Journal of Materials Chemistry A

COMMUNICATION

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

A Facile Access to Stiff Epoxy Vitrimer with Excellent Mechanical Properties via Siloxane Equilibration

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1. Experimental Section

1.1 Materials.

Diglycidyl ether ethoxylated bisphenol A (DGEBAEO) were synthesized in our laboratory before. [24] 3-aminopropyldimethoxymethylsilane and hydroxyl-terminated poly(dimethylsiloxane) (PDMS, viscosity: 1500 cp) were purchased from Jiangxi Xinghuo Organic silicone Plant. Potassium hydroxide (KOH) and triethylenetetramine (TETA) were supplied by Beijing Chemical Reagents Company (China). All reagents were used as received without further purification.

1.2 Preparation.

(1) Synthesis of PAMS and K-PAMS: 13.5 g 3-aminopropyldimethoxymethylsilane and 3.6 g water were added into a 100ml three-necked round bottom flask and reacted with refluxing at 90 °C for 6 h. The water and generated methanol were removed through vacuum distillation, and PAMS product was obtained. A certain ratio of PAMS and KOH were added into a 100 ml three-necked round bottom flask equipped with a thermometer, a nitrogen gas inlet, a mechanical stirrer and a distilling condenser. The mixture was stirred at 110 °C for 4 h until no more water produced, and the obtained viscous liquid was K-PAMS. The adopted molar ratios of siloxane units [-$SiCH_3(CH_2CH_2CH_2NH_2)O$-] in PAMS to KOH were 6:1, 3:1 and 3:2, and the corresponding K-PAMS samples were named as K_1, K_2, and K_3, respectively. K-PDMS was synthesized from PDMS and KOH in the same way, and the adopted molar ratios of siloxane units [-$Si(CH_3)_2O$-] in PDMS to KOH was 3:1.

(2) Preparation of cured samples (Scheme 1): A stoichiometric amount of DGEBAEO and K-PAMS was weighed and added into a beaker and the mixture was stirred thoroughly and degassed under vacuum. Then the mixture was casted into a preheated Teflon mould, and cured at 80 °C for 1 h and 110 °C for 2 h in a convection oven. Samples named as V_0, V_1, V_2, and V_3 were obtained by adopted PAMS, K_1, K_2, and K_3 as hardeners, respectively.

(3) Recycling of V_2 sample: About 3g V_2 sample was cut into pieces, then placed into a rectangular mould (50 mm × 50 mm) and hot pressed at 130 °C and 10 MPa for 40 min. The mould was cooled to room temperature and a recycled sheet sample was unmolded. Dumbbell and rectangular shape specimens were cut from the sheet using a full-automatic cutter cuting machine in order to determine the tensile and dynamic mechanical properties of the recycled material, respectively.

1.3 Characterization.

The Fourier transform infrared spectroscopy (FT-IR) measurement was performed on a BRUKER TENSOR-27 FTIR spectrometer at room temperature in the range of 4000-600 cm^{-1} with a 4 cm^{-1} resolution over 32 scans. For uncured samples, they were prepared by solution (CH_3OH) casting onto a KBr window. For cured samples, the measurements were conducted by equipping with a diamond ATR attachment. ^{29}Si nuclear magnetic resonance (NMR) were acquired on a 400 MHz Avance 400 spectrometer using deuterated dimethyl sulfoxide as solvent, tetramethylsilane (TMS) as external reference, and chromium acetylacetonate as nonpolar paramagnetic relaxation agent. ^{1}H-NMR spectra with deuterated dimethyl sulfoxide as solvent was recorded using a Bruker Avance 400 MHz NMR spectrophotometer at room temperature. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a autoflex III MALDI-TOF mass spectrometer (Bruker, Billerica, Germany) with a nitrogen laser emitting at a wavelength of 335 nm in the linear mode and pulsed for 3 ns. The flight tube was evacuated to 10^{-7} Pa. All measurements were performed in a linear mode with positive-ion detection. The morphology of crack surface and elements distribution were observed by a Hitachi S4800 scanning electron microscope (SEM, Hitachi, Japan) equipped with an energy dispersive X-ray (EDX) analyser at an activation voltage of 10 kV. The sample was coated with thin gold layers about 10 nm. A high-resolution transmission electron microscope (HRTEM; JEOL, JEM-2100F, 200 kV) and energy dispersive X-ray spectroscopy (EDS) mapping were also performed. Dynamic mechanical analysis (DMA) was carried out using a TA Instruments Q800 in film tension mode under air atmosphere with a sample size of 30 mm × 4 mm × 1 mm, and three experiments were conducted.

1) Thermal mechanical property test: The glass transition temperature (T_g), defined by the peak temperature of loss factor curves (tan δ), and storage modulus at different temperatures were measured at a frequency of 1 Hz and a heating rate of 5 °C min^{-1}. The cross-linking density (ν) and molecular weight between cross-links (M_c) were evaluated by the following equation:

$$E = 3\nu RT = \frac{3\rho RT}{M_c} \qquad (1)$$

Where E is the storage modulus at T_g+50 °C, ρ is the density of cured sample (measured by pyknometer method), R is the gas constant and T refers to the absolute temperature.

2) Stress relaxation test: The time and temperature dependent of stress relaxation was also tested by DMA. A sample was initially preloaded by a 1×10^{-3} N force to maintain straightness and heated. After reaching the testing temperature, it was allowed 20 min to reach thermal equilibrium. Then a 1% strain was applied on the sample and the strain was maintained throughout the test, and the decrease of stress was recorded.

3) Recyclability test: The storage modulus of original and recycled samples was measured by DMA with a constant strain of 0.1% and an isothermal (35 °C) frequency sweep (1-15Hz) five times for each sample. The storage modulus was averaged by at least three frequency sweeps for each sample at 1Hz.

Tensile strength measurement was performed on an Instron Universal Tester Model 3365 according to GB/T 1040-2006. Dumb-bell test specimens were used for test at a strain rate of 2 mm min^{-1}, and the result was the average of at least five samples.

Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449F3 in N_2 atmosphere at 10 °C min^{-1}. Differential scanning calorimetry (DSC) was performed on a TA instruments Q100 Differential Scanning Calorimeter. Samples were heated from 20 to 200 °C at a rate of 10 °C min^{-1} under a nitrogen atmosphere. In order to test the T_g of each sample, two cooling-heating runs were performed and the data were obtained from the second heating curves.

The gel fraction of cured resin was determined by Soxhlet extraction method. Acetone was chosen as solvent, and the extraction were carried out at 56 °C for 24 hours. After that, the insoluble polymer was dried at 80 °C to the constant weight (W_2). The original weight of the sample was expressed as W_0. Therefore, the gel fraction (GF) was calculated according to the formulas: $GF = W_2 / W_0$.

2. Supplement Results and Discussion

2.1 Characterization of K-PAMS

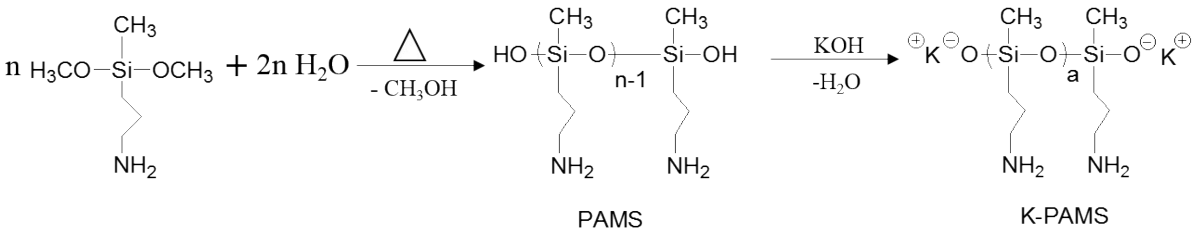
The chemical structures of K-PAMS were confirmed by FT-IR, ^1H and ^{29}Si nuclear magnetic resonance (NMR) (Figure S1-S3). Figure S1 shows the FT-IR spectrum of PAMS and all K-PAMS. As the potassium hydroxide concentration increased, the doublet peak at 1000-1100 cm^{-1} (ν_{as} (SiOSi)) was gradually becoming a single peak, indicating the number of repeat siloxane units was decreasing. Figure S2 gives the ^1H NMR spectrum of PAMS and K-PAMS. ^1H NMR of samples (400MHz, DMSO, δ): PAMS (0.05, s, 3H; $–CH_3$), (0.47, t, 2H; Si-CH_2-); K-PAMS (0.05, s, 3H; $–CH_3^1$), (-0.10, s, 3H; $–CH_3^2$), (-0.25, s, 3H; $–CH_3^3$), (0.47, t, 2H; Si-CH_2^1-), (0.33, t, 2H; Si-CH_2^2-), (0.20, t, 2H; Si-CH_2^3-). With the introduction of KOH, the chemical shifts corresponding to proton of $–CH_3$ and Si-CH_2- varies from one peak to three peaks and obviously moves to high field region. The two original peaks (0.05, s, 3H; $–CH_3^1$) and (0.47, t, 2H; Si-CH_2^1-) are becoming smaller and eventually disappeared while adjacent new peaks (-0.10, s, 3H; $–CH_3^2$), (-0.25, s, 3H; $–CH_3^3$), (0.33, t, 2H; Si-CH_2^2-) and (0.20, t, 2H; Si-CH_2^3-) become stronger, indicating that more and more -(SiO) - and –SiOH units are terminated by –SiOK groups and the oligomer chains become shorter with an increasing of KOH concentration. Figure S3 shows the ^{29}Si NMR spectra of various K-PAMS and PAMS. ^{29}Si NMR of PAMS (400MHz, DMSO, δ): (-16.5, s; -Si-OH), (-20.8~-22.5, m; -O-Si-O-). For K-PAMS, there was an increase of peaks at -20~-25.6 ppm when KOH was introduced, which were attributed to –O-Si-O- linked to -(SiO) -, -SiOH or SiOK unit. However, each peak cannot be accurately confirmed. Owing to the stronger conjunctive effect of (p-d)π bonding in Si-OK, the two original peaks moved to higher field region with the increasing KOH content, which shows same tendency as to ^{1}H NMR. The molecular weight of PAMS and K-PAMS was determined by MALDI-TOF, shown in Figure S4. MALDI-TOF m/z of PAMS (Figure S4a): 1929 (n=16), 2046 (n=17), 2163 (n=18), 2280 (n=19), 2397 (n=20), 2514 (n=21) $[M+K]^+$; K_2 (Figure S4b) :835 (n=6), 952 (n=7), 1069 (n=8), 1186 (n=9),1303 (n=10), 1420 (n=11), 1537 (n=12) $[M+K]^+$. According to the feeding molar ratios of PAMS/KOH, the calculated siloxane segment number ($K^{+}\ {}^{-}O[CH_3Si(CH_2CH_2CH_2NH_2)O]_{n-1}[CH_3Si(CH_2CH_2CH_2NH_2)O]^{-}K^{+}$) in K_2 was 6. It is seen that the MOLDI-TOF result is close to the calculated molecular weight, confirming that the molecular chain becomes shorter with the increase of KOH content.

2.2 Curing behavior

The curing behavior of DGEBAEO/K-PAMS system was studied by DSC. Figure S5a gives the non-isothermal DSC curves of DGEBAEO curing with K_2, PAMS, TETA and K-PDMS (K_2). Only one exothermic curing peak was observed for DGEBAEO/PAMS, and the curing peak temperature was close to that of DGEBAEO/TETA, indicating that they had similar curing reactivity. For DGEBAEO/K-PAMS system, there were two exothermic peaks in the curing curves. According to the position of peaks, and comparing to the curing peaks of DGEBAEO cured by PAMS and K-PDMS, the curing peak of DGEBAEO/K-PAMS at lower temperature was attributed to the curing reaction between epoxy and amine groups, while the peak at higher temperature was attributed to the ring-opening of epoxy attacked by silanolate anion. In order to further determine the chemical crosslinks of DGEBAEO/K-PAMS under the given curing condition (80 °C 1h, 110 °C 2h), an isothermal procedure at 80 °C was set for 1h firstly, and then a non-isothermal DSC scan was conducted (Figure S5b). No obvious exothermic peak was observed in the curve of DGEBAEO/K-PAMS, indicating that the curing reaction has almost finished after curing at 80 °C for 1 h. However, the DGEBAEO/K-PDMS exhibited an obvious exothermic peak centered at 150 °C, and the exothermic enthalpy is the same as that of without the isothermal process, indicating that the reaction between epoxy groups and silanolate anions didn't happen at 80 °C. The above results presented that only the reaction between epoxy and amino groups happened in DGEBAEO/K-PAMS system at the given curing condition, and most of the chemical crosslinks in the cured network were formed by the epoxy-amino linkage.

2.3 Thermal property

Figure S6 gives the DMA and DSC curves of V_0-V_3. With the increase of KOH content, T_g of the cured resins decreased first and then increased. It is known that T_g is proportional to the crosslink density and potassium ion concentration. The crosslink density values (ν and M_c) were calculated from the DMA data (Table S1). The crosslink density was decreasing as the KOH concentration increased, for the reason that the oligomer chain of K-PAMS got shorter. Therefore, the decrease of K-PAMS's T_g is definitely due to the decrease of crosslink density, while the increase of T_g is attributed to the increasing strong ionic interaction of potassium silanolate groups, which limits the chain motions.



Scheme S1. Synthesis route of K-PAMS.

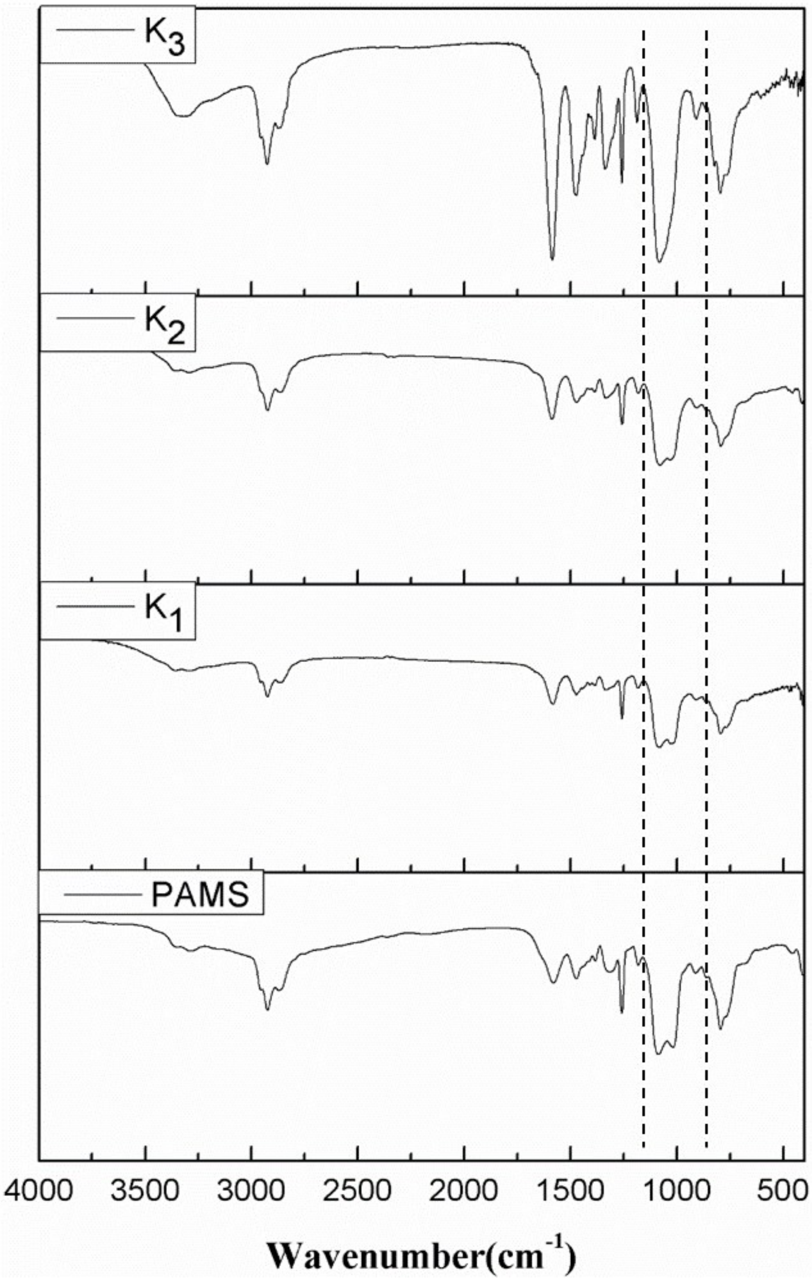


Figure S1. FT-IR spectra of the K-PAMS and PAMS.

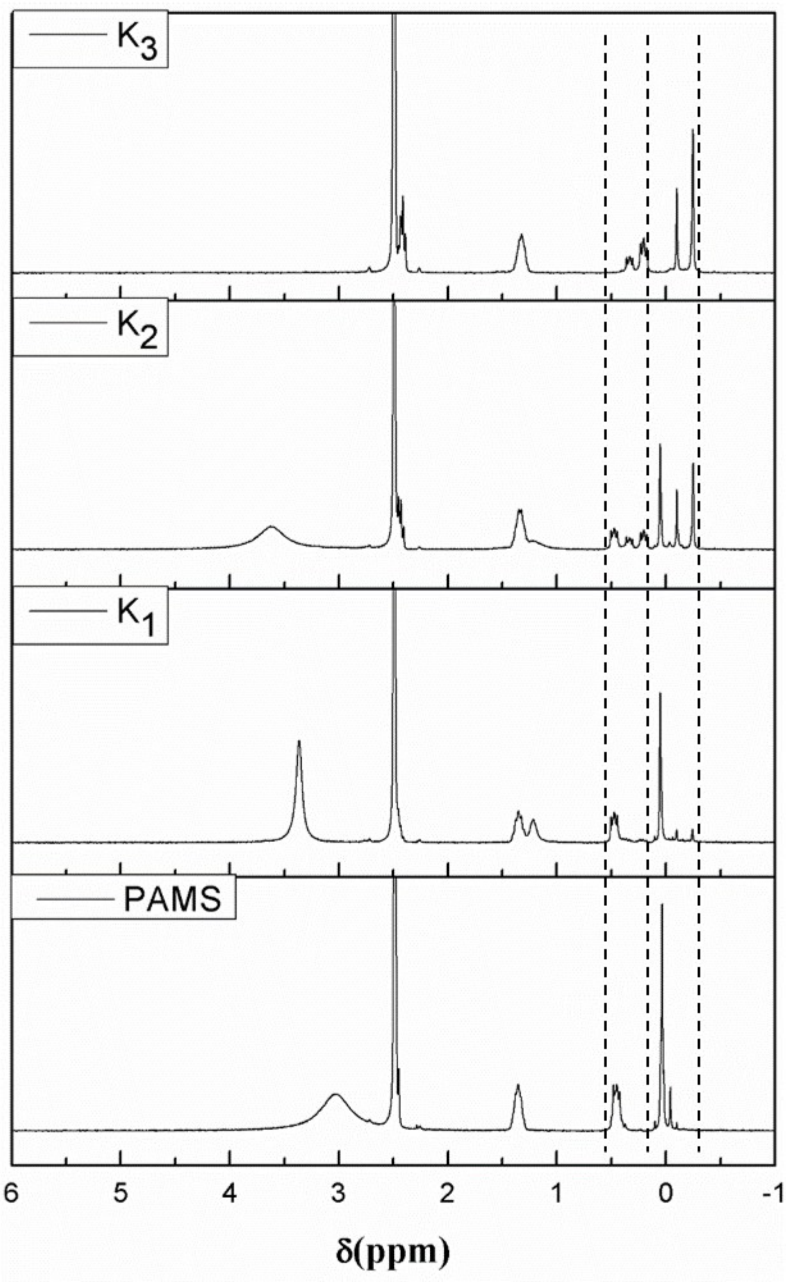


Figure S2. ^{1}H NMR spectra of K-PAMS and PAMS.

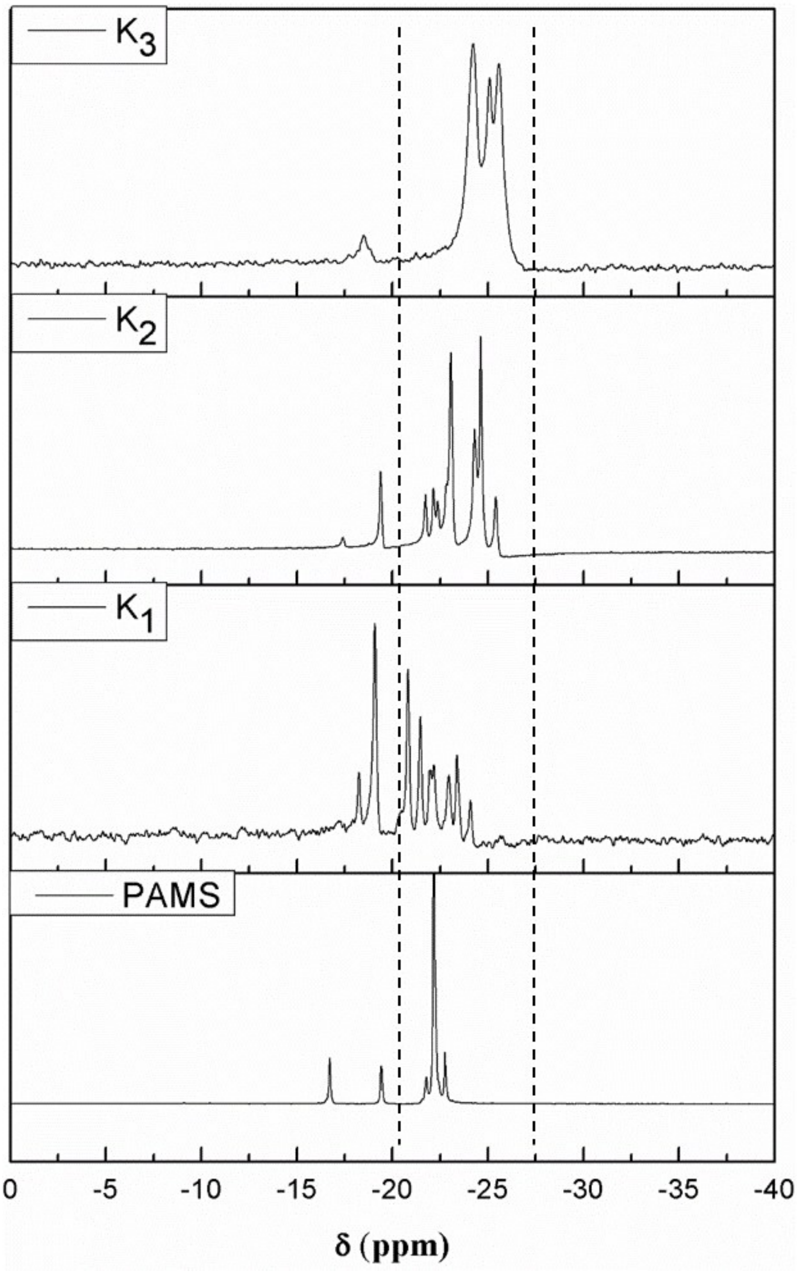


Figure S3. ^{29}Si NMR spectra of K-PAMS and PAMS.

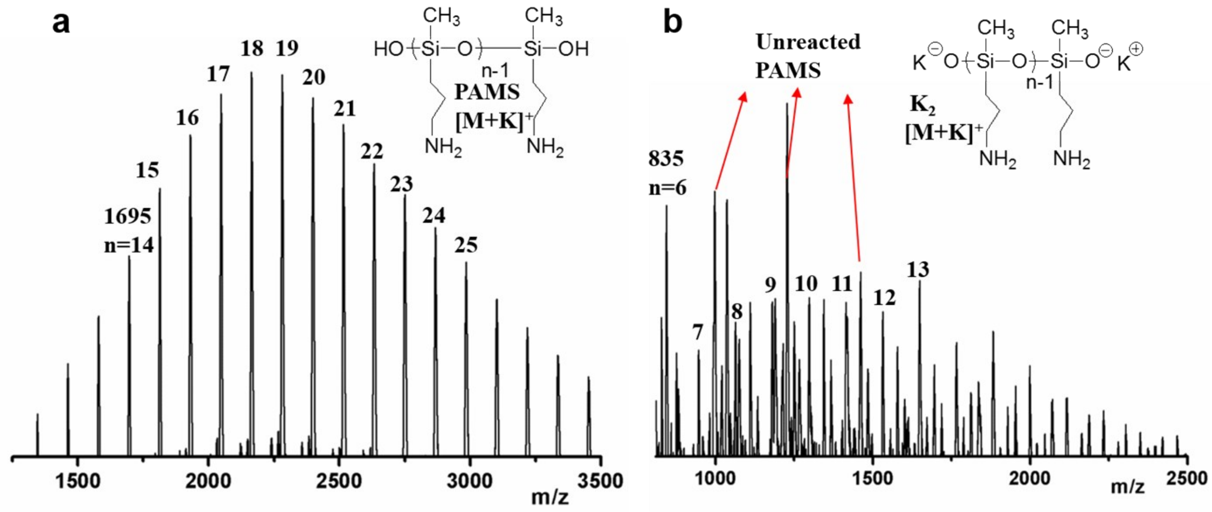


Figure S4. MALDI-TOF mass spectra of a) PAMS and b) K_2.

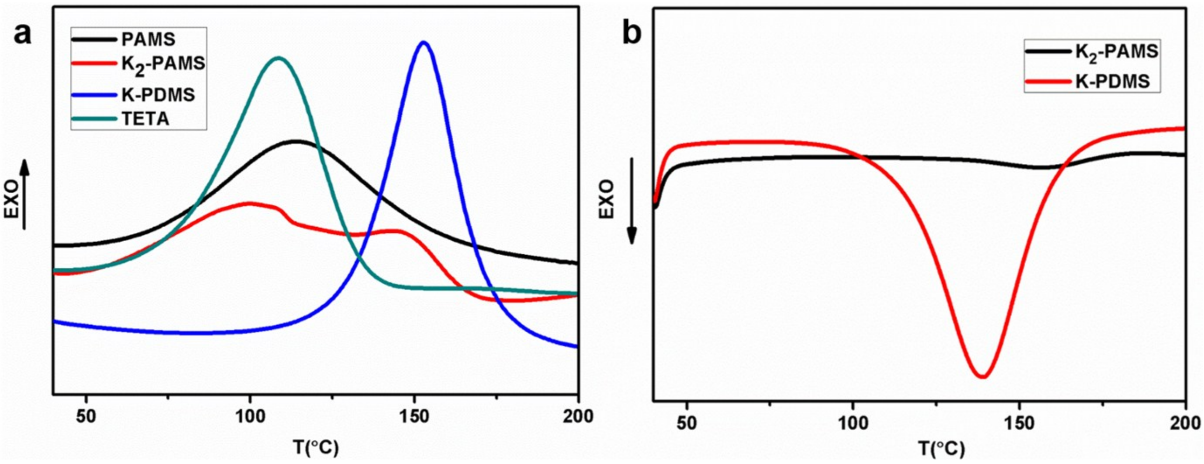


Figure S5. a) Non-isothermal DSC curves of DGEBAEO curing with different curing agents; b) non-isothermal DSC curves of DGEBAEO curing with K_2 and K-PDMS after an isothermal DSC process at 80 °C for 1 h.

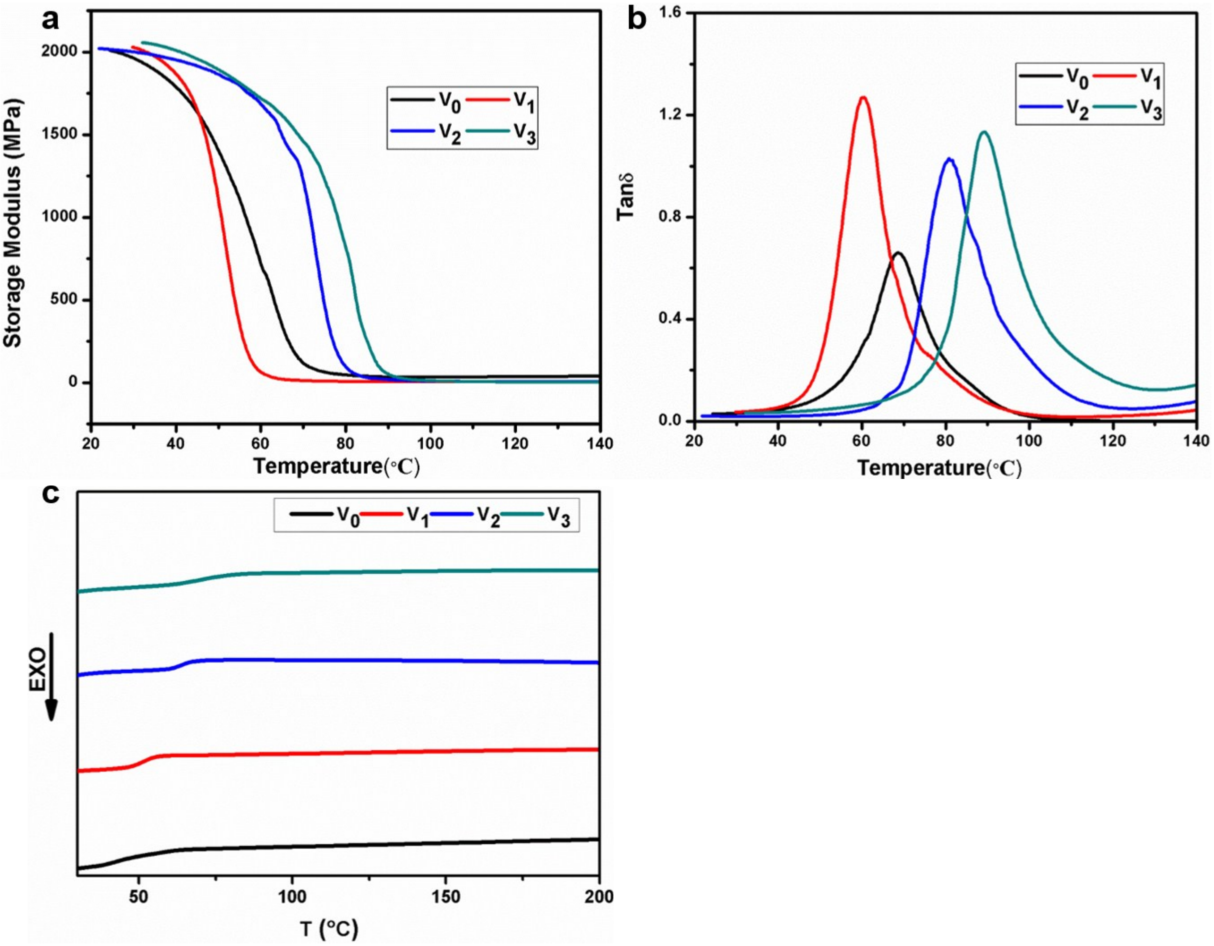


Figure S6. DMA and DSC curves of four cured samples.

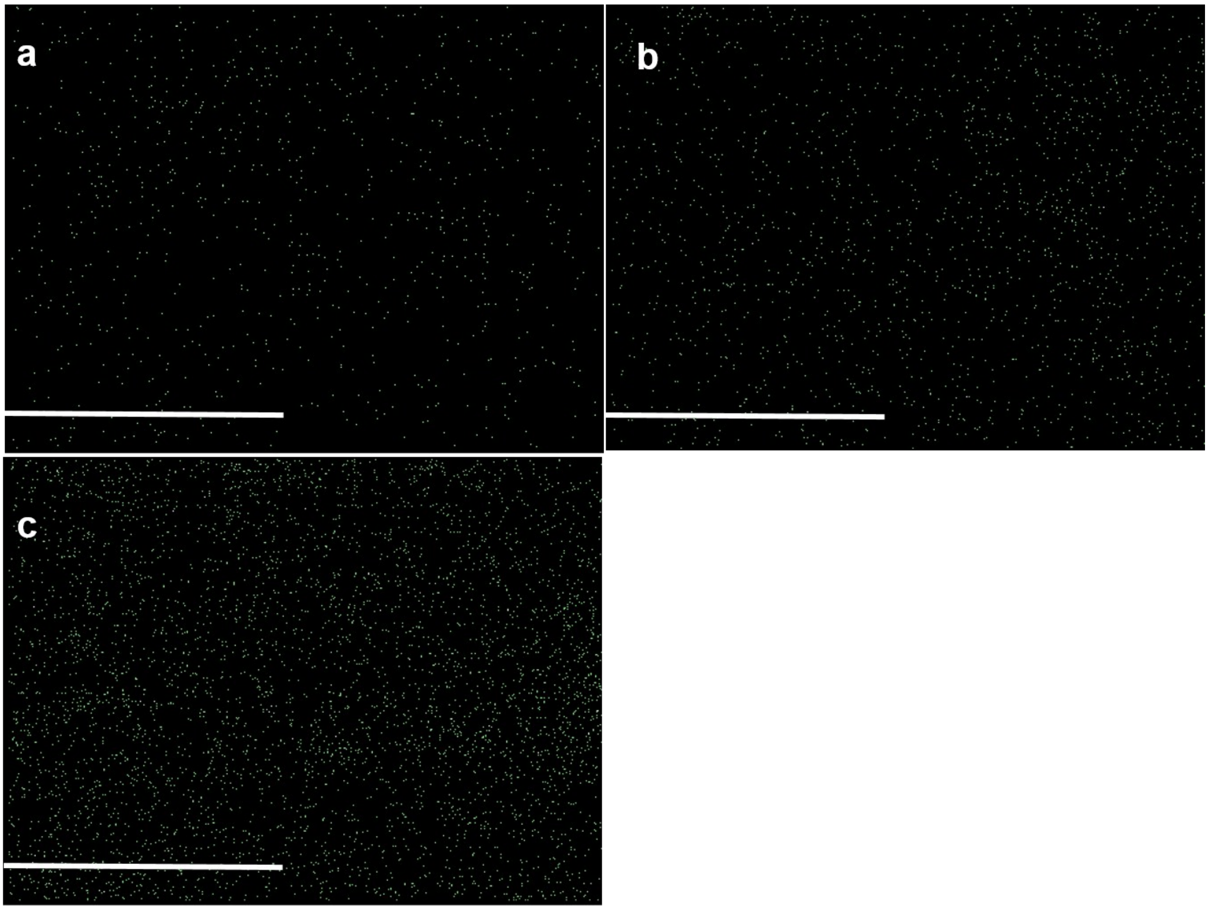


Figure S7. SEM-EDS map of K element distribution in: a) V_1, b) V_2, c) V_3 samples (Scale bars: 6 μm).

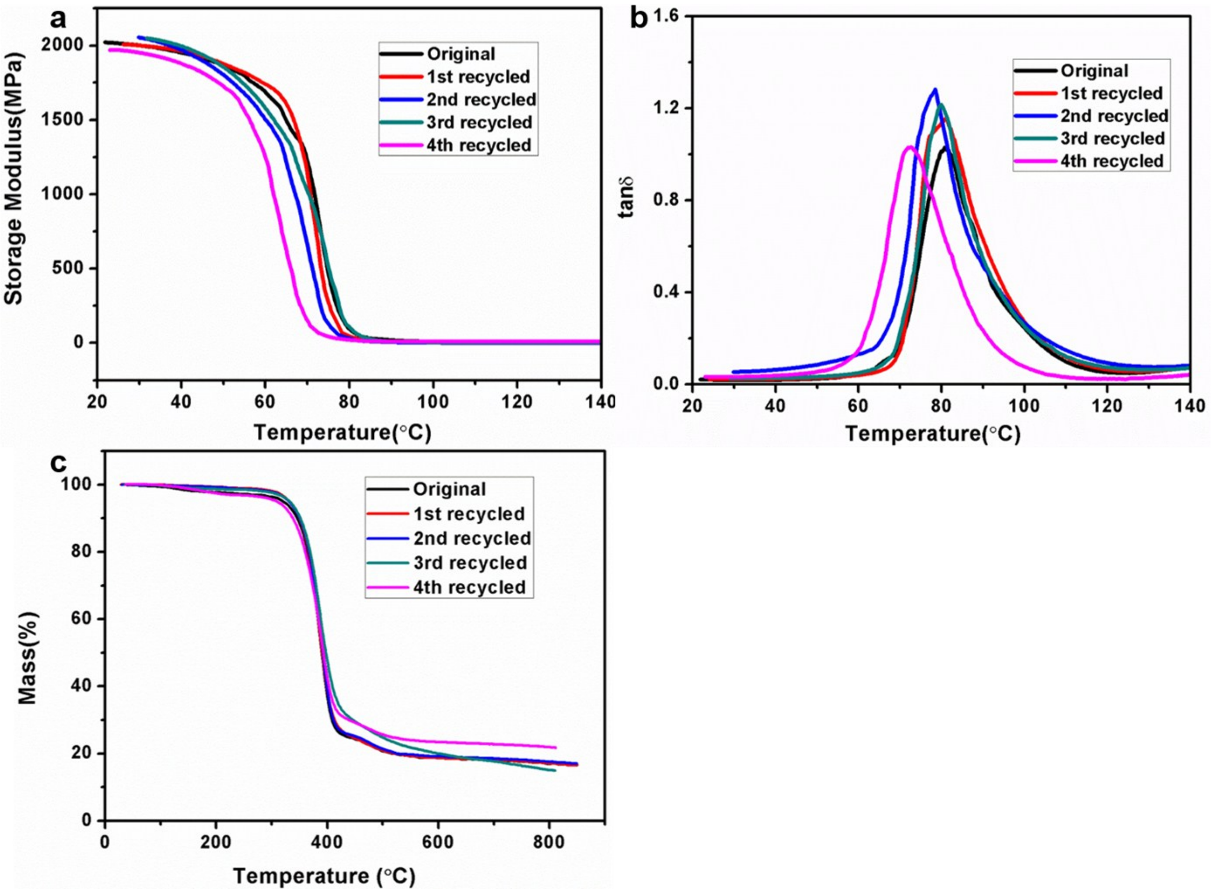


Figure S8. DMA and TGA curves of original and recycled samples.

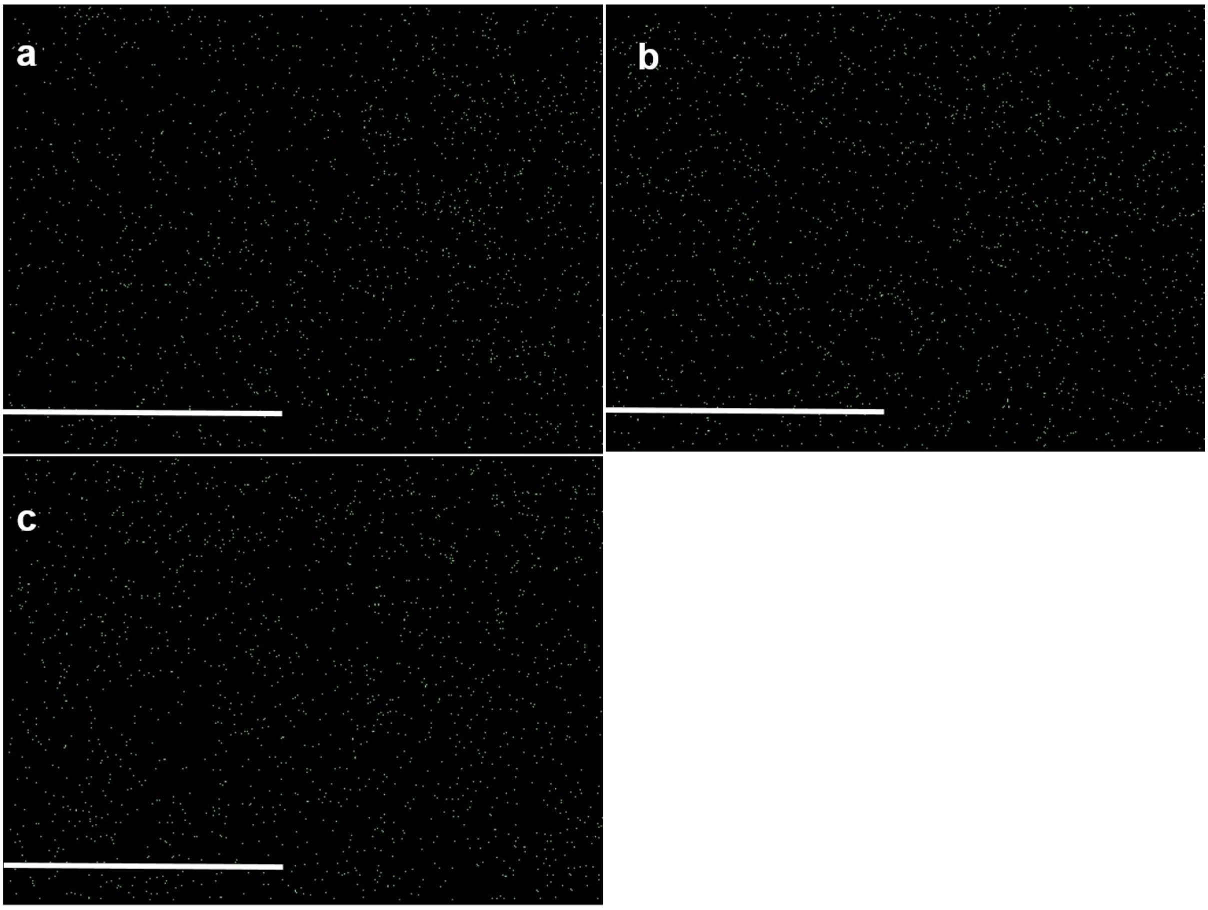


Figure S9. SEM-EDS map of K element distribution in V_2 sample: a) original, b) 1st recycled, c) 2nd recycled (Scale bars: 6 μm).

Table S1. DMA, DSC and gel fraction data of four cured samples.

Samples	T_g/ °C (DSC)	T_g/ °C (DMA)	GF/%	E/MPa T_g+50°C	ρ/ g cm^{-3}	ν/ mol m^{-3}	M_c/ Kg mol^{-1}	Relaxation times /s (110°C)
V_0	57	68	100	36	1.1830	3692	0.32	/
V_1	52	60	94	7.0	1.1866	733	1.62	1867
V_2	63	83	96	4.0	1.1959	406	2.95	205
V_3	70	89	100	4.8	1.2049	466	2.58	854

Table S2. Mechanical and thermal properties of original and recycled vitrimers.

Vitrimers	Tensile strength (MPa)	Strain at break (%)	Young's modulus (MPa)	T_d/ °C (IDT)
Original	45.18±0.80	7.42±0.29	1962±17.2	358
Recycled 1	47.34±3.15	6.66±0.41	1995±15.7	357
Recycled 2	42.89±2.66	5.71±0.24	1985±60.8	359
Recycled 3	45.53±1.19	4.64±0.32	1998±21.9	353
Recycled 4	45.83±7.88	5.26±0.74	2020±33.8	352