

**Supplementary Materials to:**  
**Recycling of Vitriimer Blends with Tunable Thermomechanical**  
**Properties**

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**1. Synthesis of Vitrimers**

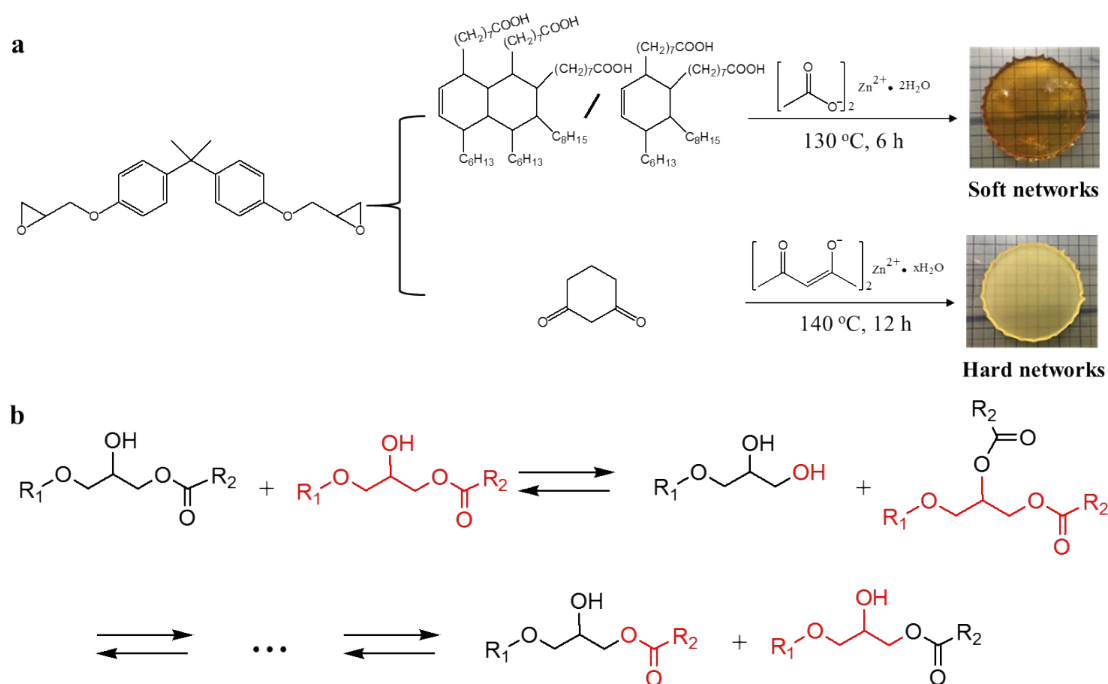
All the chemical products are commercially available and were used as received without further purification. Pripol 1040, a mixture of C18 fatty acids derivatives containing about 23 wt.% dimers and 77 wt.% trimers, was kindly provided by Uniqema (Singapore). Diglycidyl ether of bisphenol A (DGEBA), zinc acetate dihydrate ( $\text{Zn}(\text{Ac})_2 \cdot 2 \text{H}_2\text{O}$ ), zinc acetylacetonate and glutaric anhydride were purchased from Sigma Aldrich, Singapore.

Soft networks were prepared from the reaction of fatty acids (Pripol 1040) with DGEBA (Fig. S1a). Firstly, the fatty acids and the catalyst (zinc acetate dihydrate, 5 mol% to the -COOH groups) were mixed in a round-bottom flask at 100 °C. Then the temperature was gradually increased and maintained at 180 °C under vacuum until no gas evolution was observed and catalyst particles were fully solubilized (~2 h). DGEBA under melt state was introduced into the above mixture and manually stirred at 130 °C until the solution became homogeneous and translucent where the molar ration between -COOH and epoxy is 1:1. Then the resulting mixture was quickly poured into a Teflon mold with a Teflon film cover, and placed into an oven for 6 h at 130 °C.

Hard networks were obtained by the reaction between DGEBA and glutaric anhydride with zinc acetylacetonate dihydrate as catalyst where the stoichiometry between epoxy and anhydride is 1: 0.5. Zinc catalyst corresponding to 5% epoxy equivalents was first mixed with DGEBA by heating at around 130 °C for 10 min, followed by adding the anhydride (Fig. S1a). The resulting miscible mixture was poured into a Teflon mold and cured at 140 °C for 12 h.

The generated two vitrimer materials are transesterification based with different glass transition temperature. [1, 2] During the transesterification, new ester and new hydroxyl

groups are generated from the reaction between existing ester and hydroxyl groups where the dynamic covalent bonds evolve simultaneous breaking and reconnecting (Fig. S1b).



**Figure S1.** Synthesis of vitrimers used in this study (a) and a scheme of reversible transesterification (b).

## 2 Computational Modeling

### 2.1 Thermoviscoelastic model for the pure vitrimer

For the pure vitrimers with hard or soft network, a multibranch thermoviscoelastic model was employed where one equilibrium branch and several thermoviscoelastic nonequilibrium branches were arranged in parallel (Fig. 1a) [3]. The stress relaxation behavior was described by the Maxwell elements in the nonequilibrium branches where a spring and a dashpot were in series connected. The total stress can be calculated as

$$\sigma = E_{eq}e + \sum_{m=1}^n E_{non}^m \int_0^t (\partial e / \partial s) \exp \left[ - \int_s^t dt' / [\tau_m(T)] \right] ds ,$$

where  $E_{eq}$  is the elastic modulus of the equilibrium branch,  $E_{non}^m$  and  $\tau_m$  are the elastic modulus and temperature dependent relaxation time of the  $m^{th}$  nonequilibrium branch,  $e$  is the mechanical strain. The relaxation time  $\tau_m(T)$  of each dashpot at any predefined temperature could be determined based on time-temperature superposition principle (TTSP) by calculating the product of shift factor  $\alpha^{shift}(T)$  and its relaxation time at reference temperature  $\tau_m^R$  as

$$\tau_m(T) = \alpha^{shift}(T) \tau_m^R .$$

The shift factor could be determined by the Williams-Landel-Ferry (WLF) equation [4] or the Arrhenius-type equation [5] depending on whether the temperatures  $T$  is above or below the reference temperature  $T_{ref}$ . For the case of  $T > T_{ref}$ , the shifting factor can be calculated by the WLF equation as

$$\log_{10} [a^{shift}(T)] = -C_1 (T - T_{ref}) / [C_2 + (T - T_{ref})], T > T_{ref} ,$$

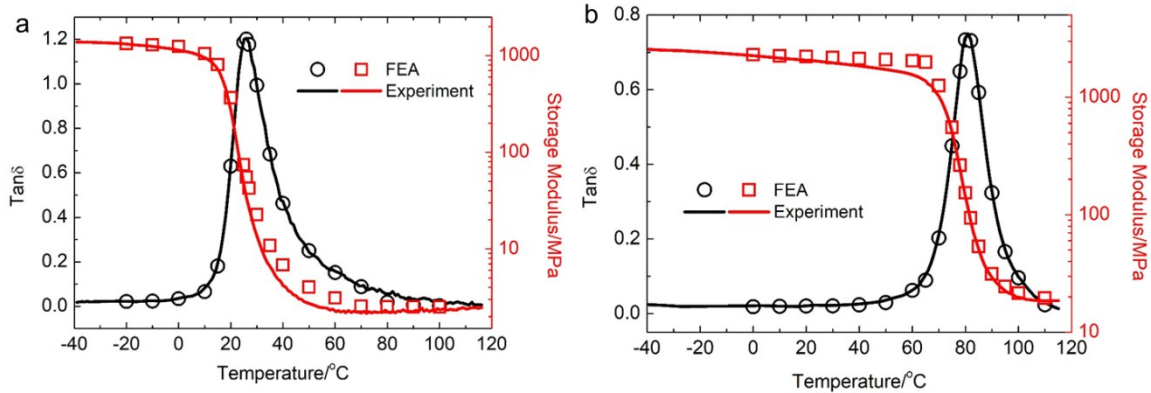
where  $C_1$ ,  $C_2$  and  $T_{ref}$  are the material parameters to be determined. For the case of  $T < T_{ref}$ , the shifting factor can be calculated by Arrhenius-type equation as

$$\ln[a^{shift}(T)] = -AF_c/k \cdot (1/T - 1/T_{ref}), T < T_{ref},$$

where  $A$ ,  $F_c$  and  $k$  are the material constant, configurational energy, and Boltzmann's constant, respectively.

The DMA test results of temperature-dependent storage modulus and loss factor ( $\tan\delta$ ) were employed to identify the material parameters by using the nonlinear regression (NLREG) method [6]. For more details regarding the multibranch model and corresponding material parameter characterization method, readers can refer to [7]. The characterized material parameters for the hard and soft vitrimer can be found in the Supplementary Materials (Table S1).

## 2.2 Finite element simulations

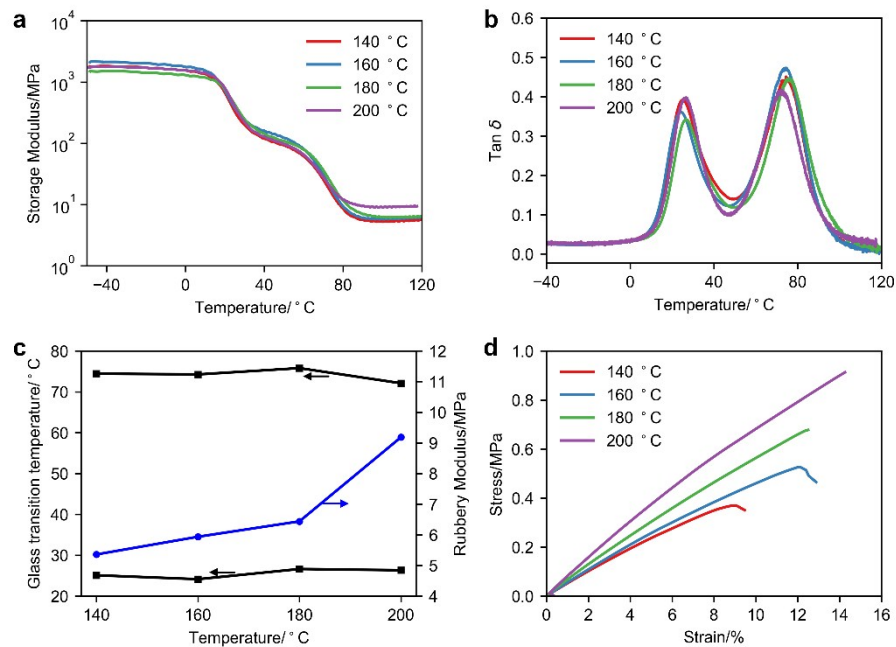


**Figure S2.** Storage modulus and  $\tan\delta$  of soft and hard epoxies (a and b) as a function of temperature. Solid lines illustrate experimental results and dash lines denote the prediction by using finite element (FE) simulations.

## 3. Effect of treating temperature

To study the effect of heating temperature, the mixed vitrimer powders (Soft: Hard=1:1) were thermally treated for 2 h under a controlled pressure of 16 MPa at 140 °C,

160 °C, 180 °C and 200 °C, respectively. Similar to the previous case controlling the heating time, the heating temperature also barely affects the glass transition temperatures of the vitrimer blends (Fig. S3a-c). However, the rubbery modulus gradually increased from 5.2 MPa to 9.2 MPa when the thermal treating temperature varied from 140 °C to 200 °C, which reveals the enhancement of interface bonding with treating temperature. This could also be confirmed from the uniaxial tension results shown in Fig. S3d that both Young's modulus and break strain of the vitrimer blends at rubbery state gradually increase from 4.6MPa and 9% to 6.4 MPa and 14% when the thermal treatment temperature increases from 140 °C to 200 °C.



**Figure S3.** Effect of heating temperature on thermomechanical performance of recycled vitrimer blends. Storage modulus (a) and  $\tan\delta$  (b) as a function of temperature. (c) The effect of heating temperature on glass transition temperature and rubbery modulus. (d) Strain-stress behavior of recycled materials with 50 % of hard network at high temperature (rubbery state). All the samples were prepared by mixing 50% of soft network and 50%

*hard network polymer powders resulting from the utilization of 0.5 mm trapezoidal perforation sieve rings under the same controlled pressure for 2 h.*

**Table S1** Multi-branch model parameters of the base materials.

Branch	Hard epoxy		Soft Epoxy	
	$E_{non}^m$ (Pa)	$\tau_m^R$ (s)	$E_{non}^m$ (Pa)	$\tau_m^R$ (s)
1	132239765.00	2.00E-08	64567404	2.00E-06
2	66873322.40	3.69E-07	54363567.6	0.0001
3	77107465.80	3.46E-06	24930358.7	0.000984641
4	77424006.30	4.53E-05	39429196.8	0.003584918
5	81428324.70	0.000757574	63394962.1	0.047476914
6	76693348.00	0.01	140856791	0.550618278
7	10.00	0.1	93646422.7	10
8	337349777.00	0.240560449	55144806.1	25.72054
9	257295428.00	2	57900723.4	69.5397871
10	225525527.00	9.68970711	114407039	208.240547
11	180718468.00	33.9636354	181993240	799.680574
12	171804570.00	88.2348799	245907176	3037.60726
13	212674786.00	272.429878	162848723	10000
14	186405023.00	840.435276	68831915.6	28485.0772
15	183346151.00	2650.01774	33582521.4	91936.9122
16	121976875.00	9476.41625	14921074.1	418493.137
17	57230280.70	53613.6628	2602216.12	8492087.35
18	41825070.90	20000	6840264.03	2000000
19	12399142.10	639054.077	1606586.71	28404183.7
20	26372070.20	202561.526	1298391.71	10000000
21	8773527.12	2129341.98	999927.987	695774986



22	5683777.83	10000000	687604.712	1.00E+10
23	3209143.93	75830700.6		
24	1730592.19	749304252		
$C1$	20		20	
$C2$	42		49	
$T_{ref}(^{\circ}\text{C})$	65		6	
$AF_c/k$	-13000		-18000	
$E_{eq}(\text{Pa})$	18600000		2400000	

## Reference

[1] D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, *Science*, 2011, **334**, 965-968.

[2] M. Capelot, D. Montarnal, F. Tournilhac and L. Leibler, *J. Am. Chem. Soc.*, 2012, **134**, 7664-7667.

[3] K. Yu, Q. Ge and H. J. Qi, *Nat. Commun.*, 2014, **5**, 3066.

[4] M. L. Williams, R. F. Landel and J. D. Ferry, *J. Am. Chem. Soc.*, 1955, **77**, 3701-3707.

[5] E. A. Di Marzio and A. J. Yang, *J. Res. Natl. Inst. Stan.*, 1997, **102**, 135.

[6] P. Sherrod, Phillip H. Sherrod, Nashville, TN Available: <http://www.nlreg.com/index.htm>, 2015.

[7] C. Yuan, Z. Ding, T. Wang, M. L. Dunn and H. J. Qi, *Smart Mater. Struct.*, 2017, **26**, 105027.