Supporting information

Preparation of lignin-based vinylogous urethane vitrimer materials and their potential use for on-demand removable adhesives

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S† Figures and tables

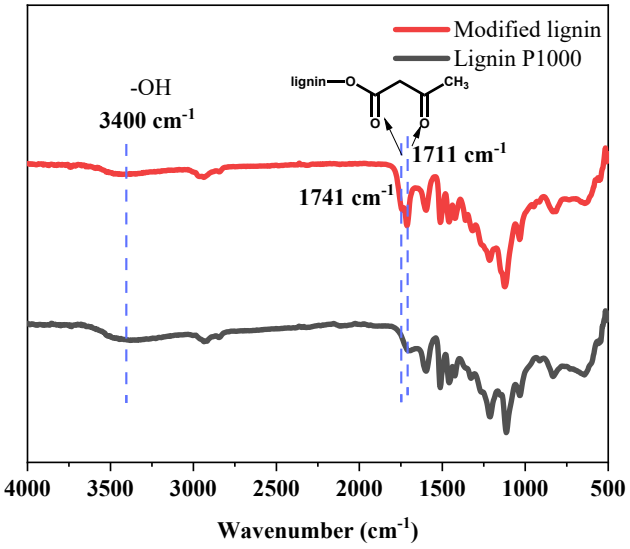

Fig. S1† FTIR spectra of modified lignin and unmodified lignin.

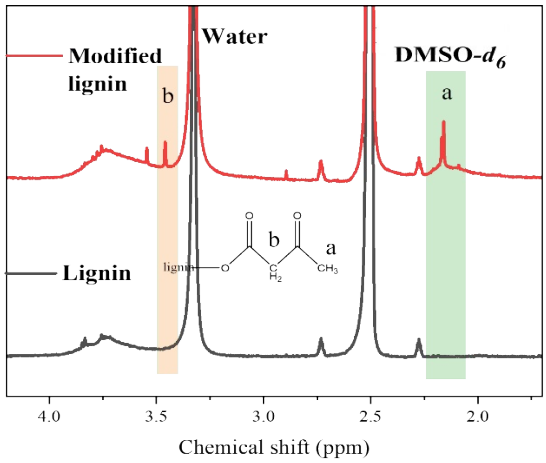

Fig. S2† ^{1}H-NMR spectra of modified lignin and unmodified lignin (DMSO-d_6).

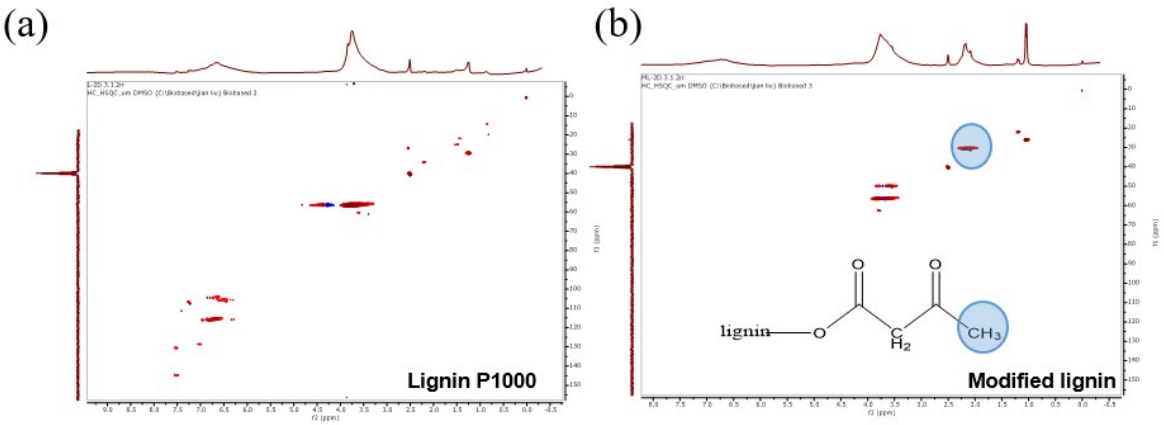

Fig. S3† (a) 2D-HSQC NMR spectra of unmodified lignin (DMSO-d_6); (b) 2D-HSQC NMR spectra of modified lignin (DMSO-d_6).

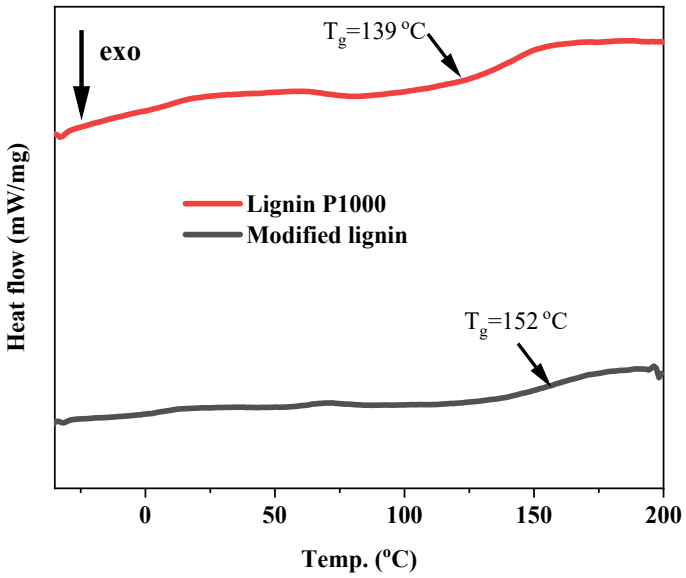

Fig. S4† DSC (second heating curve) of modified lignin and unmodified lignin.

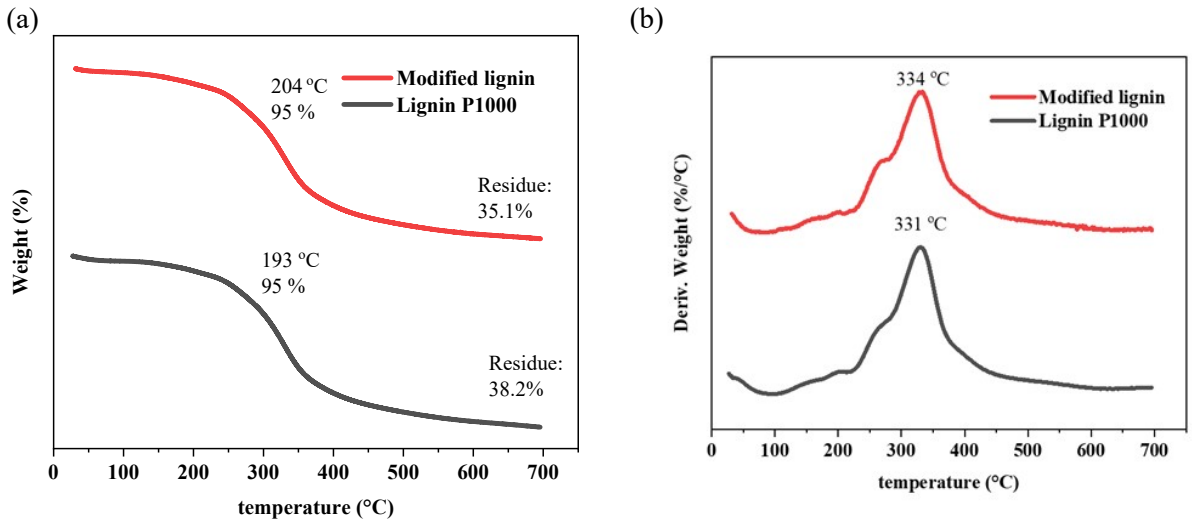

Fig. S5† (a) TGA of modified lignin and unmodified lignin (10 °C/min, nitrogen atmosphere). (b) DTGA of modified lignin and unmodified lignin (10 °C/min, nitrogen atmosphere).

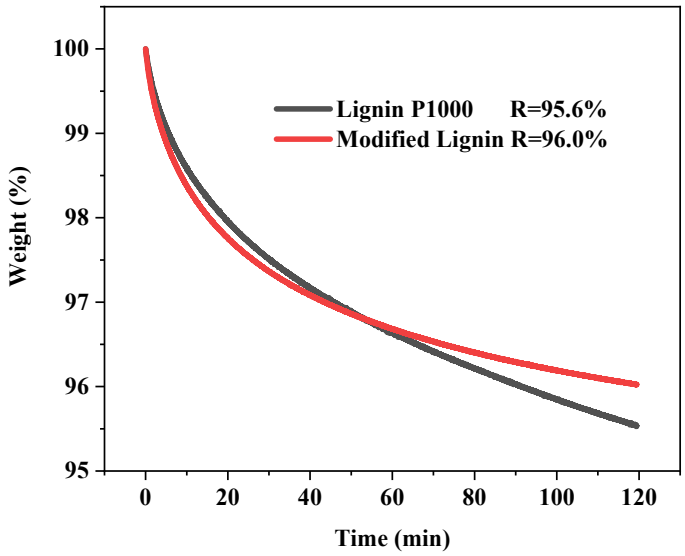

Fig. S6† Isothermal TGA curves of modified lignin and unmodified lignin at 170 °C (post-curing conditions). R = residue.

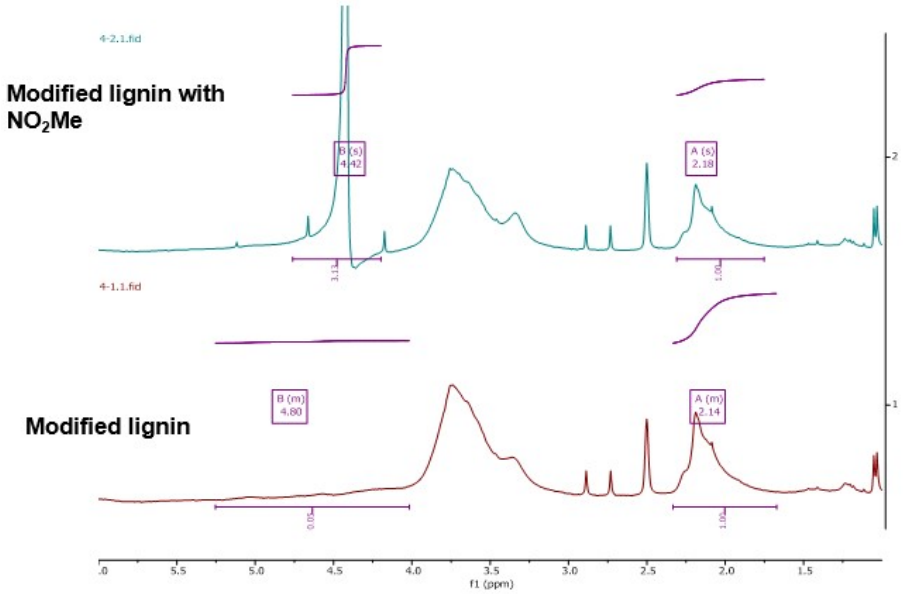

Fig. S7† Quantitative ^{1}H NMR was used to calculate the degree of modification (DMSO-d_6).

$$Molality_{OAcAc} = m_{OAcAc} = {}^{OAcAc_{mole}}\!/_{modified\ lignin_{kg}} = \left(\frac{mass_{NO_2Me(g)}}{molar\ mass\ _{\overline{NO_2Me(mole)}}^{NO_2Me(g)}}\right) \times \left(\frac{OAcAc_{in}}{NO_2Me_{in}}\right.$$

$$\left(\frac{sample\ mass_g}{1000\ \frac{g}{kg}}\right) = \frac{0.0152\ g}{61.04\ g/mol} \times \frac{1}{(3.13 - 0.05)} \div 0.0332\ g \times 1000\ g/kg = 2.43\ mo$$

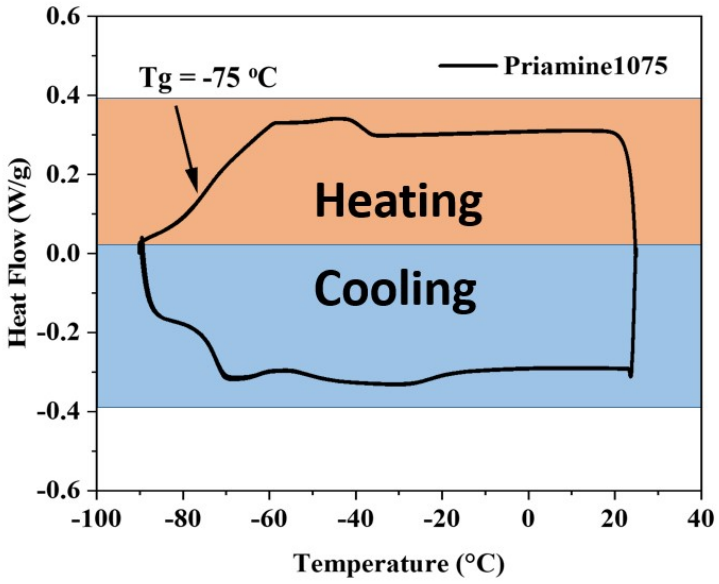

Fig. S8† DSC (second heating and cooling) of Priamine™ 1075.

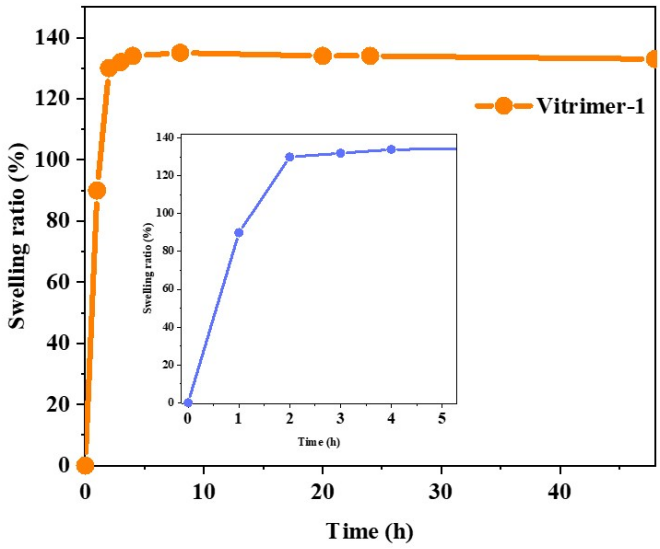

Fig. S9† Swelling ratio of Vitrimer-1 in 2-MeTHF solvent at room temperature with time.

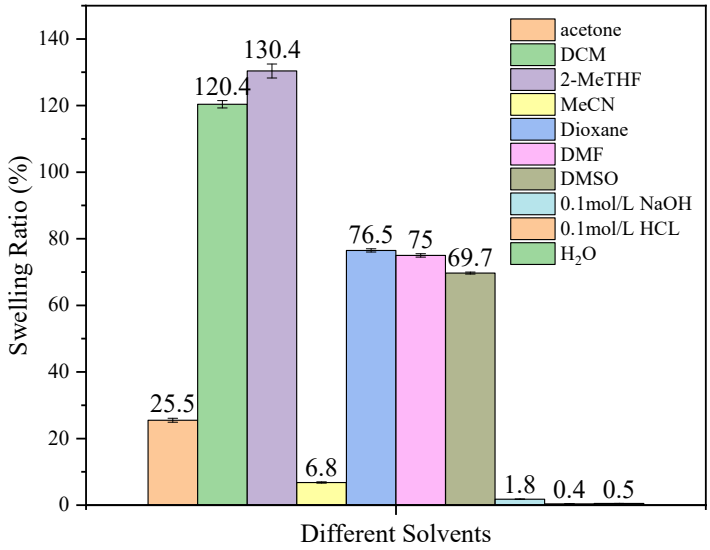

Fig. S10† Swelling ratio of Vitrimer-1 in different solvents at room temperature.

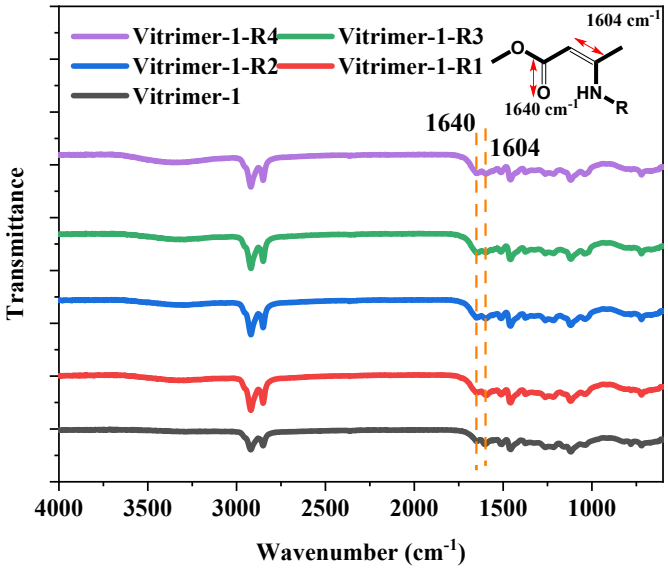

Fig. S11† FTIR spectra of recycled samples.

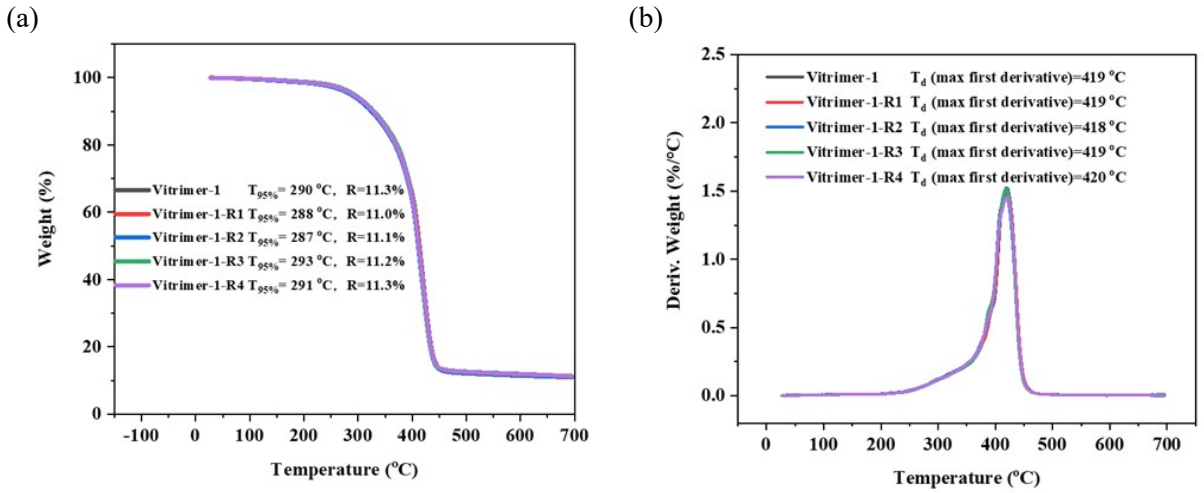

Fig. S12† (a) TGA curves of recycled samples (10 °C/min, nitrogen atmosphere). (b) DTGA curves of recycled samples (10 °C/min, nitrogen atmosphere).

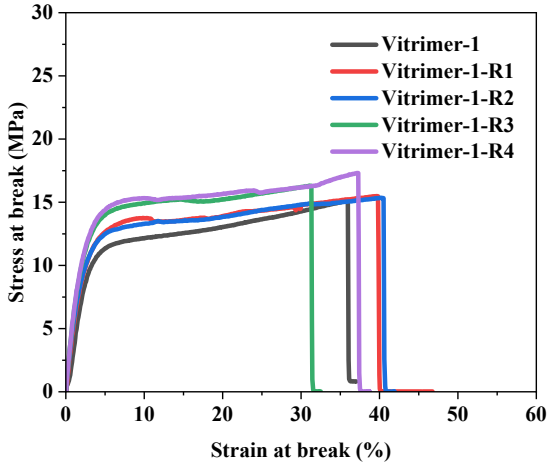

Fig. S13† Tensile properties of recycled samples

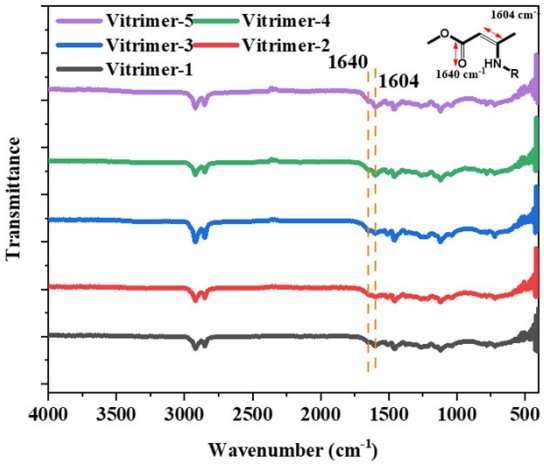

Fig. S14† FTIR spectra of different ratios' vitrimer samples.

(a) (b)

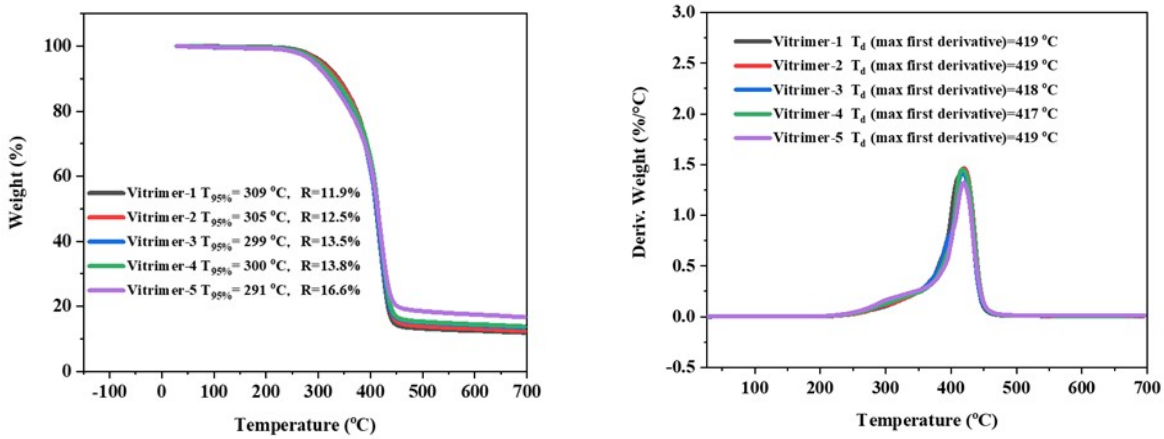

Fig. S15† (a) TGA curves of different ratios' vitrimer samples (10 °C/min, nitrogen atmosphere). (b) DTGA curves of different ratios' vitrimer samples (10 °C/min, nitrogen atmosphere).

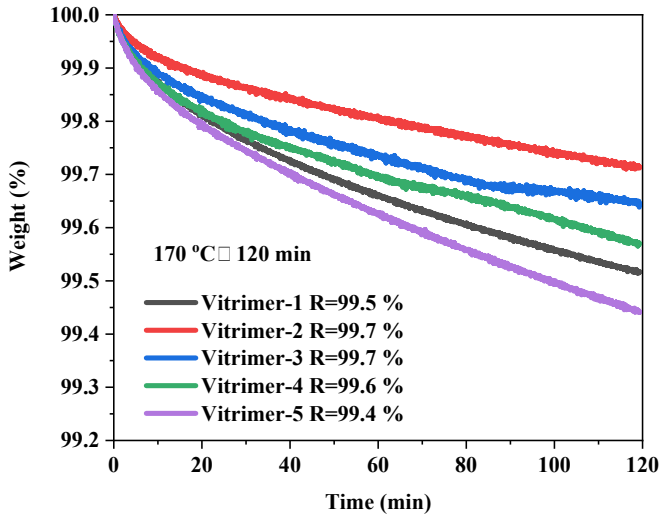

Fig. S16† Isothermal TGA curves at 170 °C of vitrimer samples with different ratio's Priamine™ 1075 and 1, 10 diaminodecane.

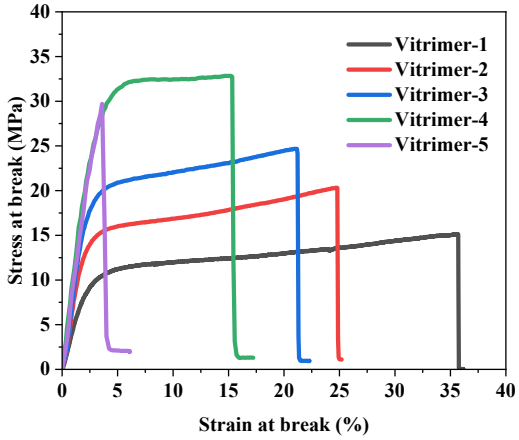

Fig. S17† Tensile properties of vitrimers with different ratio's Priamine™ 1075 and 1, 10 diaminodecane.

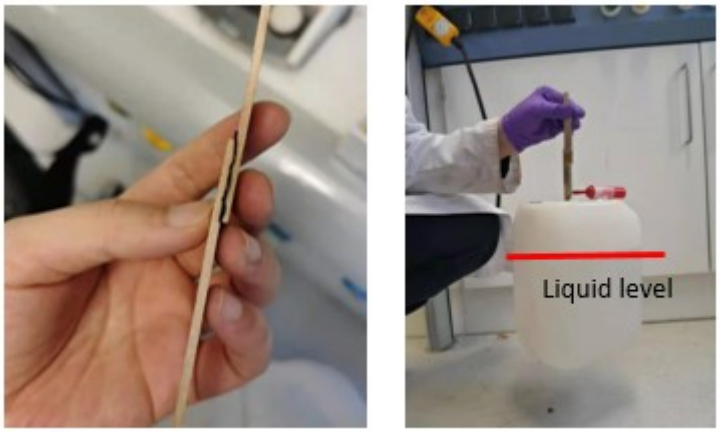

Fig. S18† Photos of shear test samples

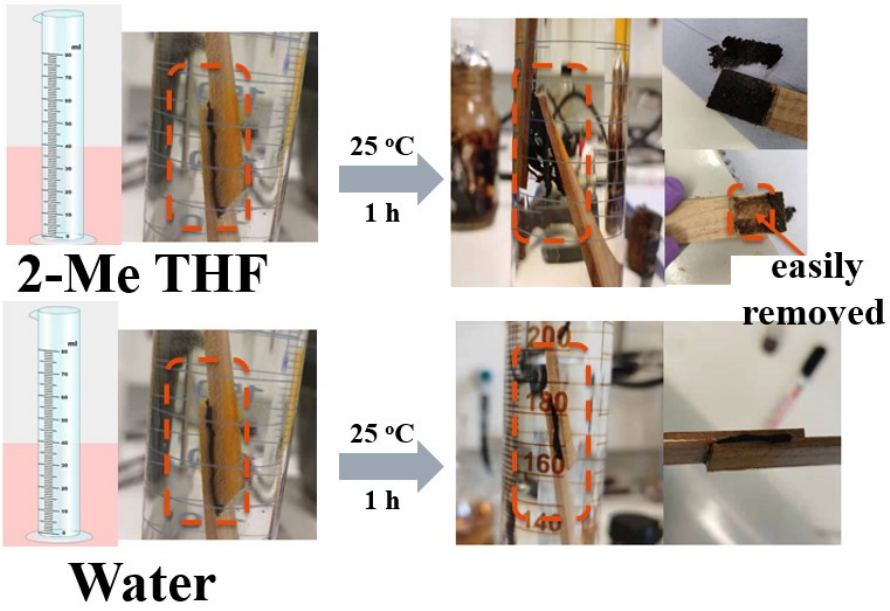

Fig. S19† Solvent removal of adhesives at room temperature.

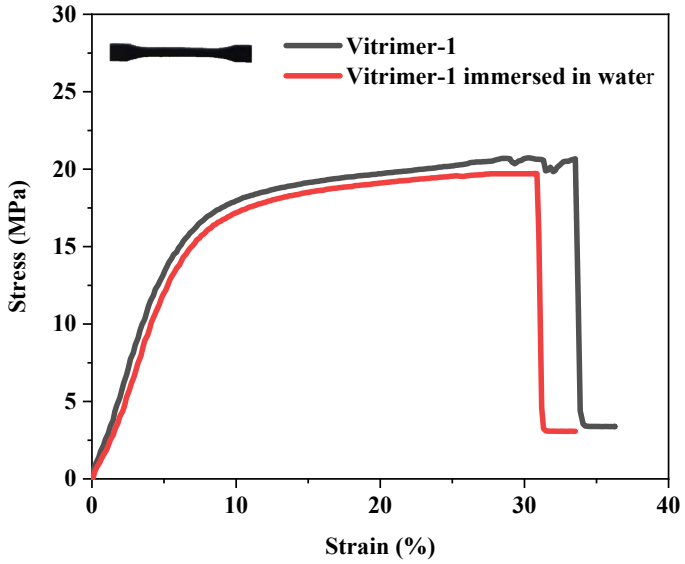

Fig. S20† Tensile test curves of materials in different solvents.

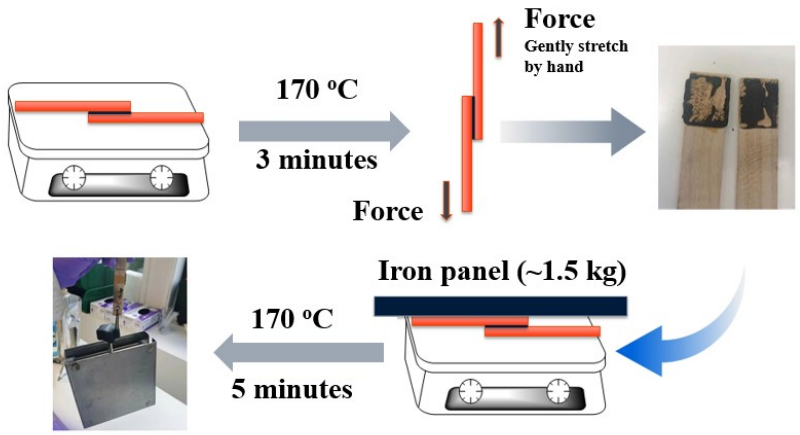

Fig. S21† Heat removal of adhesives at 170 °C.

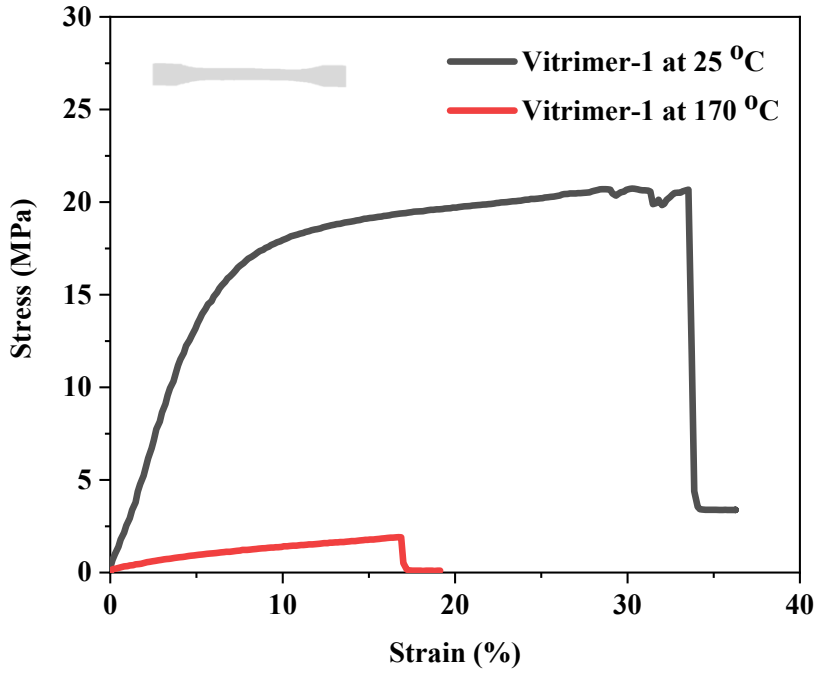

Fig. S22† Tensile test curves of materials at different temperatures.

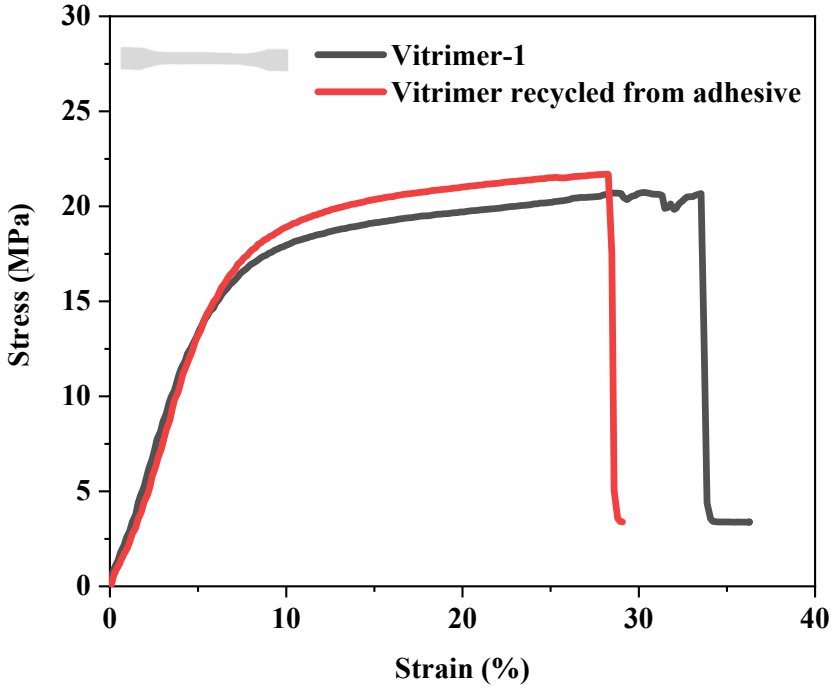

Fig. S23† Comparison of tensile test curves of free standing film materials before and after recycling.

Calculations for stress relaxation derived activation energy

Equation obtained from Arrhenius law: $y = 16.058x - 33.261$ ($R^2 = 0.9981$)

Which corresponds to $\ln(\tau^*) = 16.058 * 1000/T - 33.261$

The Arrhenius law related to the activation energy is $\tau^* = \tau_0 \exp(E_a/RT)$ ($R = 8.314$)

Therefore: $\ln(\tau^*) = \ln(\tau_0) + E_a/RT$

Identifying this to the experimental equation: $E_a/R = 16.058 * 1000$

$E_a = 16.058 * 1000 * 8.314 = 130.5$ kJ/mol

Table S1. Comparison of this work with conventional adhesives.

Case	Vitrimer adhesive **This work**	Thermosetting adhesive e.g. phenol formaldehyde	Thermoplastic adhesive e.g. poly(ethylene-vinyl acetate) (PEVA)
Adhesive state	**Solid**	Liquid	Solid
Bonding method	**Heating**	Heating	Heating
Melting properties	**No**	No	Yes
Solubility in solvent	**No**	No	Yes
Rebonding properties	**Yes**	No	Yes
Removal properties	**Yes**	No	Yes

References

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