Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Shape memory epoxy vitrimers based on DGEBA crosslinked with dicarboxylic acids and their blends with citric acid

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1. Formulations used to obtain the polymers

Table S1 shows the amount of each reagent needed for a typical synthesis of every vitrimer analyzed in this manuscript.

Table S1. Formulations used to synthesize the epoxy-acid vitrimers.

Label	**DGEBA**		**CA.H_2O**		**SA**		**GA**		**1MI**		**R**
	g	meq	g	meq	g	meq	g	meq	g	mmol	
CS11	4.0	23.0	0.731	10.4	1.055	10.4	0	0	0.0944	1.15	1.1
S12	4.0	23.0	0	0	1.935	19.2	0	0	0.0944	1.15	1.2
S15	4.0	23.0	0	0	1.548	15.3	0	0	0.0944	1.15	1.5
S20	4.0	23.0	0	0	1.161	11.5	0	0	0.0944	1.15	2.0
G15	4.0	23.0	0	0	0	0	1.011	15.3	0.0944	1.15	1.5

2. Calculation of the shape fixity and recovery ratios

The parameters used to evaluate the shape memory performance are shape fixity (R_f) and shape recovery (R_r) ratios. R_f and R_r are defined as follows for each cycle (N):

$$\boldsymbol{R_f(N) = \frac{\gamma_{unloaded}(N) - \gamma_{permanent}(N)}{\gamma_{max}(N) - \gamma_{permanent}(N)} . 100\%} \quad \text{(Eq. S1)}$$

$$\boldsymbol{R_r(N) = \frac{\gamma_{max}(N) - \gamma_{permanent}(N)}{\gamma_{max}(N) - \gamma_{permanent}(N-1)} . 100\%} \quad \text{(Eq. S2)}$$

where γ_{max} and $\gamma_{unloaded}$ are the strain values in the temporary form under stress at 100ºC, and after releasing the stress at room temperature; $\gamma_{permanent}$ is the strain value measured at 100ºC when no stress is applied.

Figure S1 shows schematically the values used to calculate R_f and R_r for the Nth cycle of a shape memory test.

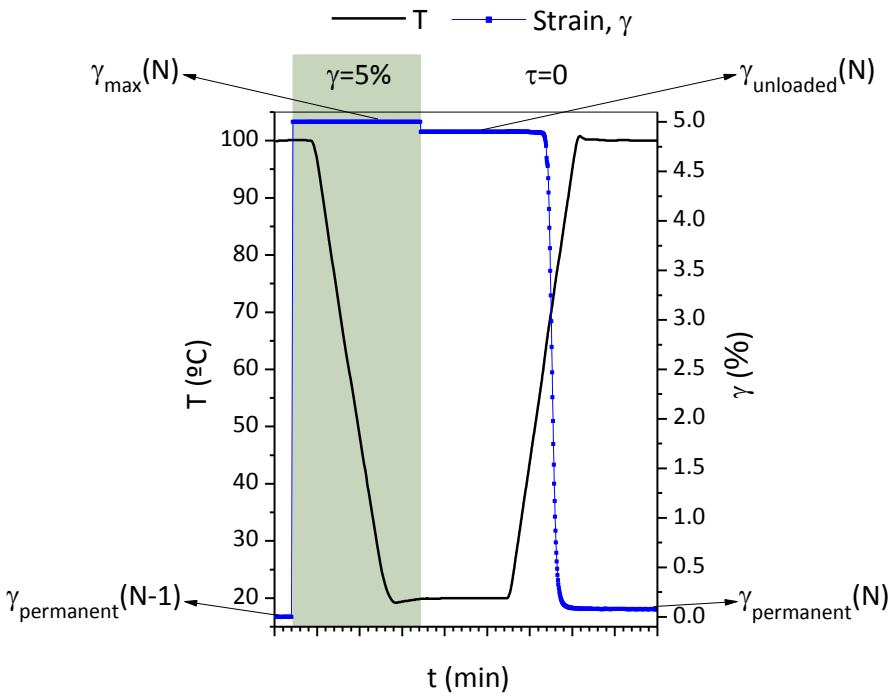

Figure S1. Schematic temperature- and deformation-time curves for the Nth-cycle in a shape memory test.

3. Network parameters of the epoxy-acid-imidazole vitrimers

Table S2 summarizes important network parameters that are useful to explain some of their properties. Assuming that all the vitrimers have similar densities, it can be stated that the trends in mass concentrations (expressed in mmol/g) will hold when expressed as volume concentration (mmol/cm^3).

Table S2. 1MI, phenyl groups and -OH mass concentration in the epoxy-acid vitrimers.

Label	M_{tot}	1MI		Phenyl	-OH	**[1MI]**	**[Phenyl]**	**[-OH]**
	g	g	mmol	mmol	mmol	**mmol/g**	**mmol/g**	**mmol/g**
CS11	5.880	0.0944	1.15	23.64	24.59	0.196	4.02	4.18
S12	6.029	0.0944	1.15	23.64	19.52	0.191	3.92	3.24
S15	5.642	0.0944	1.15	23.64	15.62	0.204	4.19	2.77
S20	5.255	0.0944	1.15	23.64	11.82	0.219	4.50	2.25
G15	5.105	0.0944	1.15	23.64	15.62	0.225	4.63	3.06

4. Calculation of activation energy for the transesterification reaction

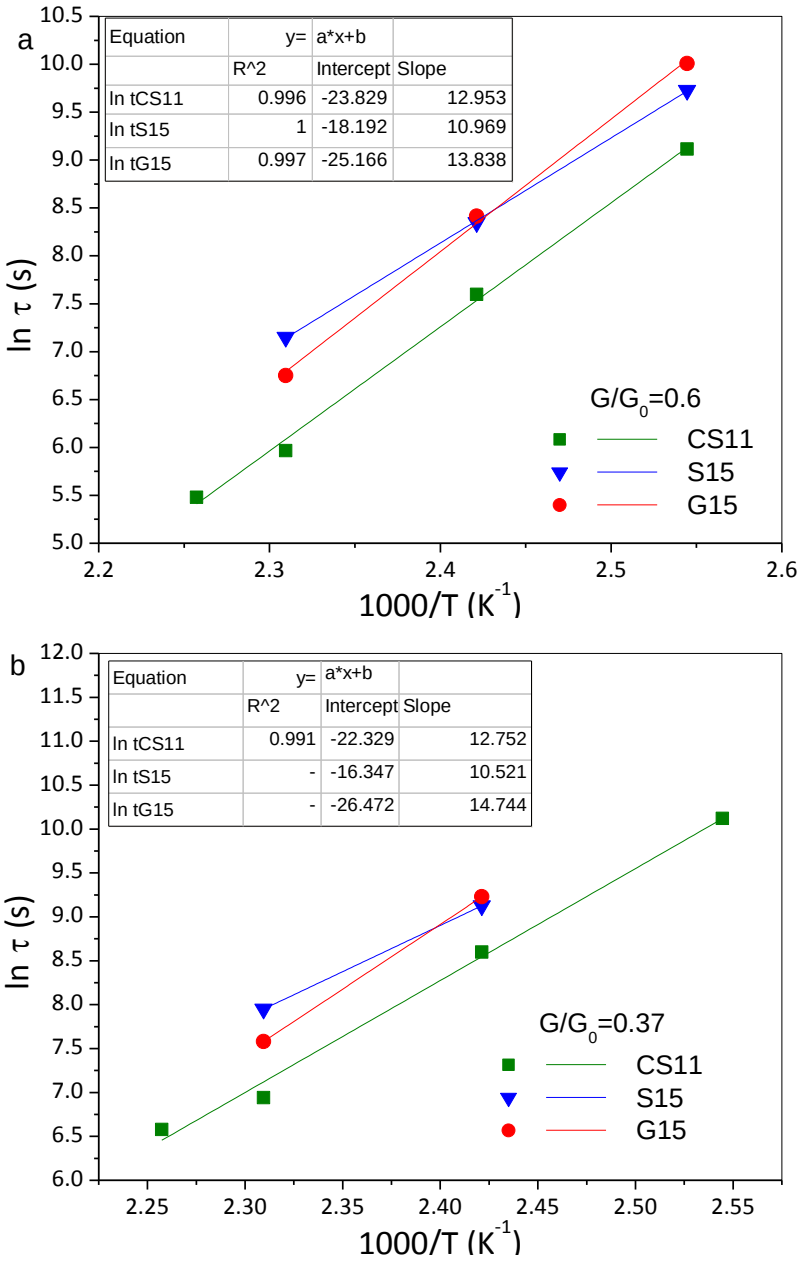

Figure S2. ln τ vs 1000/T for 40% (a) and 63% (b) relaxation for CS11, S15 and G15 vitrimers, and the corresponding fitting to Eq. 1.

The temperature of topology freezing (T_v) was defined as the temperature at which the vitrimer takes 1 day (86400 s) to achieve a stress relaxation of 63%. From the extrapolation of the experimental data fitting for G/G_0 = 0.37 (Figure S2b), T_v values of 105ºC, 107ºC and 117ºC were obtained for CS11, S15 and G15 respectively.