reaction, the mixture was cooled down to room temperature. Both THF and ammonia were removed by rotary evaporation. Finally the product was freeze dried to remove any trace of water. A white solid was obtained. The solid product was vacuum distilled with a Kugelrohr at 180°C. Yield of APP: 80.8%, 6.3g. Purity of APP (LC-MS, 214 nm, m/z, ES+, $[M+H]^+$= 168.1, $C_9H_{13}NO_2$): 100%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.40 (s, 2H), 2.54-2.70 (m, 2H), 3.69 (m, 1H), 3.8-4.0 (m, 2H), 4.88 (s, 1H), 6.93 (m, 3H), 7.27 (m,2H).

1.6 Model Compound study

APP ***(2)*** (69.2 mg, 0.41 mmol) was added to octyl VU ***(1)*** (20 mg, 0.08 mmol) in benzene-d_6 (1.5 mL). To obtain a pseudo-first order reaction at low conversions, five equivalents of APP were used. The mixture was heated (80, 100 and 120 °C) in a pressure tube and NMR spectra were measured at different time intervals. The model compound reaction could be followed by comparing the integration of two distinct sharp signals at 1.48 ppm and 1.53 ppm from the remaining N-octyl VU and the formed N-3-phenoxypropan-2-ol VU ***(3)***, respectively.

1.7 Curing of bio-based VU-networks

Prior to network synthesis, the viscous freeze-dried DHAP-MHQ was frozen in liquid nitrogen, to weigh the exact required mass in a vial. In a speed mixer cup, CDM-AA was molten at 90°C. Afterwards, the frozen DHAP-MHQ was added together with the trifunctional crosslinker, tris(2-aminoethyl)amine, to the molten CDM-AA. For the networks containing DGE-MHQ, also the epoxy was added in a molten state. As soon as everything in the polypropylene cup was molten, the cup was placed in a DAC 150.1 FVZ speed mixer, for 2 minutes at 3500 rpm. Then, the network was further cured at 90°C in a heating block for 30 min, followed by further curing at 100°C for 2h30 and post-curing in a vacuum oven at 120°C for 15 minutes.

1.8 Characterization

Nuclear Magnetic Resonance (NMR). Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 or a Bruker Avance II 400 spectrometer at 25°C and measured in DMSO-d_6, D_2O or benzene-

d_6. The chemical shifts (δ) are presented in parts per million (ppm) relative to the deuterated solvent used as the internal reference.

Thermogravimetric Analysis (TGA). The thermogravimetric analyses were performed on a Mettler-Toledo TGA/SDTA 851. The dynamic thermogravimetric measurements were recorded in a nitrogen atmosphere from +25 °C to 600 °C, with a heating rate of 10 °C /min. The isothermal thermogravimetric measurements were recorded in a nitrogen atmosphere at 150°C or 180°C for 120 min.

Differential Scanning Calorimetry (DSC). DSC analyses were measured on a Mettler Toledo 1/700 instrument. The measurements were performed under a nitrogen atmosphere with a heating rate and cooling rate of 10°C/min from -20 °C to 140 °C.

Fourier Transform Infrared Spectroscopy (FTIR). IR spectra were recorded on a Perkin-Elmer SPECTRUM 1000 FTIR spectrometer equipped with a diamond ATR probe.

Mass Spectrometry (MS). Electrospray ionization mass spectrometry (ESI-MS) and liquid chromatography mass spectrometry (LC-MS) were performed on an Agilent 1100 series LC/MSD system equipped with a diode array detector and single quad MS detector (VL), equipped with an electrospray source (ESI-MS). UV detection allowed to detect eluting compounds (λ = 214 nm). LC-MS spectra were analysed using ACD/Spectrus software.

Rheological experiments. Amplitude Sweeps, stress-relaxation, creep and frequency sweep measurements were performed on an Anton-Paar Physica MCR 301 rheometer and an Anton-Paar Physica MCR 302 rheometer with 8 mm as plate diameter. The material samples have a diameter of 8mm and thickness of 1mm. 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 100%. Time-frequency sweeps were measured using a frequency of 1Hz, a constant force of 0.5 or 1 N, and a variable shear strain that was ramped up logarithmically from 0.01% to 100%. Creep experiments were performed using a constant force of 1 N for different temperatures from 30 to 50°C in time intervals of 20°C. An applied shear stress of 2000 Pa was applied for 5000 seconds and followed as a function of time.

Solubility and swelling tests. Samples of 2 – 4 mm diameter, 1 mm of thickness and a weight around 15 mg were added to a vial, and then immersed in 20 mL of THF for 24 h at 25 °C. After the mass of the swollen sample was measured, the solvent was removed by leaving the sample under vacuum 6 h at 120 °C and overnight at 50°C until complete dryness. The soluble fraction and swelling ratio were calculated using Equation 1 and 2, respectively.

$$Soluble\ fraction\ (\%) = \frac{m_{initial} - m_{final}}{m_{initial}}\ x\ 100\ \% \qquad [1]$$

$$Swelling\ ratio\ (\%) = \frac{m_{swollen} - m_{dry}}{m_{dry}}\ x\ 100\ \% \qquad [2]$$

Reprocessing. The networks were (re)processed using compression moulding. For the first processing, the samples were first ground and dried in a vacuum oven at 40°C overnight and then brought into the rectangular mould (recycling 0) (A, 70 mm × 40 mm × 2 mm; B, 30 mm × 15 mm × 2 mm). For reprocessing, the materials were broken into small pieces and placed in the mould. All the materials were pressed at 150°C for 15 minutes with an applied pressure of 2 tons. Homogeneous materials were obtained for all formulations.

2. Optimised synthesis of DGE-MHQ & DHAP-MHQ

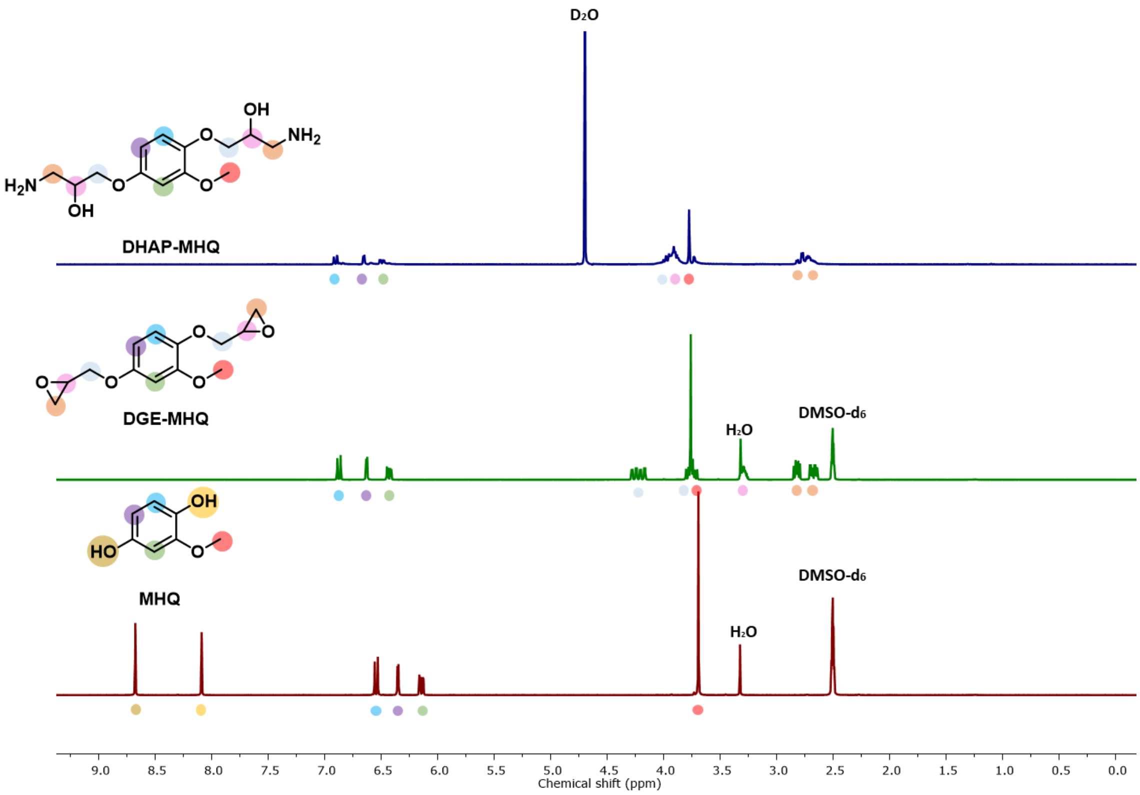

Figure S1. Stacked ^{1}H NMR spectrum in DMSO-d_6 for MHQ and DGE-MHQ and in D_2O for DHAP-MHQ.

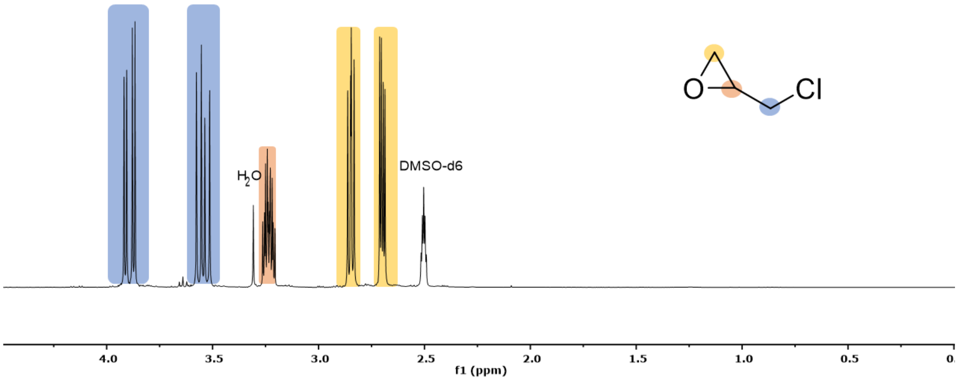

Figure S2. ^{1}H NMR spectrum in DMSO-d_6 of recovered epichlorohydrin in glycidylation step.

Calculations for process mass intensity (PMI):

$$PMI\ (g\ g^{-1}) = \frac{m_{reactant}+m_{reagent}+m_{catalyst}+m_{solvent}+m_{work-up\ chemical}+m_{work-up\ solvent}}{m_{product}} \quad [1]$$

PMI for DGE-MHQ (this work):

$$PMI = \frac{30g_{MHQ} + 594g_{epichlo} + 9{,}8g_{ptc} + 20g_{NaOH} + 100g_{H2O} + 100g_{H2O} + 675g_{EtOAc_{\rho\,=0.9\,\mathrm{g/mL}}} + 150g_{\ brine}}{49g} = 34{,}3\ g/g$$

PMI for DGE-MHQ (e.g. with silica column 1g product to 30 g silica & 6-4 Petroleum ether-EtOAc):

$$\begin{aligned} PMI = (&30g_{MHQ} + 594g_{epichlo} + 9{,}8g_{ptc} + 20g_{NaOH} + 100g_{H2O} + 100g_{H2O} + 675g_{EtOAc_{\rho\,=0.9\frac{\mathrm{g}}{\mathrm{mL}}}} \\ &+ 150g_{\ brine} + 1500g_{silica} + \ 693\ g_{petroleum\ ether_{\rho=\,0.77\frac{\mathrm{g}}{\mathrm{mL}}}} \\ &+ 540\ g_{EtOAc_{\rho\,=0.9\frac{\mathrm{g}}{\mathrm{mL}}}})/49g \quad = 88\ g/g \end{aligned}$$

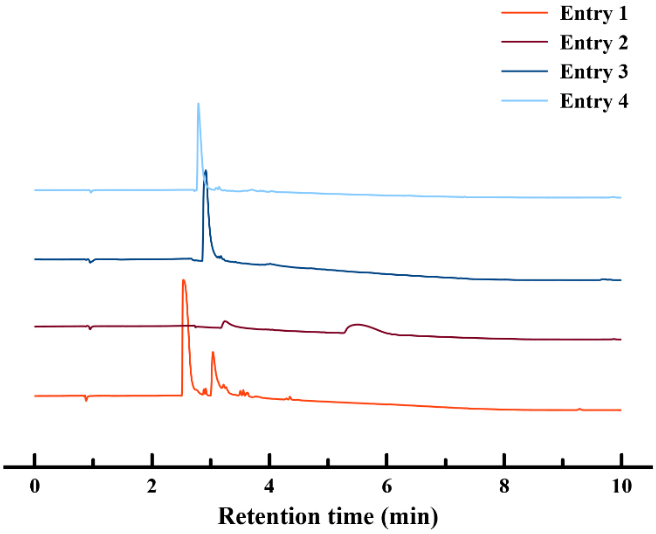

Figure S3. LC-MS traces at 214 nm, for DHAP-MHQ, synthesised in different conditions (see Table 1).

3. Model compound study

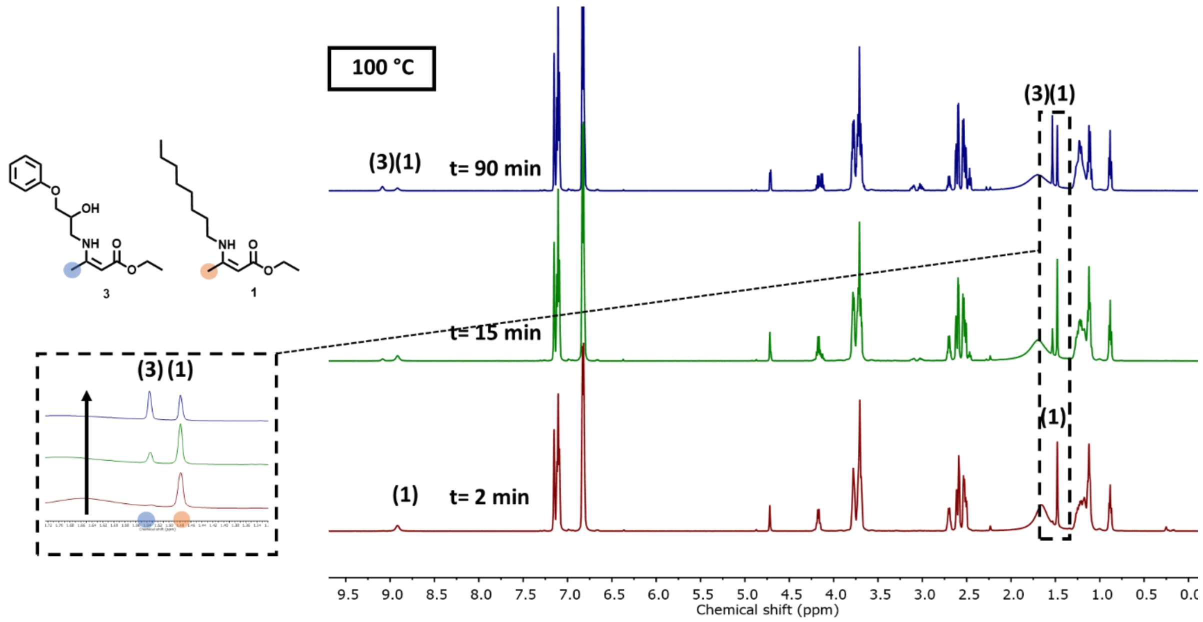

Figure S4. ^{1}H NMR recorded in C_6D_6 at different times in order to follow the kinetic of formation of compound (3) at 100°C (see Fig. 3 in the main manuscript).

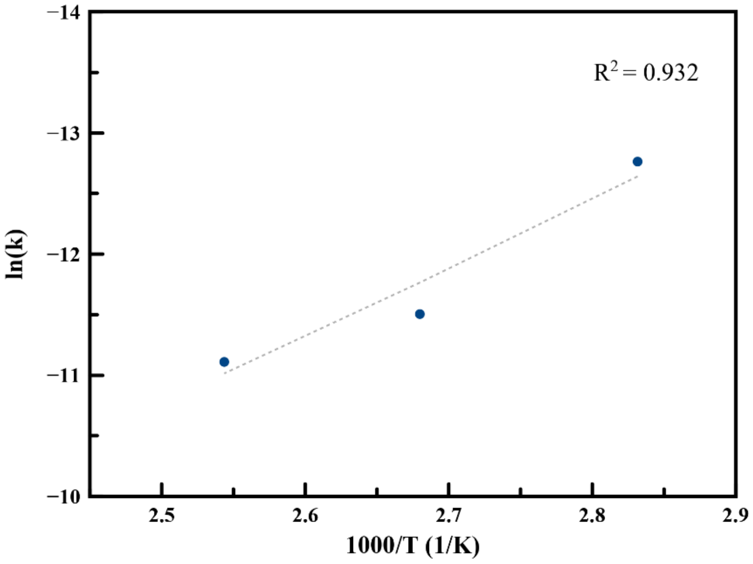

Figure S5. Calculation of the apparent Ea (at 120, 100 and 80 °C) of the model compound study with the Arrhenius equation. (y = -5.77 x + 3.70) (E_a = 48 ± 13 kJ mol^{-1})

4. Properties of the bio-based materials

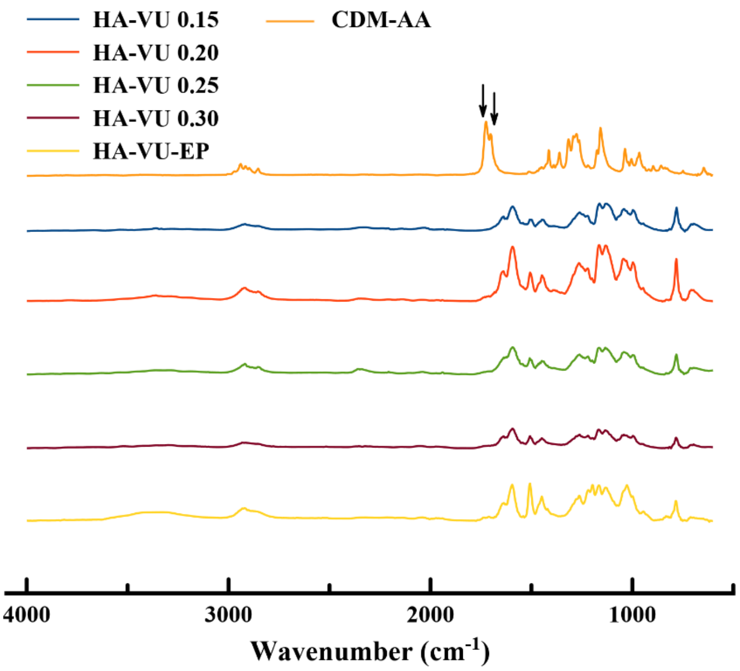

Figure S6. ATR-FTIR absorbance of CDM-AA and all cured materials. The CDM-AA vibration bands at 1720 and 1700 cm^{-1} have disappeared for the materials.

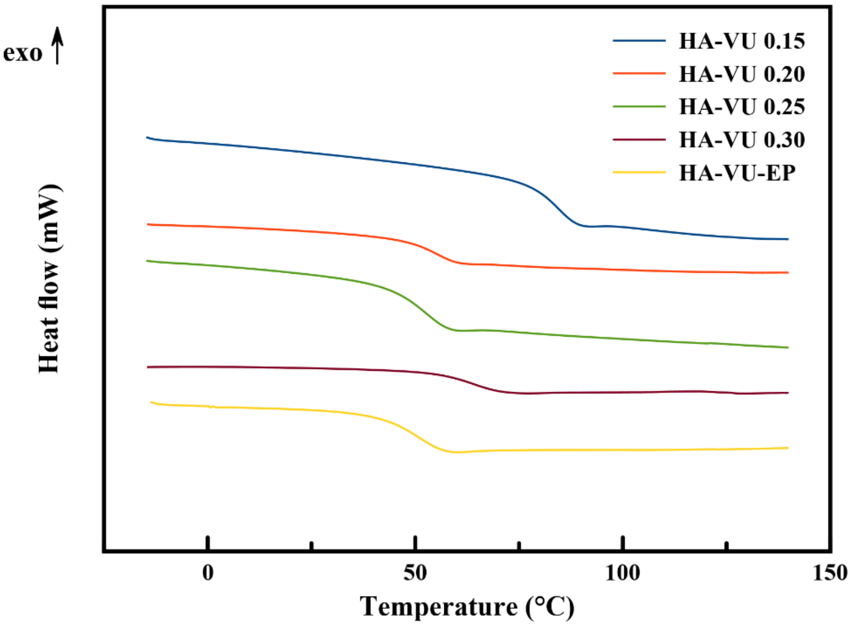

Figure S7. DSC thermograms of all materials obtained at a heating rate of 10°C min^{-1}.

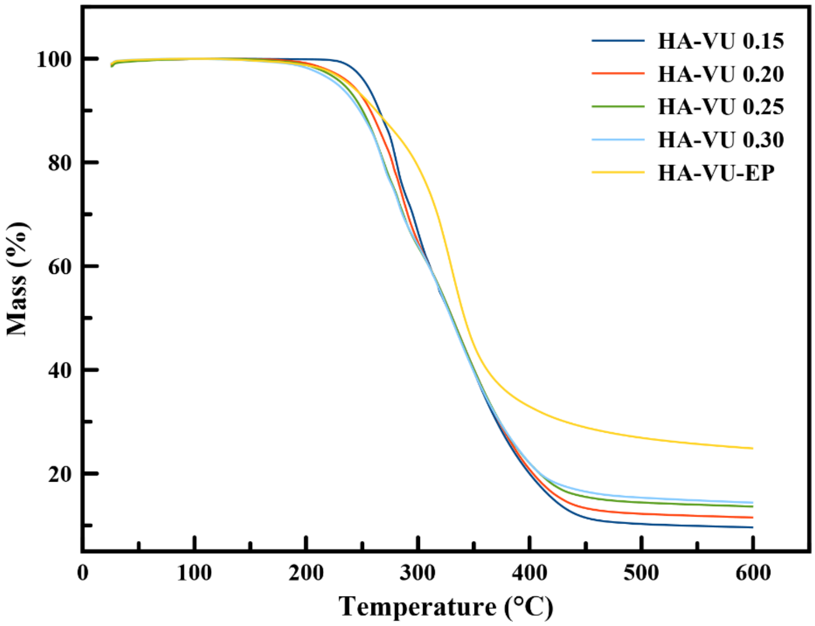

Figure S8. TGA thermograms of all the materials obtained at a heating rate of 10°C min^{-1}.

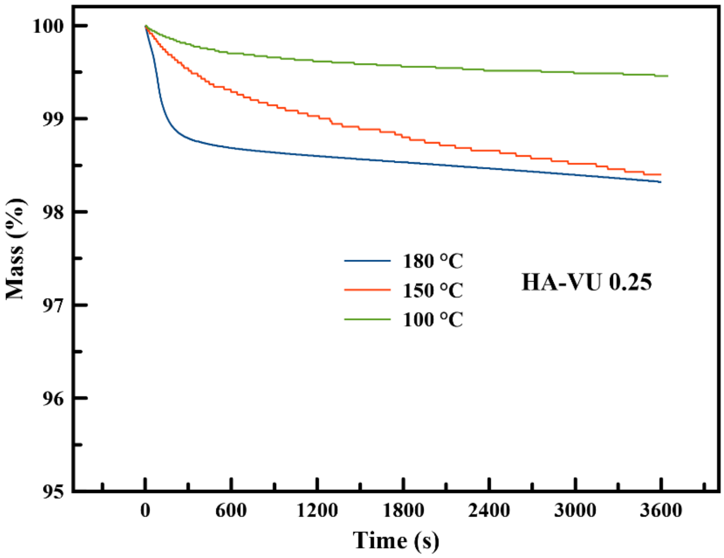

Figure S9. Isothermal TGA of HA-VU 0.25.

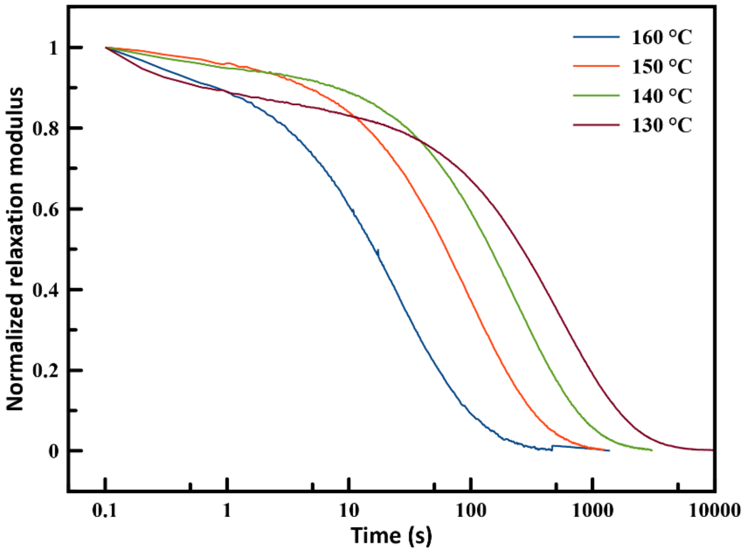

Figure S10. Stress relaxation for 1% strain of HA-VU 0.15.

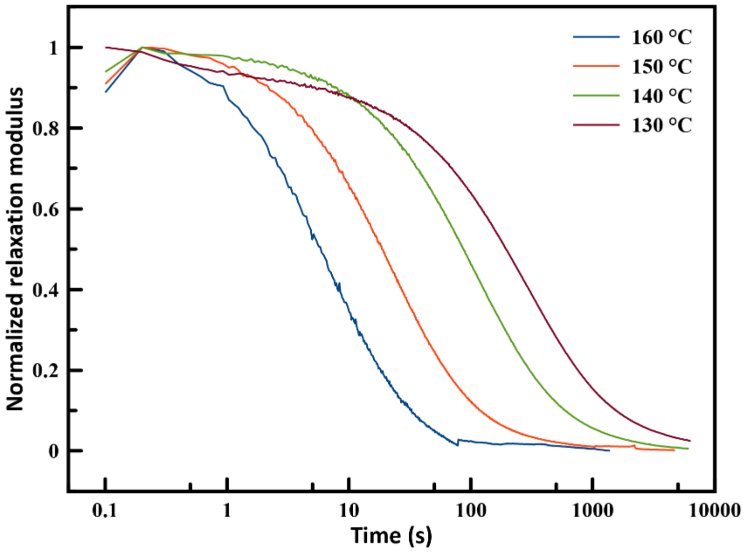

Figure S11. Stress Relaxation for 1% strain of HA-VU 0.20.

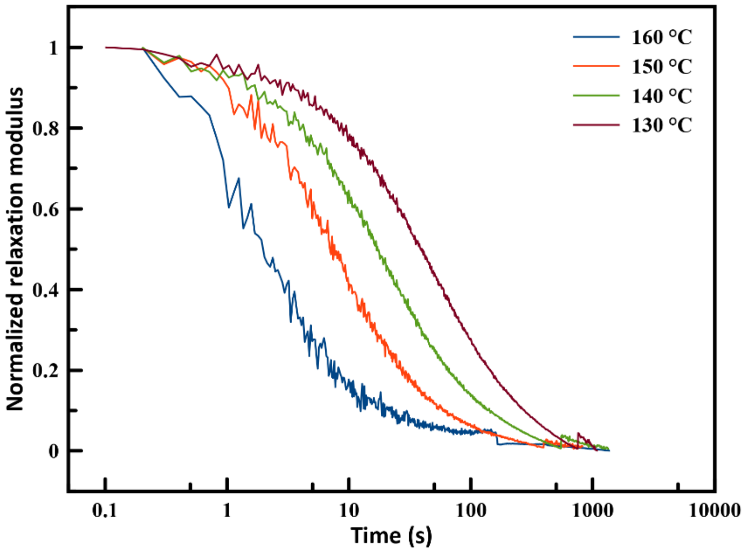

Figure S12. Stress relaxation for 1% strain of HA-VU 0.30.

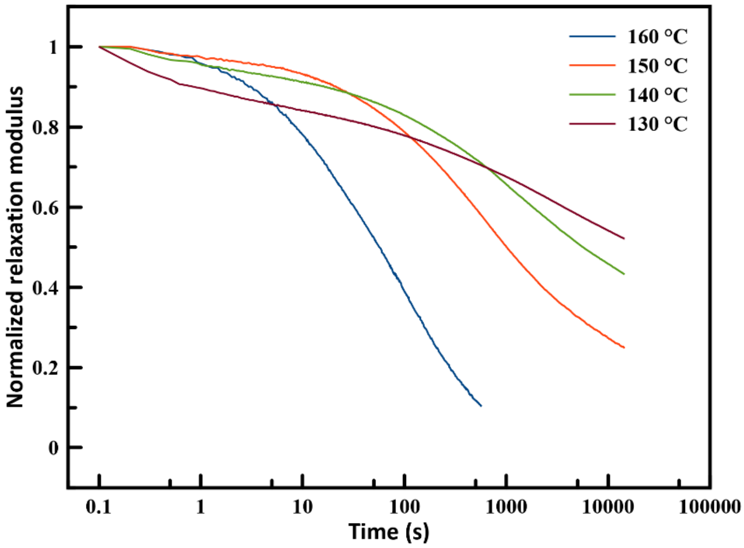

Figure S13. Stress relaxation for 1% strain of HA-VU-EP.

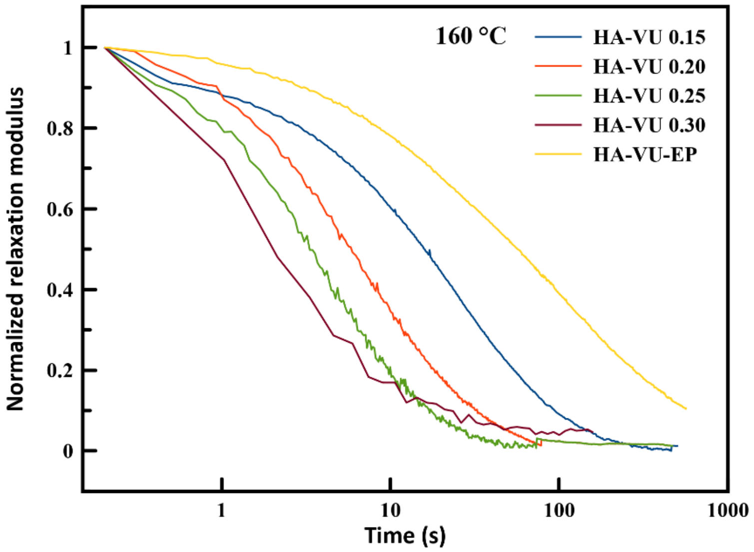

Figure S14. Stress Relaxation for 1% strain of all materials at 160°C.

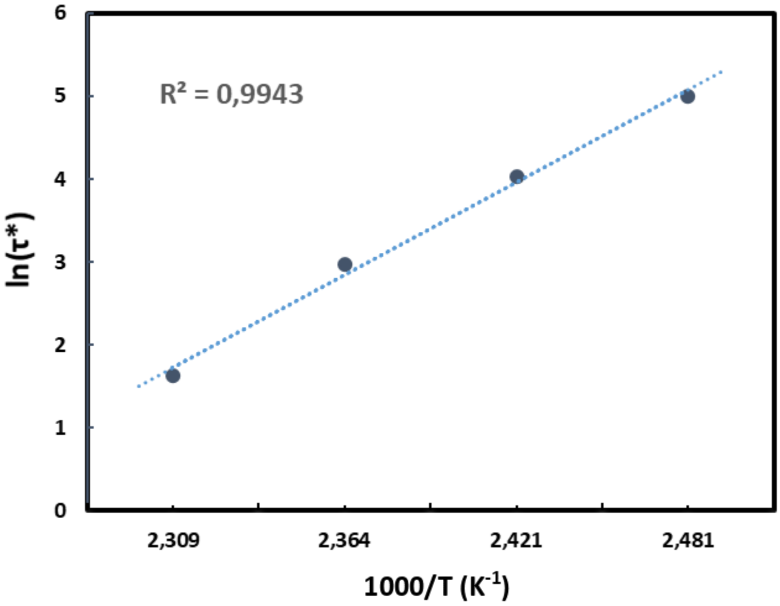

Figure S15. Fitting of the relaxation times (at 160,150, 140, 130 °C) of HA-VU 0.25 to the Arrhenius equation. (y = 19.48 x – 42.23) (E_a = 162 ± 11 kJ mol^{-1})

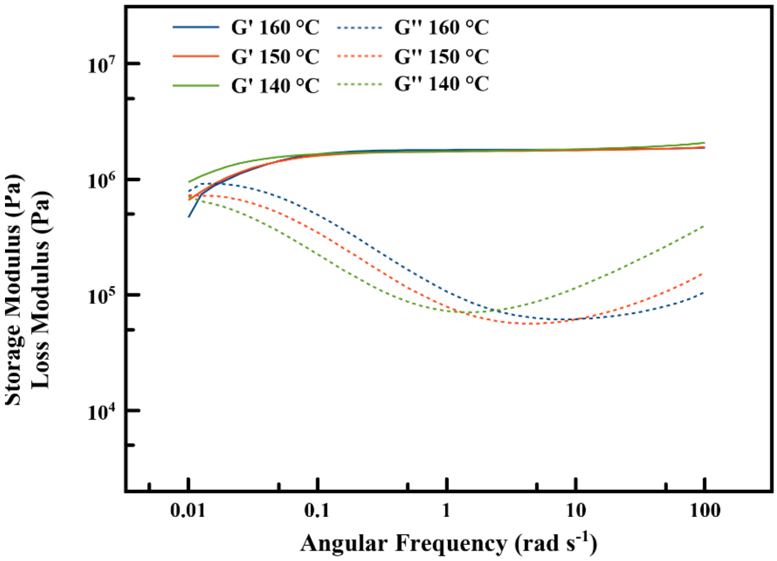

Figure S16. Frequency Sweep measurements of HA-VU 0.15.

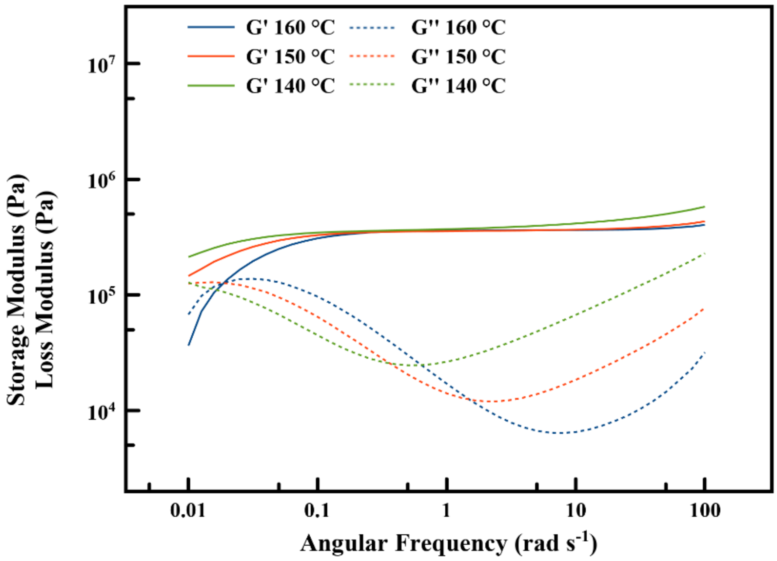

Figure S17. Frequency Sweep measurements of HA-VU 0.20.

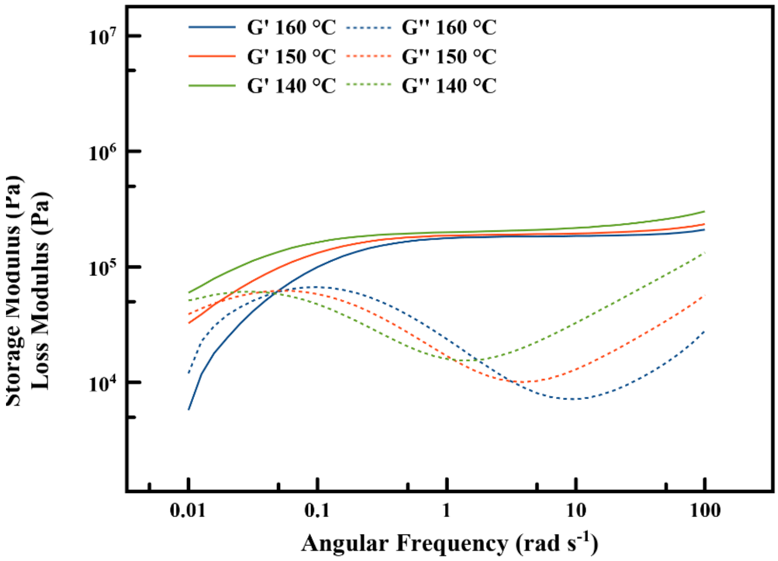

Figure S18. Frequency Sweep measurements of HA-VU 0.30.

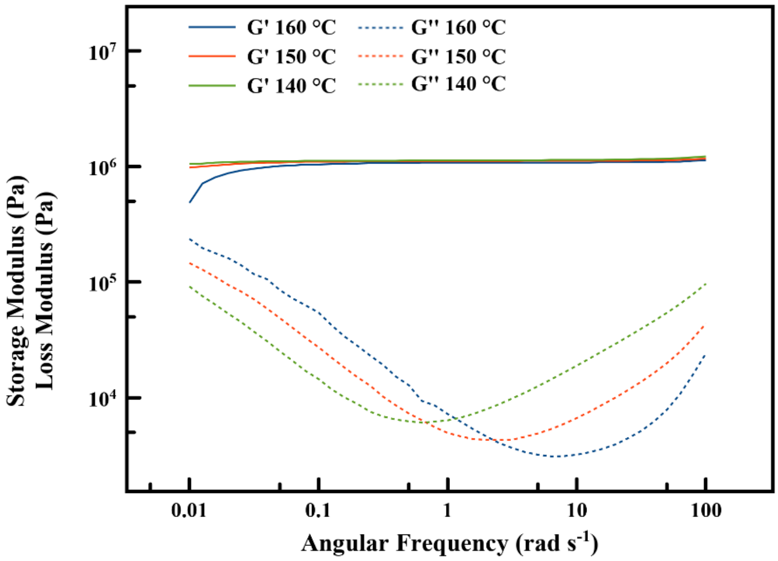

Figure S19. Frequency Sweep measurements of HA-VU-EP.

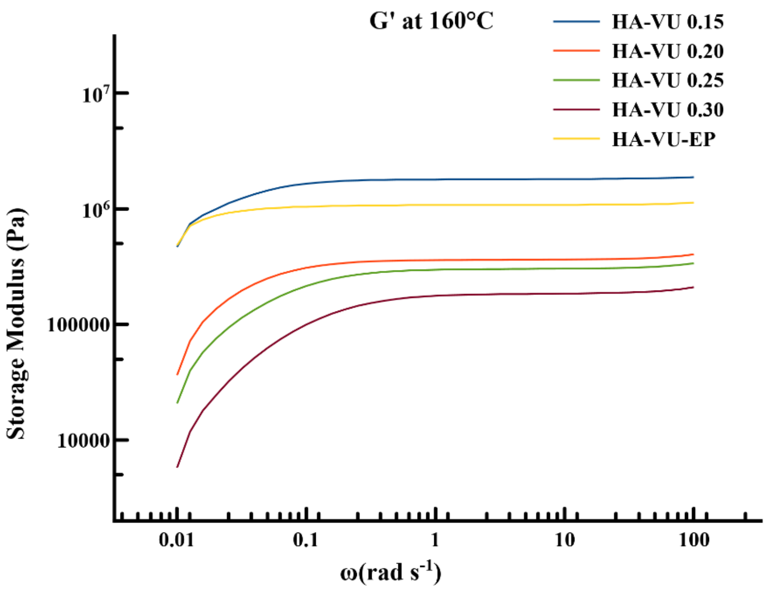

Figure S20. Storage moduli at 160°C obtained from frequency sweeps, for all materials.

Crosslinking density[7,8] (for values of crosslinking densities, see Table 2)

$$v' = \frac{G'}{R\,T} \qquad [3]$$

5. Recyclability study

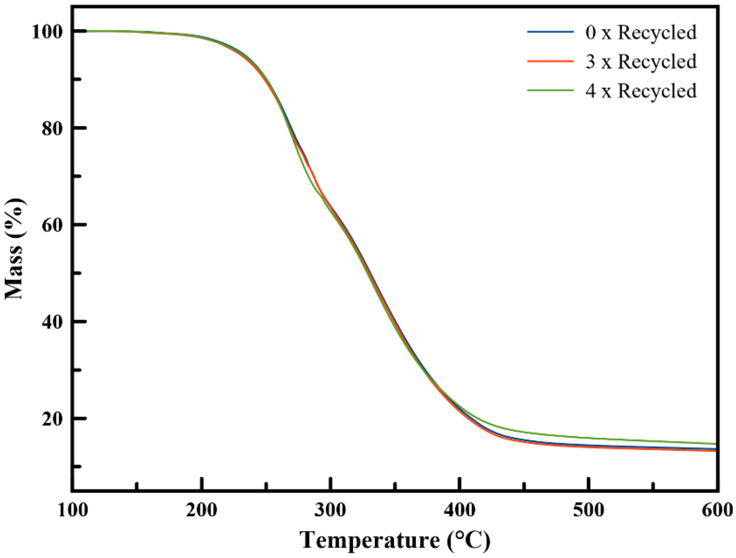

Figure S21. TGA thermogram of HA-VU 0.25 (0 x recycled) and after 3rd and 4th recycling processes (Heating rate 10°C/min)

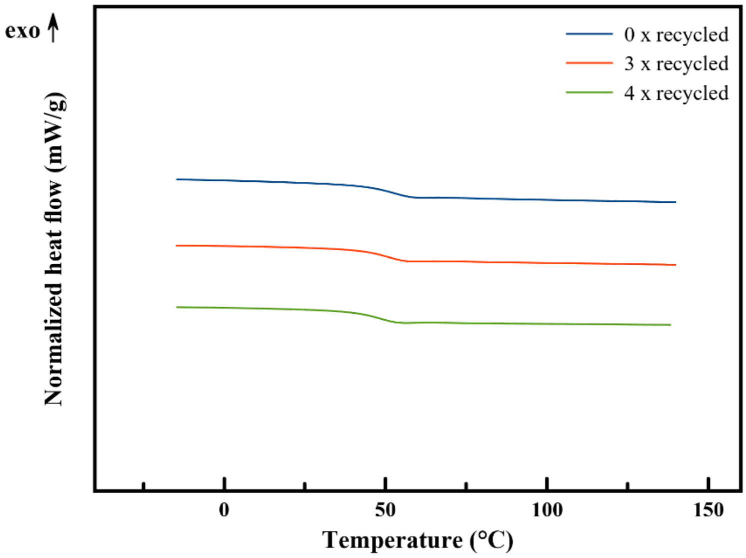

Figure S22. DSC thermogram of HA-VU 0.25 (0 x recycled) and after 3 and 4 recycling processes (Heating rate 10°C/min)

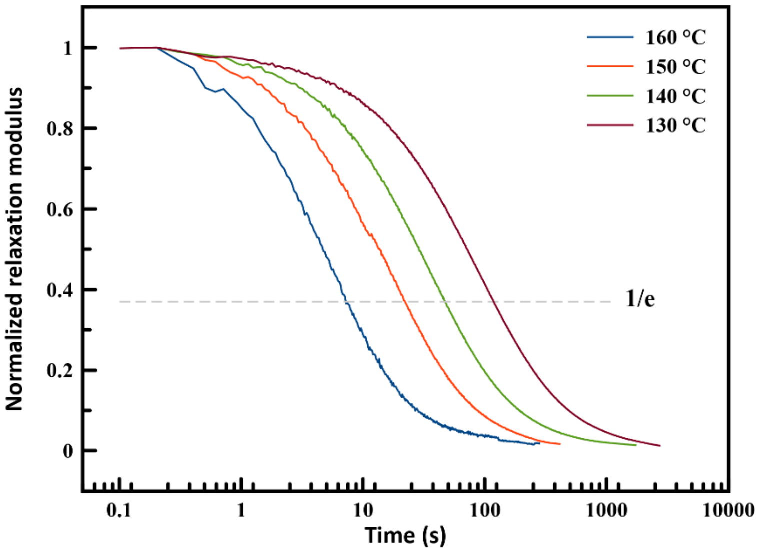

Figure S23. Stress Relaxation for 1% strain of HA-VU 0.25 4th recycling.

6. References

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