

Electronic Supplementary Information for

Reprocessable Vinylogous Urethane Cross-linked Polyethylene via Reactive Extrusion

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Experimental

Size exclusion chromatography (SEC): SEC was performed at 160 °C on a *Polymer Laboratories PLXT-20* Rapid GPC Polymer Analysis System (refractive index detector and viscosity detector) with three *PLgel Olexis* (300 • 7.5 mm, Polymer Laboratories) columns in series. 1,2,4-Trichlorobenzene (TCB) was used as eluent at a flow rate of 1 mL•min⁻¹. The molecular weights were calculated with respect to polyethylene standards (*Polymer Laboratories*). A *Polymer Laboratories PL XT-220* robotic sample handling system was used as auto-sampler.

Nuclear Magnetic Resonance (NMR): High-temperature NMR spectra were recorded on a *Bruker AVANCE III* (500 MHz) equipped with a cryogenically cooled probe head at 120 °C in tetrachloroethane (TCE-*d*₂). ¹H-NMR chemical shifts are given in reference to the residual solvent peak of TCE at 6.00 ppm.

Calculation of content of MEA, HEMA, and Ethylene in mol% inside copolymers. For ease of calculation, the total integral of the MEA and HEMA signal are set to a value of 4 (4 protons).

This allows to determine the content of both methacrylate co-monomer as follows:

$$\text{Mol\%}_{\text{Methacrylate}} = \frac{\frac{4}{4}}{1 + \left(\frac{\text{ACH2backbone} - 3}{4}\right)}$$

With ACH2backbone corresponding to the CH₂ signals of the polymer backbone. The factor -3 originated from the CH and CH₂ protons that belong to the methacrylate comonomer. The Amount of MEA and HEMA can then be determined by obtaining the percentage of MEA and HEMA as follows:

$$\% \text{Func}_{\text{MEA}} = \frac{A_{\text{CHME}}}{4} \rightarrow \text{Mol}\%_{\text{MEA}} = \% \text{Func}_{\text{MEA}} \times \text{Mol}\%_{\text{Methacrylate}}$$

With A_{CHME} corresponding to the integrated area of MEA methylene signals. We can simply divide by 4, because the integral of the methacrylate signals are set to 4, but it is technically the addition of MEA methylene and HEMA methylene signal strengths.

Fourier Transformed Infrared Spectroscopy (FTIR): FTIR-spectra were recorded on a *Perkin Elmer Spectrum One* equipped with a Golden Gate accessory (diamond ATR).

Rheology: Injection molded disks for rheology (diameter 25 mm, thickness 1 mm) were measured using a *TA Instruments DHR-2*, equipped with a parallel plate geometry. First, a strain sweep was carried out to determine the linear viscoelastic regime of the polymer samples. The subsequent measurements were carried out within the linear viscoelastic regime. Storage (G') were monitored during a frequency sweep from 100 – 0.01 $\text{rad}\cdot\text{s}^{-1}$ at 160 °C using a strain amplitude of 0.4 %. Stress relaxation measurements were performed at multiple temperatures between 160 °C and 220 °C, applying a step strain of 1 %, then monitoring the stress until at least 75 % of the initial stress relaxed, or until a constant stress value was observed.

Dynamic Mechanical Thermal Analysis (DMTA): Rectangular samples suitable for DMTA were cut to dimension of 3 x 5 x 0.5 mm (length x width x thickness) from injection molded bars or directly compression molded to size. Samples were measured on a *TA Instruments Q800* in tensile mode. The storage (E') and loss modulus (E'') were monitored while screening the samples during a temperature sweep from -100 to 200 °C at 3 $\text{K}\cdot\text{min}^{-1}$. An oscillation frequency of 1 Hz with an oscillation amplitude of 10 μm were applied.

Determination of gel fraction: Extruded pieces (mass of each sample ~190 mg) were first placed in a 50 mL vial, then 10 mL of xylene was added, the vial closed, heated to 100 °C, and kept for 24 h. After cooling to room temperature, the liquid is removed with a syringe, and the solid residue

washed at least three times with methanol. The samples are dried in a vacuum oven (80 °C) until the weight was constant. The gel fraction was determined according to equation 2:

$$\text{Gel fraction (\%)} = (m_{\text{final}}/m_{\text{initial}}) * 100 \% \quad (\text{S1})$$

Differential scanning calorimetry (DSC): Differential scanning calorimetry was performed on a *TA Instruments Q20* equipped with a *RCS 90* cooling system. About 4 – 8 mg of polymeric sample was weighed inside an aluminum pan and subjected to DSC measurements under nitrogen atmosphere. Unless otherwise noted, polymers were screened twice from -90 °C to 200 °C at a constant heating/cooling rate of 10 K·min⁻¹. Enthalpy, glass, melting, and crystallization temperatures were determined from the second heating and cooling cycle.

Thermogravimetric analysis (TGA): TGA measurements were performed on a *Discovery TGA* from *TA Instruments*. A small amount of sample (3 – 5 mg) was weighed and placed inside the crucible. A temperature ramp was performed from 25 °C to 600 °C at 10 °C·min⁻¹ while monitoring the weight. Isothermal TGA measurements were carried out at 150 °C and 200 °C for 30 min.

Tensile tests: Tensile tests were performed with a *Zwick* type *Z020* tensile tester equipped with a 1 kN load cell. The tests were performed on injection molded dog bones with dimensions of 75 mm x 4 mm x 2 mm. A grip-to-grip separation of 30 mm was used. The samples were pre-stressed to 0.5 N and then loaded with a constant crosshead speed of 50 mm·min⁻¹.

Materials: The poly(ethylene-co-2-[methacryloyloxy] ethyl acetoacate-co-2-hydroxyethyl methacrylate) polymers (also referred to as PE-ACAC-HEMA [PACHE] polymers) with varying amounts of ACAC content were provided by SABIC and used as received. *m*-xylylenediamine 99 % (XYDIA) was purchased from Sigma-Aldrich and used as received.

Preparation of Vitrimer samples in the Extruder:

PE vinylogous urethane vitrimers were prepared *via* reactive extrusion or melt mixing, following a similar procedure. For example, samples denoted as VitX2.6 could be obtained as follows: First, the pristine PACHE *co*-polymer (9.78 g) was fed inside a corotating twin-screw mini-extruder set to 160 °C, rotating at 100 rpm and molten until the observed torque exerted on the screws was constant (~4 – 5 min). Then, the diamine cross-linker XYDIA (0.221 g, 1.62 mmol, 0.55 EQ with respect to ACAC units) was added dropwise *via* syringe and the combined materials were reacted at 160 °C until the observed torque remained constant (usually ~10 – 15 min). The not fully airtight setup allowed water to evaporate. The hot polymer melt was then injection molded into suitable molds to prepare rectangular bars for DMTA, disks for rheology, and dog bones for tensile tests.

Calculation of activation energy and topology freezing temperature from stress relaxation measurements

Topology-freezing temperature (T_v) and *activation energy* (E_a) were determined using methodologies reported in literature.^[1-3] In order to obtain E_a , the \ln of the experimentally determined values for the relaxation time τ were plotted versus $1000/T$ according to eq (S3), which can be obtained from (S1).

$$\tau(T) = \tau_0 \cdot e^{\frac{E_a}{R \cdot T}} \quad \text{eq. (S2)}$$

R – universal gas constant; 8.31 J/(K·mol), E_a – activation energy, T – temperature

Eq (S1) can be transformed to eq (S2) to a linear function of the type $y = ax + b$:

$$\ln \tau = \frac{E_a}{R \cdot T} + \ln \tau_0 = a \cdot \frac{1000}{T} + b \quad \text{eq. (S3)}$$

Then, the E_a in kJ/mol can be determined from the slope of the fit of $\ln \tau$ vs $1000/T$ according to eq (S3)

$$E_a = a \cdot R \quad \text{eq. (S4)}$$

The topology freezing temperature (T_v) is defined as the temperature at which exchange reactions become fast enough so that the topology of the vitrimer network is no longer frozen and the material can flow. T_v is conventionally chosen at the solid to liquid transition when a viscosity of 10^{12} Pa*s is reached.^[4] The relation between the viscosity η and the characteristic relaxation time τ is given by the Maxwell relation eq (S5).

$$\eta = \frac{E' \cdot \tau}{2 \cdot (1 + \nu)} \quad \text{eq. (S5)}$$

E' – equilibrium storage modulus, ν – Poisson's ratio (for PE $\nu = 0.5$ for low strain rates^[5])

Using eq (S2) and eq (S4) T_v can be calculated from eq (6)

$$T_v = \frac{1000 \cdot a}{\ln\left(\frac{\eta \cdot (2 \cdot (1 + \nu))}{E'}\right) - b} \quad \text{eq. (S6)}$$

For sample VitX2.6, we obtain $a = 13.01$, $b = -19.67$ from the fit, and $E' = 1.94$ MPa (taken from the plateau modulus after melting at 180 °C). Thereby, with η (at T_v) = 10^{12} Pa*s, a T_v of ~110°C was determined. Using the same method for VitX1.9 yields a T_v of 31.4±14 °C.

Supporting Figures

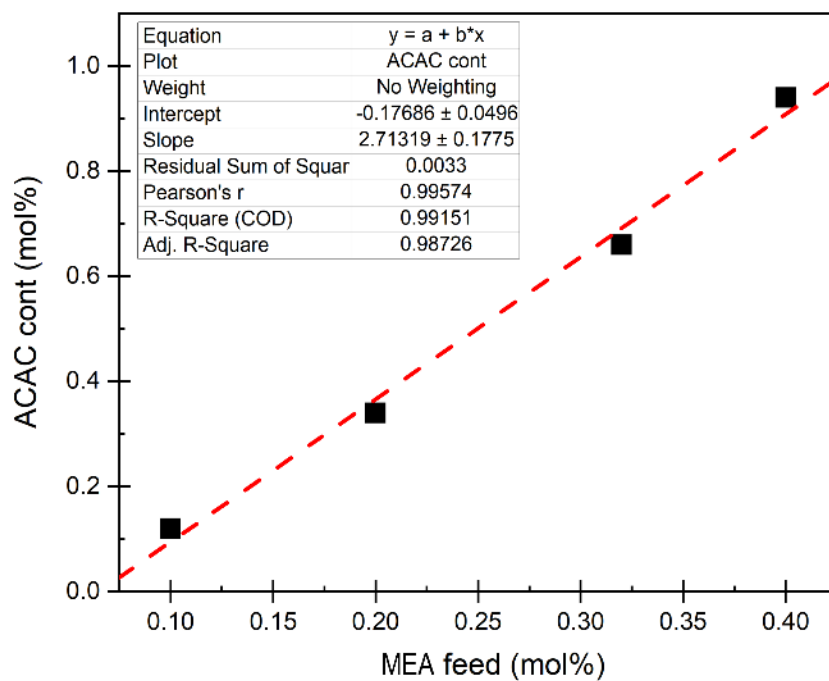


Figure S1. Plot of incorporated ACAC (in mol%) as function of comonomer feed (in mol%). The linear relationship is revealed by the fit represented by the red line.

Pristine PACHE used for preparation of VitX0.5 in TCE-d₂, 120°C, 400 MHz

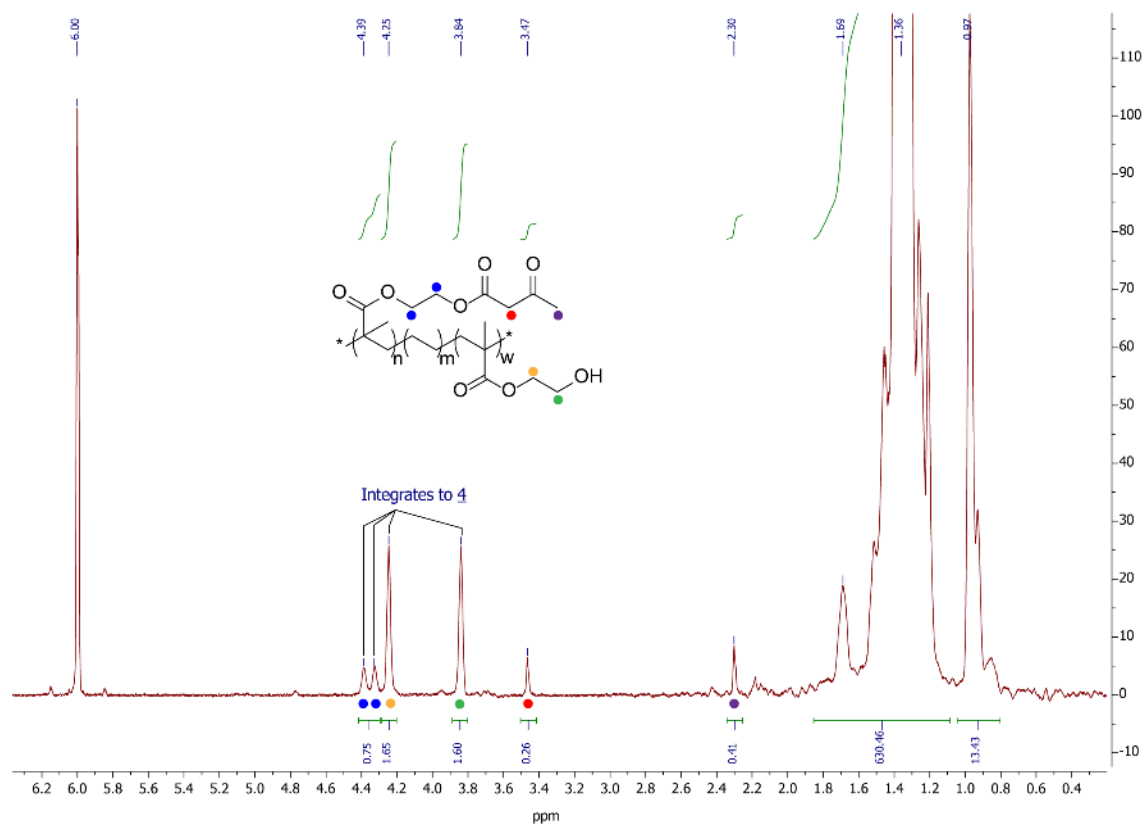


Figure S2a. High temperature ¹H NMR spectrum (120 °C, in TCE-d₂) of pristine terpolymer PACHE which was used to make sample VitX0.5.

Pristine PACHE used for preparation of VitX1.1 in TCE-d₂, 120°C, 400 MHz

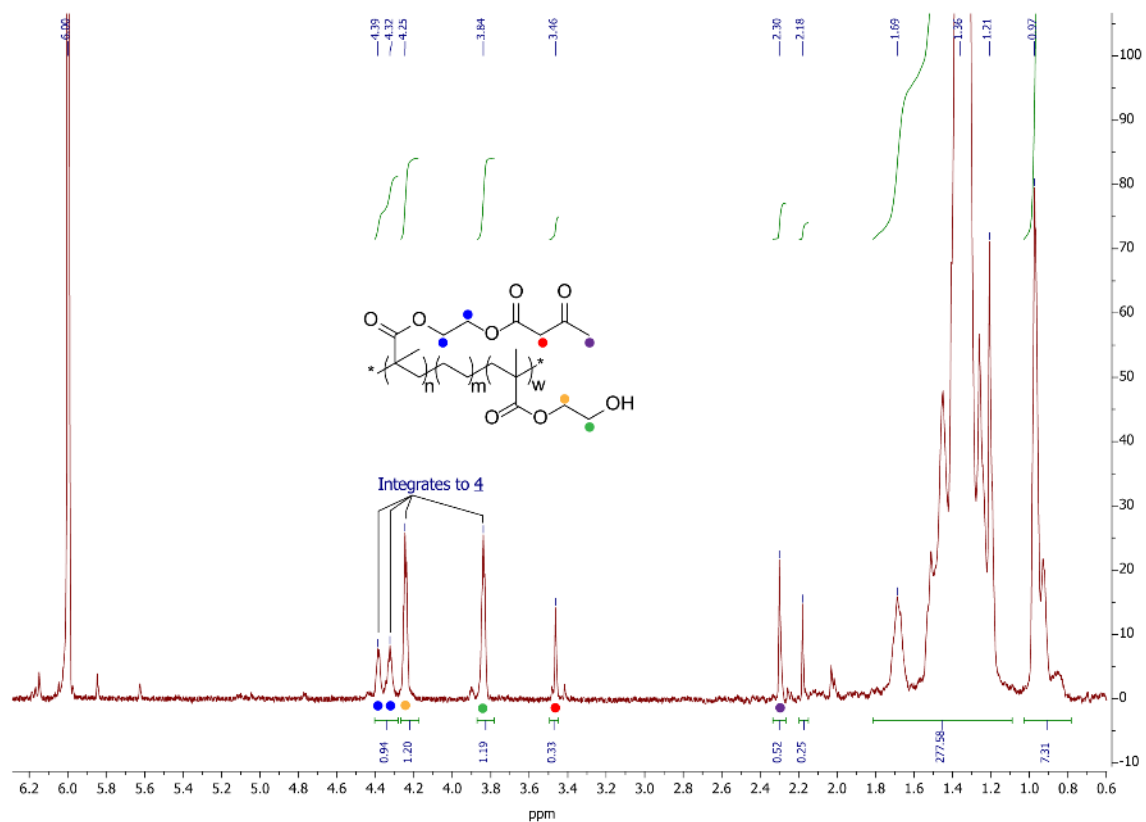


Figure S2b. High temperature ¹H NMR spectrum (120 °C, in TCE-d₂) of pristine terpolymer PACHE which was used to make sample VitX1.1.

Pristine PACHE used for preparation of VitX1.9 in TCE-d₂, 120°C, 400 MHz

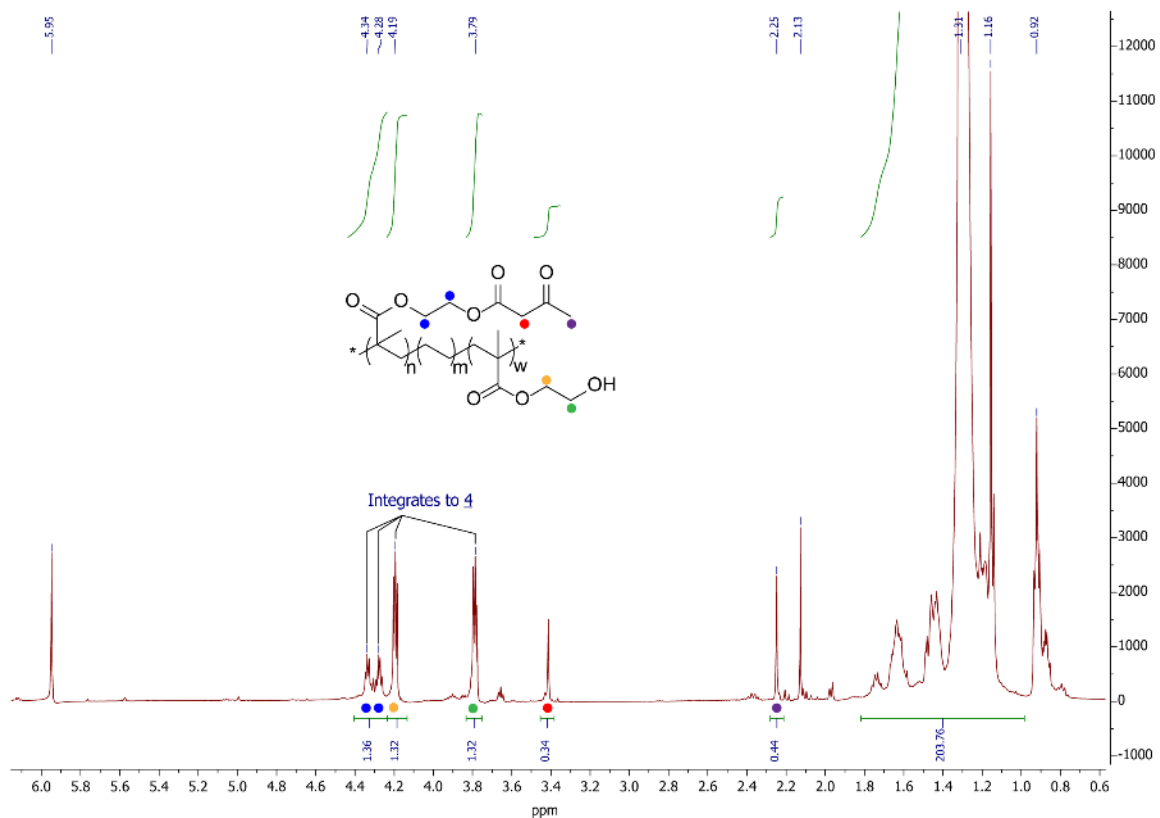


Figure S2c. High temperature ¹H NMR spectrum (120 °C, in TCE-d₂) of pristine terpolymer PACHE which was used to make sample VitX1.9.

Pristine PACHE used for preparation of VitX2.6 in TCE-d₂, 120°C, 400 MHz

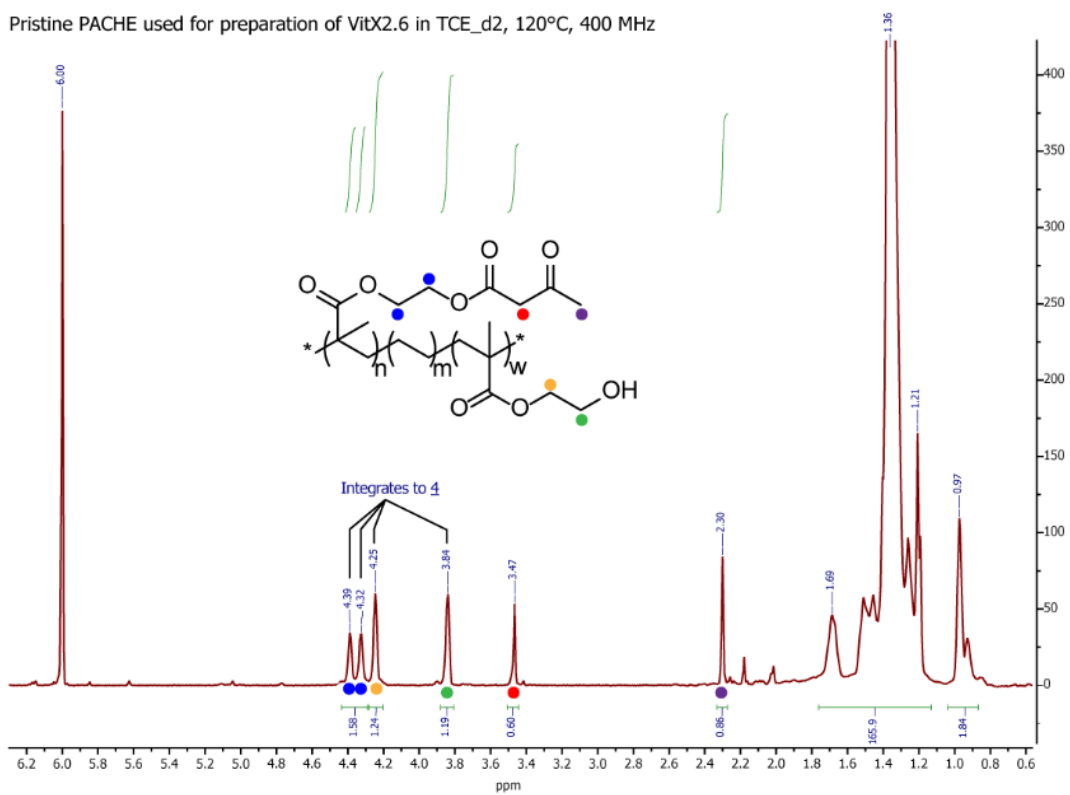


Figure S2d. High temperature ¹H NMR spectrum (120 °C, in TCE-d₂) of pristine terpolymer PACHE which was used to make sample VitX2.6.

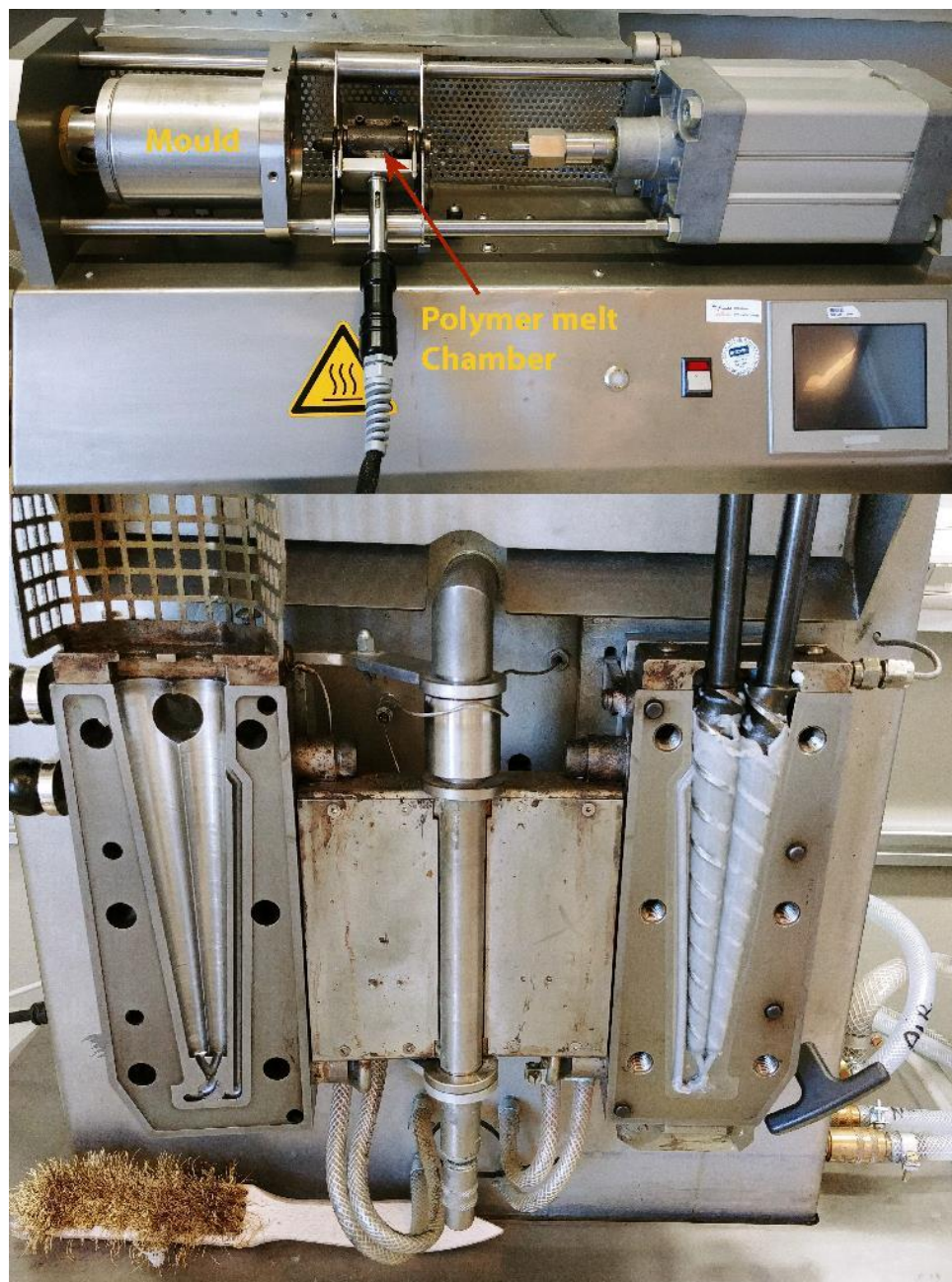


Figure S3. Picture of the injection molding machine (top) and twin-screw extruder (bottom) used for the preparation of vinylous urethane cross-linked polyethylene.

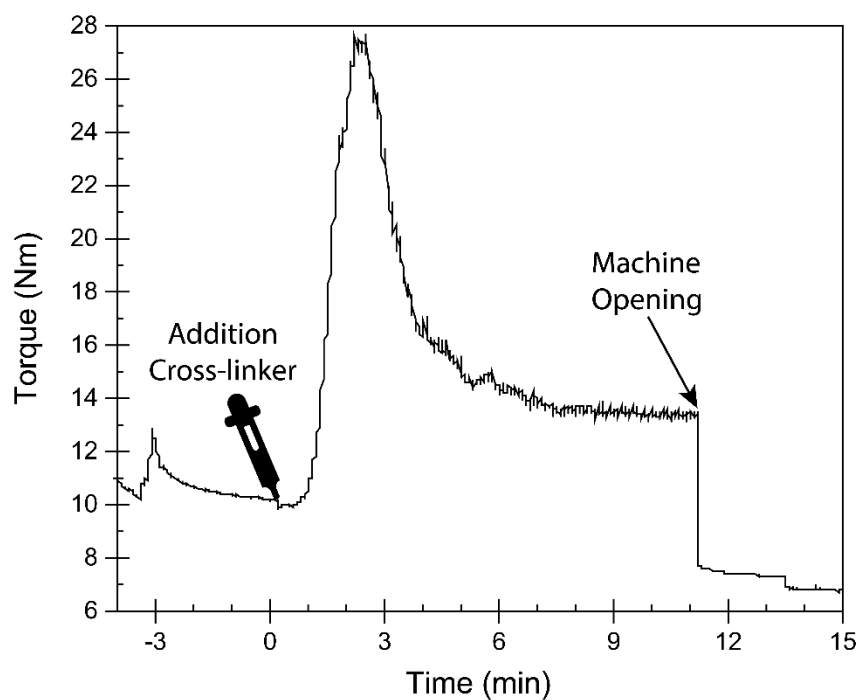


Figure S4. Torque exerted on extruder screws as a function of reaction time, obtained during preparation of sample VitX2.6. At 0 minutes, indicated by the syringe, the cross-linker was added to the polymer melt. Opening of the extruder leads to a sudden torque drop highlighted by the arrow.

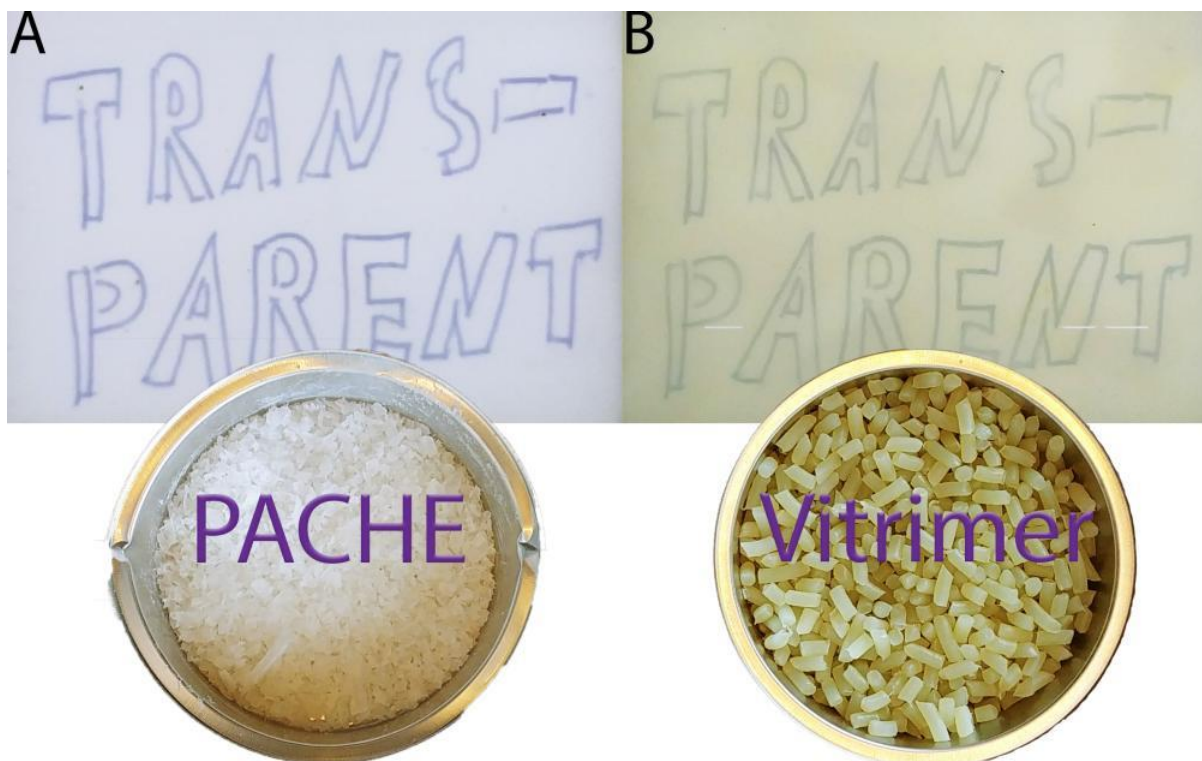


Figure S5. Examples of compression molded films over poorly sketched spelling of "transparent" on the top and picture of powdered and pelletized polymer samples (A: PACHE polymers; B: Vitrimers samples).

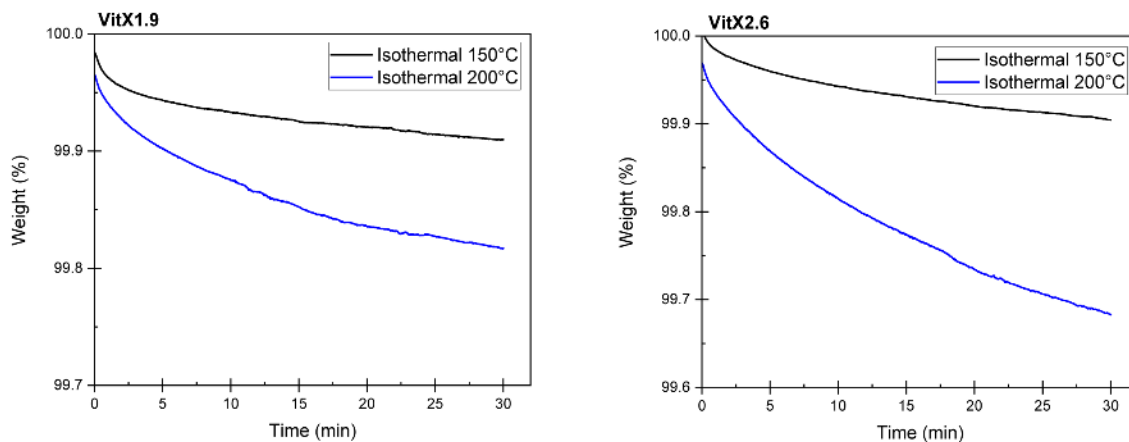


Figure S6. Isothermal TGA measurements of samples VitX1.9 (left graph) and VitX2.6 (right graph) under nitrogen at 150 °C and 200 °C. Samples were monitored over a 30 min period.



Figure S7. Pictures of gel fraction test of sample VitX1.9. Top: Vial after initial solvent removal with swollen samples. Bottom left: Pictures of swollen samples just after removal from the vial. Bottom right: Pictures of dried samples after gel fraction tests.

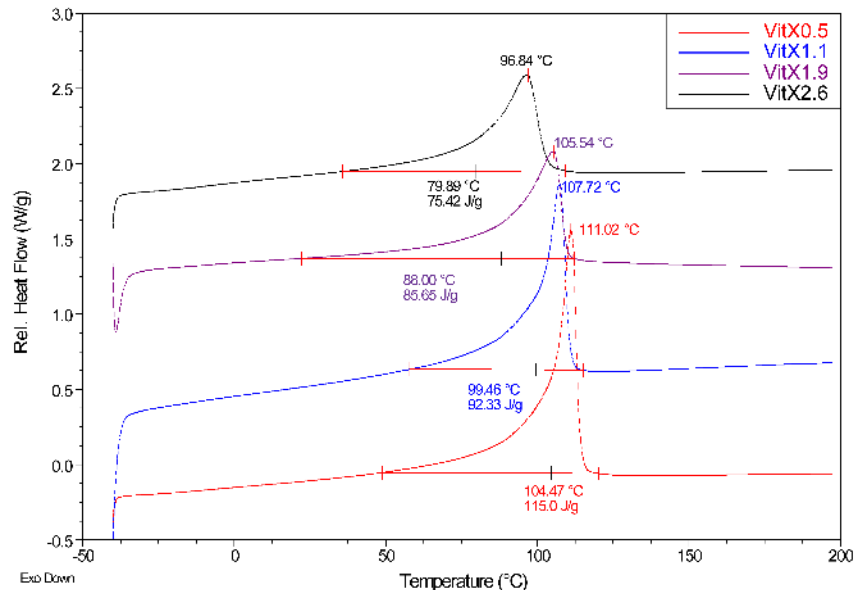


Figure S8. DSC heating curves (3rd cycle after erasion of thermal history) of Vitrimer samples.

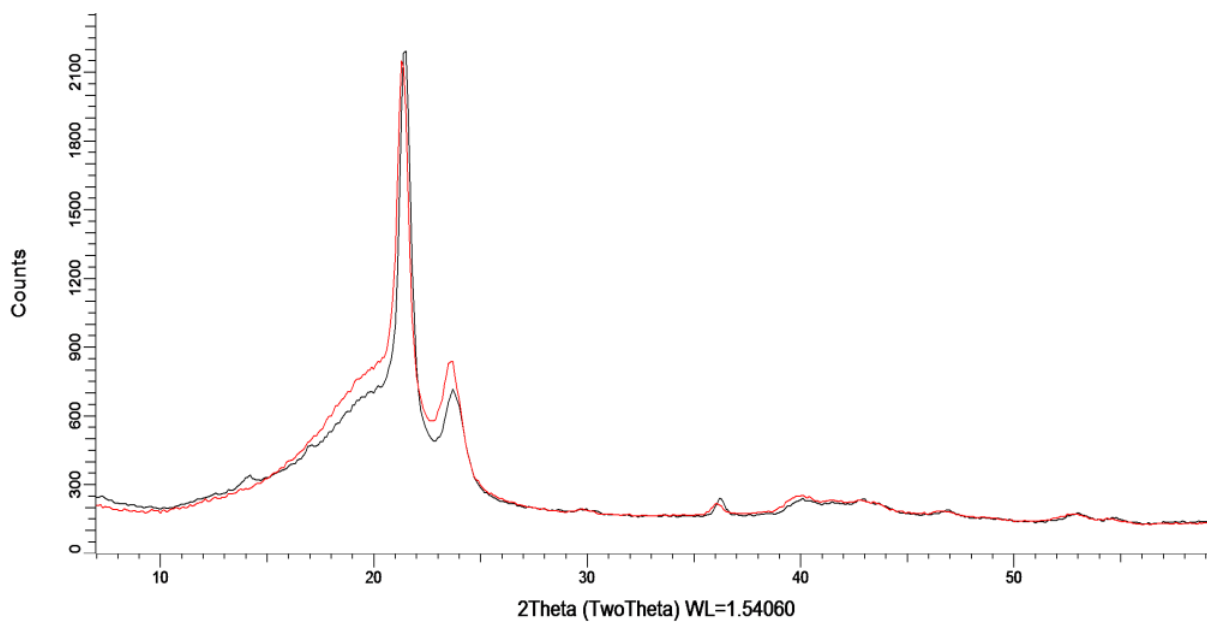


Figure S9. WAXD patterns recorded from LDPE (black line) and VitX2.6 (red line); In both cases the characteristic (110) and (200) diffraction maxima are present,^[6] corroborating that the crystalline parts of the vitrimer are made up of polyethylene.

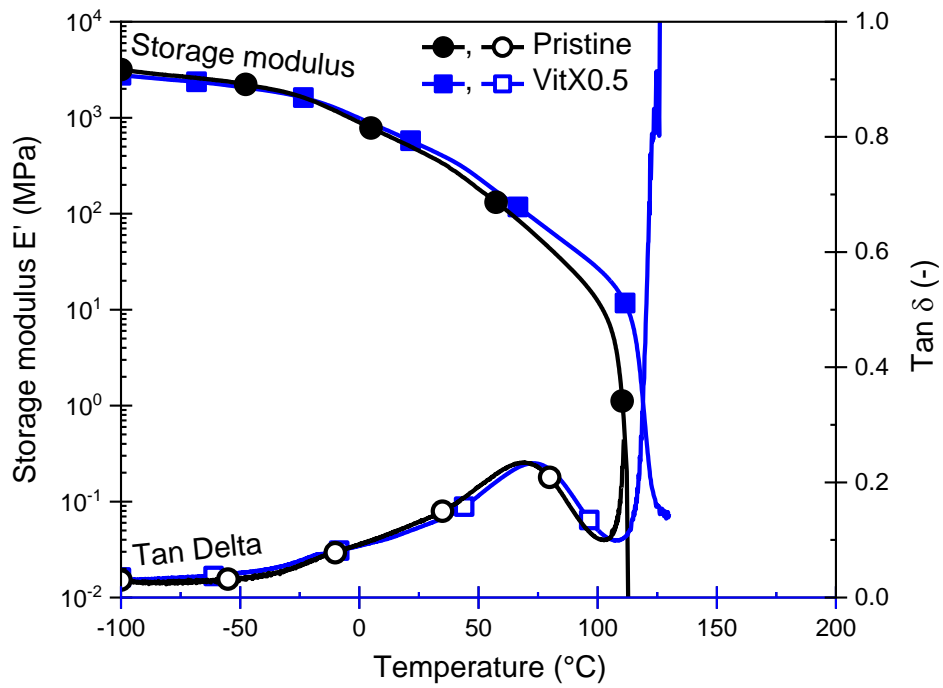


Figure S10. DMTA screening of pristine (black lines) and VitX0.5 (blue lines) between -100 °C and 130 °C. Due to melting of the sample the measurement did not continue until 200 °C. Close symbols represent data points for E', Open symbols data points for tan δ .

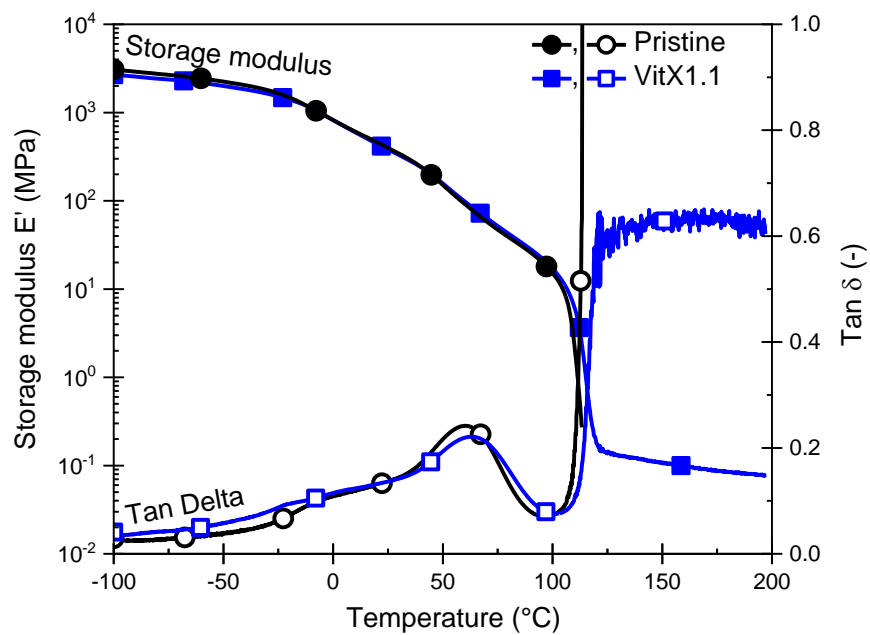


Figure S11. DMTA screening of pristine (black lines) and VitX1.1 (blue lines) between -100 °C and 200 °C. Close symbols represent data points for E', Open symbols data points for tan δ .

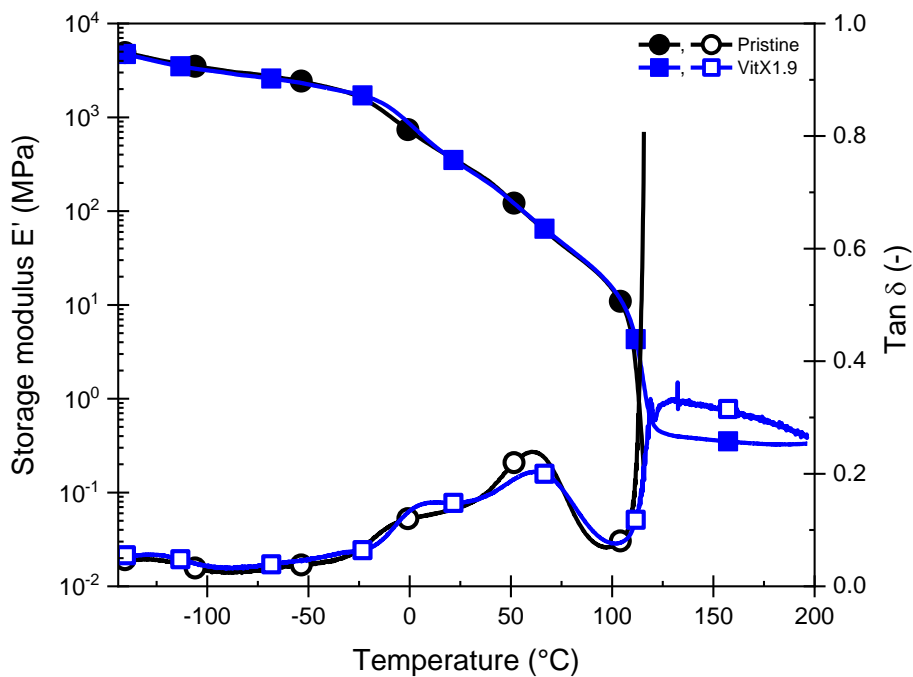


Figure S12. DMTA screening of pristine (black lines) and VitX1.9 (blue lines) between -140 °C and 200 °C. Close symbols represent data points for E', Open symbols data points for tan δ .

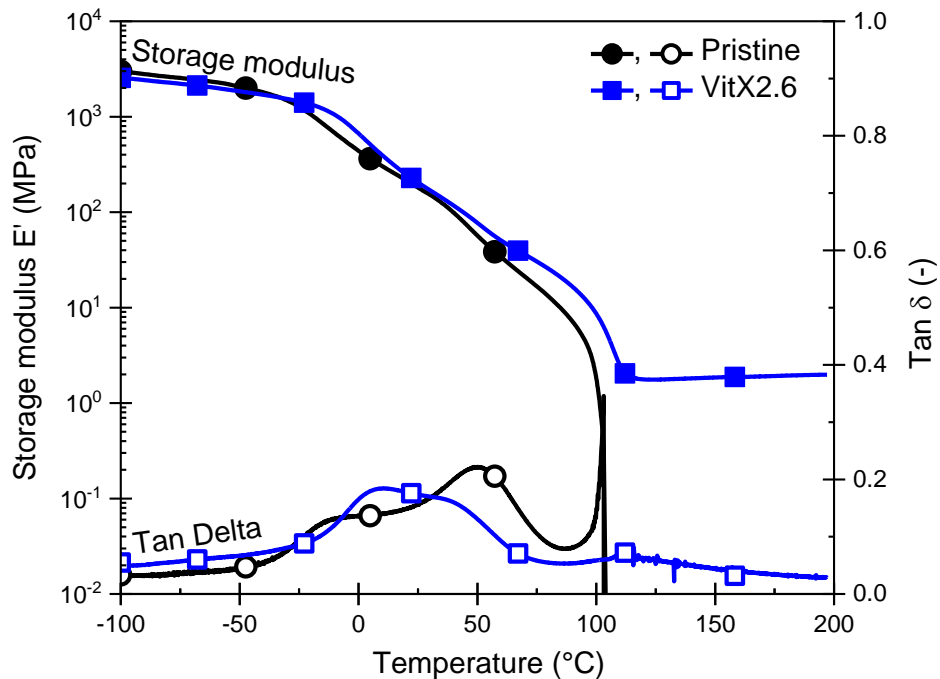


Figure S13. DMTA screening of pristine (black lines) and VitX2.6 (blue lines) between -100 °C and 200 °C. Close symbols represent data points for E' , Open symbols data points for $\tan \delta$.

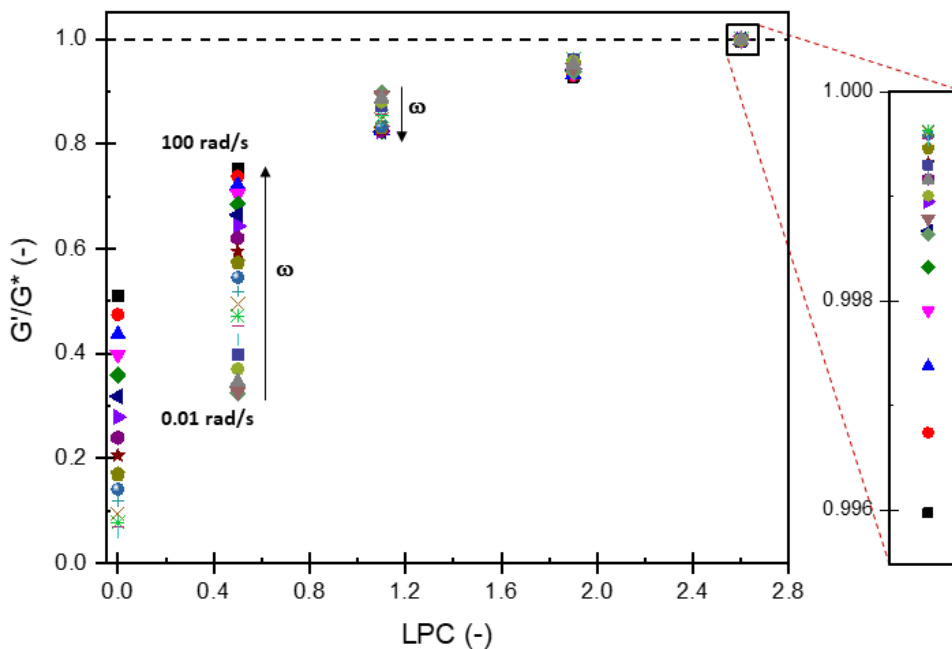


Figure S14. Plot of the normalized storage modulus (storage modulus/complex modulus, or G'/G^*) at different frequencies ($0.01 \text{ rad}\cdot\text{s}^{-1} \rightarrow 100 \text{ rad}\cdot\text{s}^{-1}$) versus links per chain (LPC) of samples VitX0.5, VitX1.1, VitX1.9, and VitX2.6. Pristine sample of VitX1.1 displayed as reference (0 LPC). Arrows highlight the direction of frequencies. Black box on the right depicts the enlarged view of data points for VitX2.6.

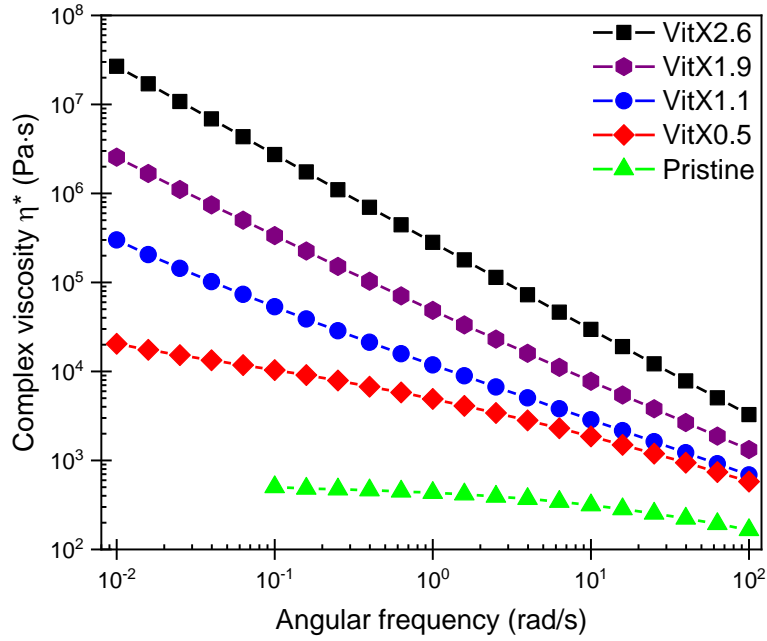


Figure S15. Plot of the complex viscosity versus angular frequency for samples VitX0.5 (red line), VitX1.1 (blue line), VitX1.9 (purple line), and VitX2.6 (black line) measured at 160 °C. The rheology of pristine polymer of Vit1.1 is displayed as a reference for a typical polymer melt (in green).

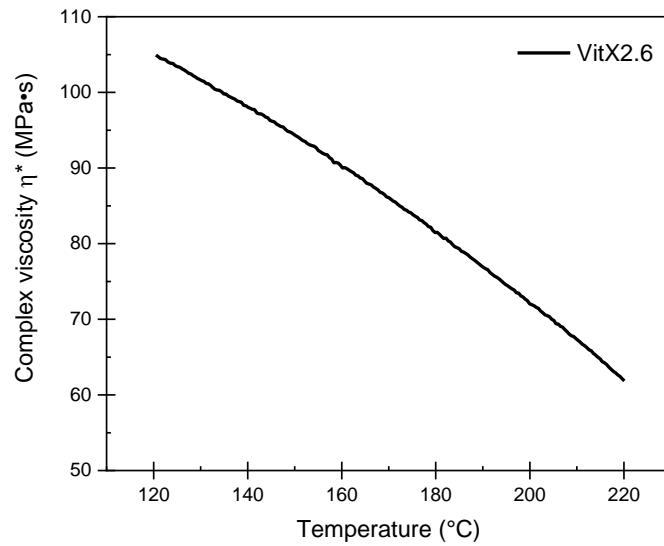


Figure S16. Plot of the complex viscosity versus temperature determined for Sample VitX2.6.

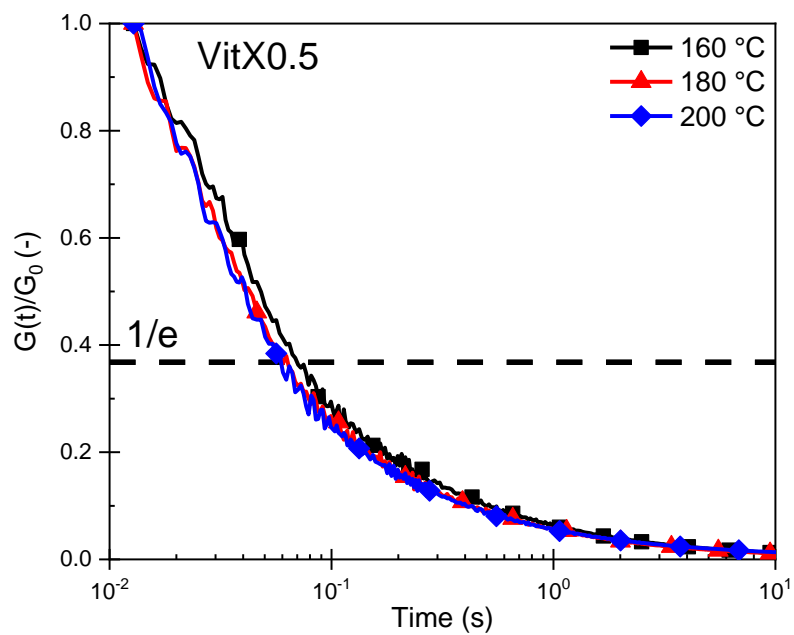


Figure S17. Normalized stress relaxation of VitX0.5 as function of time and temperature.

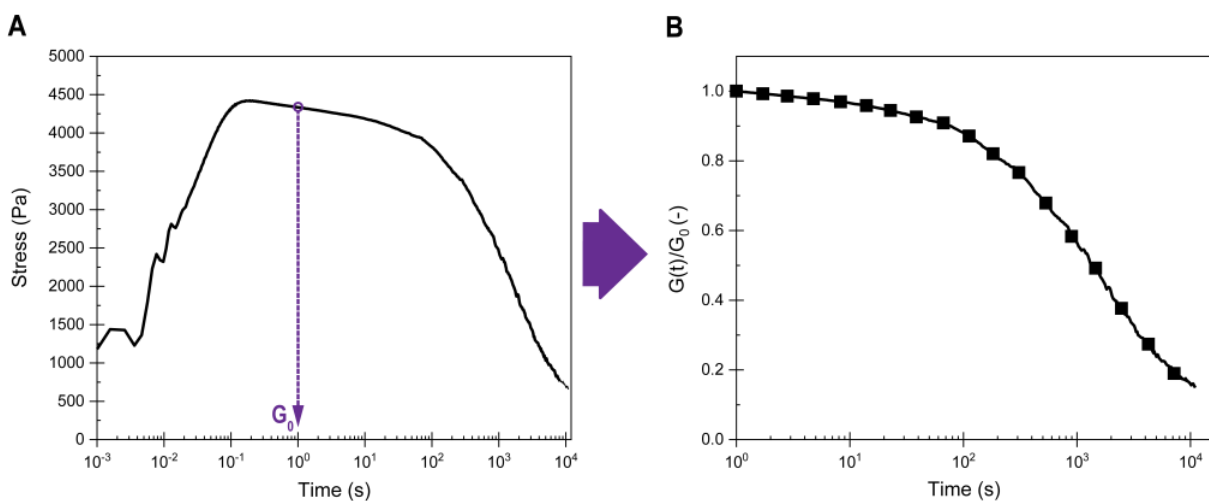


Figure S18. A: Treatment of raw stress-relaxation curves to obtain normalized spectrum. G_0 selected at $t = 1$ s for exchange reaction-controlled relaxation (VitX2.6 and VitX1.9), chosen as a stable point during the linear decline of the stress. B: Normalized treated relaxation curve.

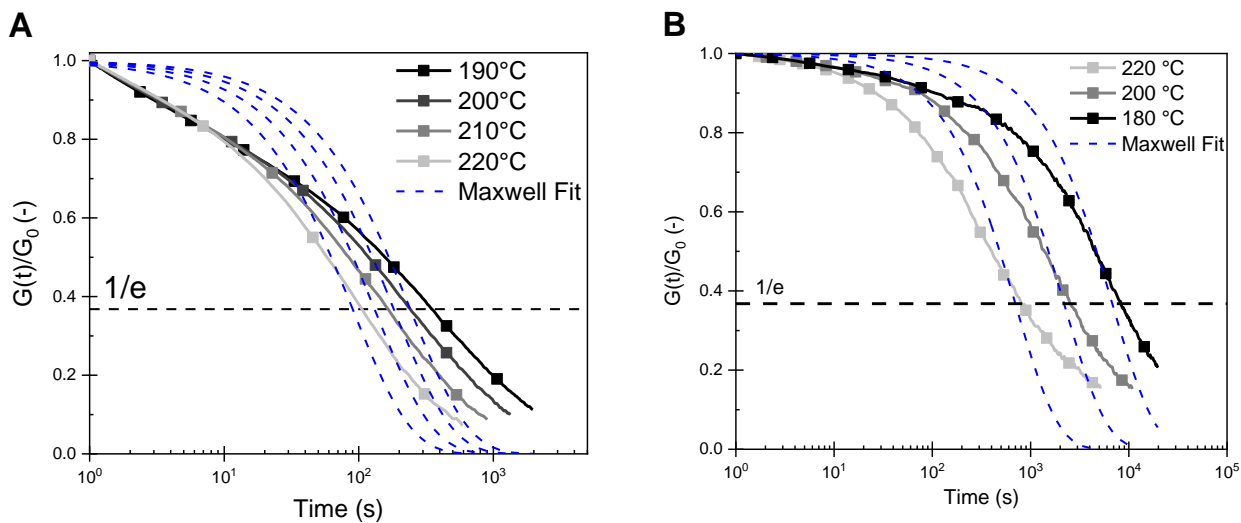


Figure S19. Maxwell Fit of samples VitX1.9 (A) and VitX2.6 (B) showcasing how the Fit does not adequately match the data. This is because the Maxwell Fitting only considers a single relaxation mode caused by one mechanism.

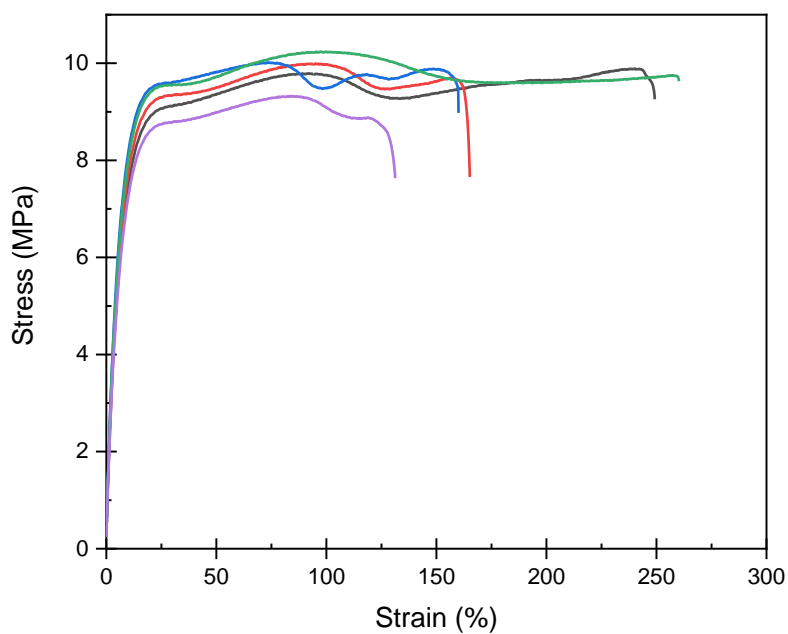


Figure S20. Stress-Strain curves (five specimen) of pristine PACHE polymer used in the preparation of sample VitX2.6.

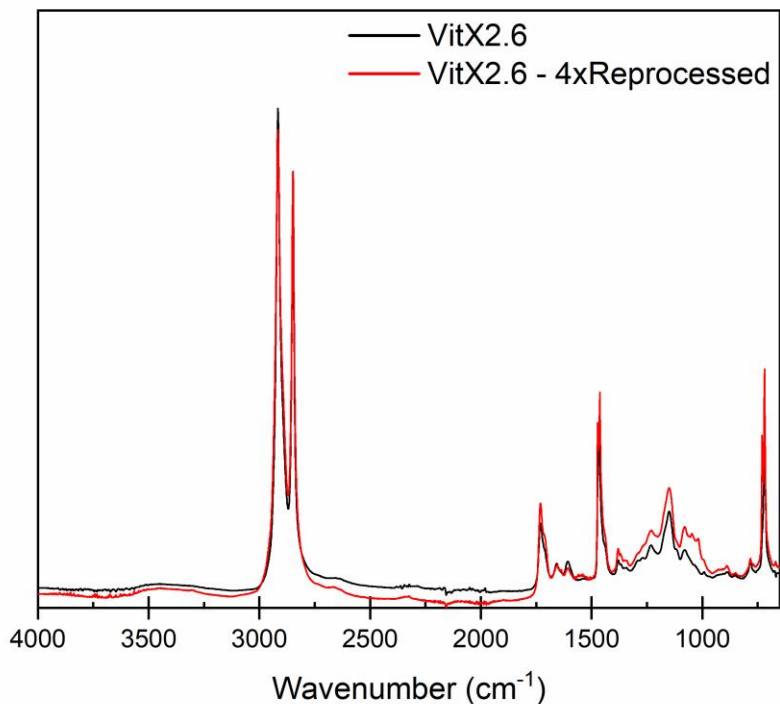


Figure S21. Superimposed ATR spectra of pristine VitX2.6 (black line) and four times reprocessed VitX2.6 (red line).

References

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