Vanillin-based dual dynamic epoxy building block: a promising accelerator for disulfide vitrimers

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Supporting Information

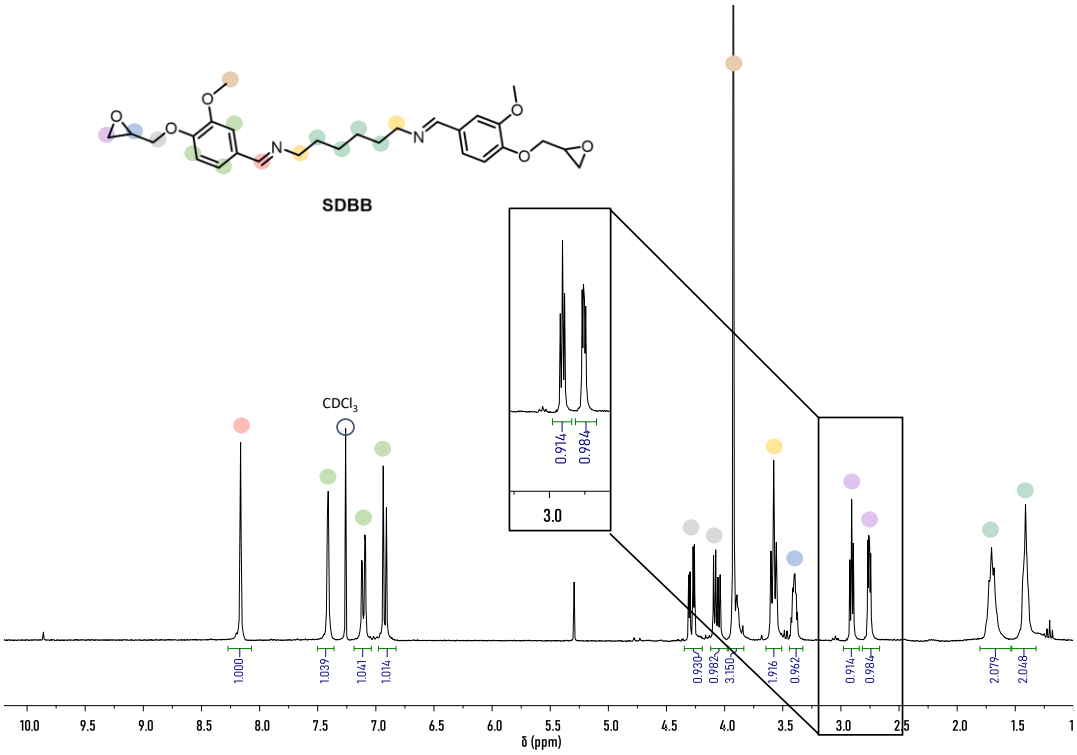

Figure S1. Quantitative ^{1}H NMR spectrum of SDBB in $CDCl_3$ at 25 °C

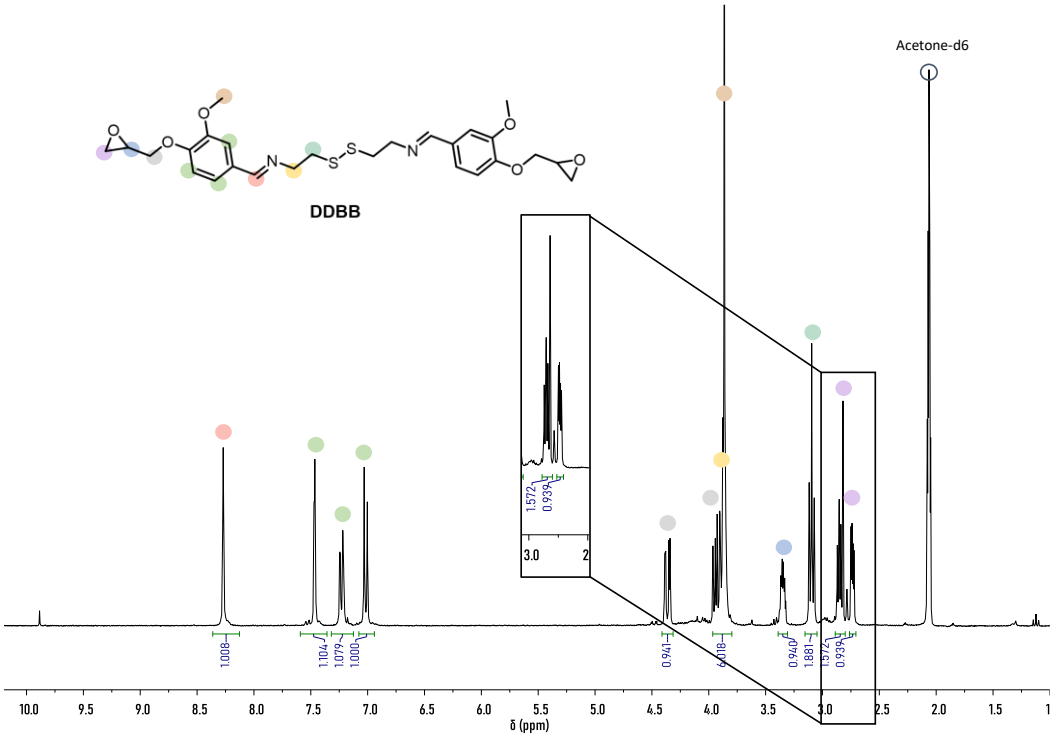

Figure S2. Quantitative ^{1}H NMR spectrum of DDBB in Acetone-d6 at 25 °C

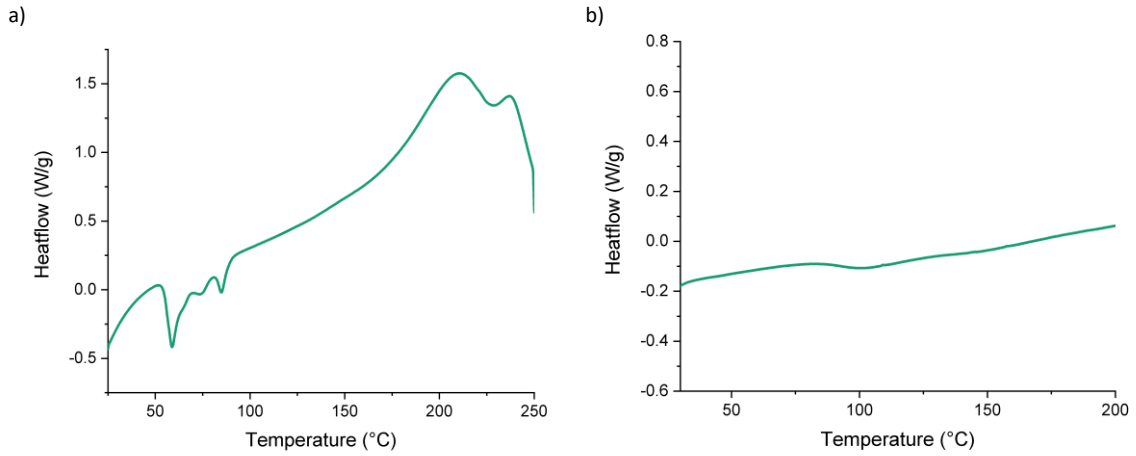

Figure S3. a) DSC thermograms obtained at heating rate of 10°C min^{-1} for DDBB b) and second heating cycle

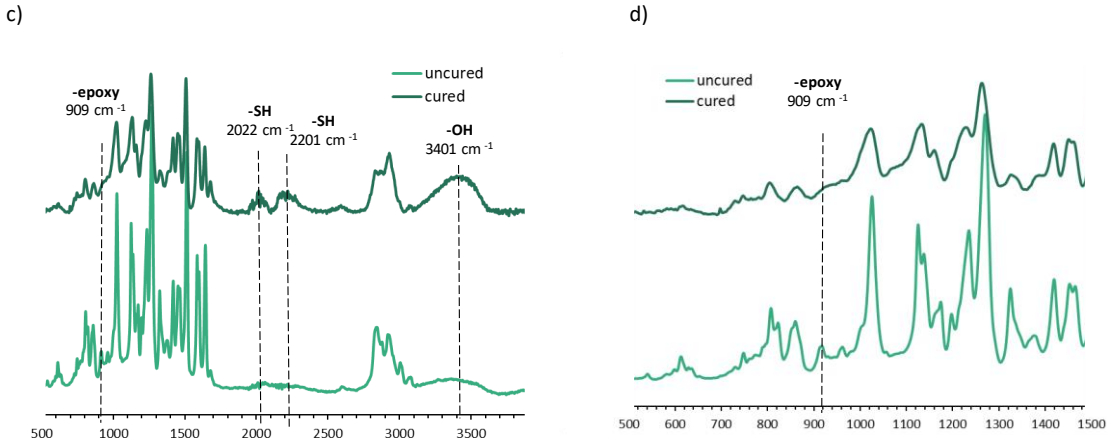

Figure S4. c) Full view of FTIR spectra of cured and uncured DDBB and d) FTIR zoom from 500 to 1500cm^{-1} of cured and uncured DDBB

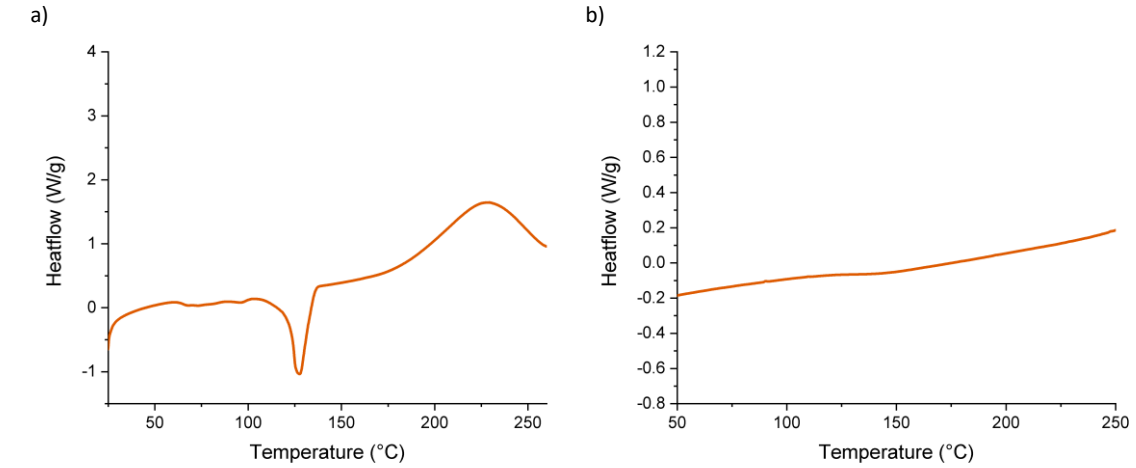

Figure S5. a) DSC thermograms obtained at heating rate of 10°C min^{-1} for SDBB b) and second heating cycle

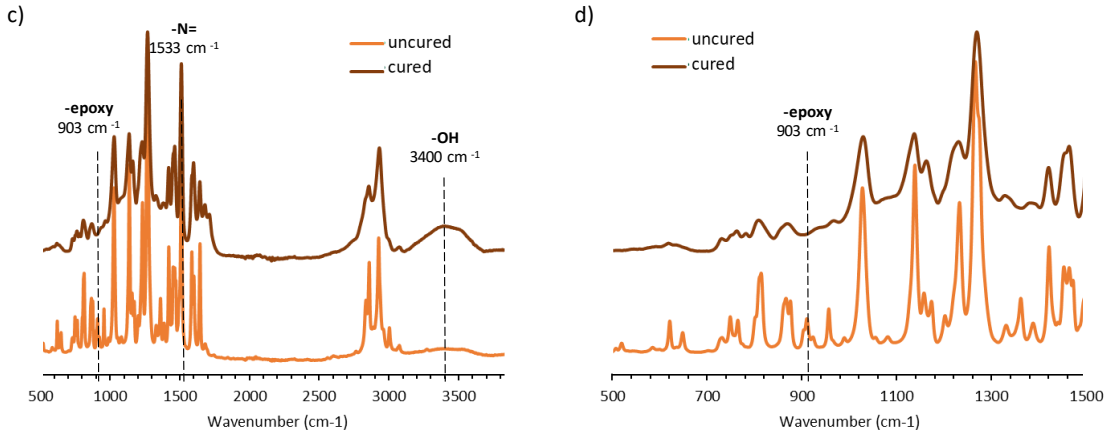

Figure S6. c) Full view of FTIR spectra of cured and uncured SDBB and d) FTIR zoom from 500 to 1500cm^{-1} of cured and uncured SDBB

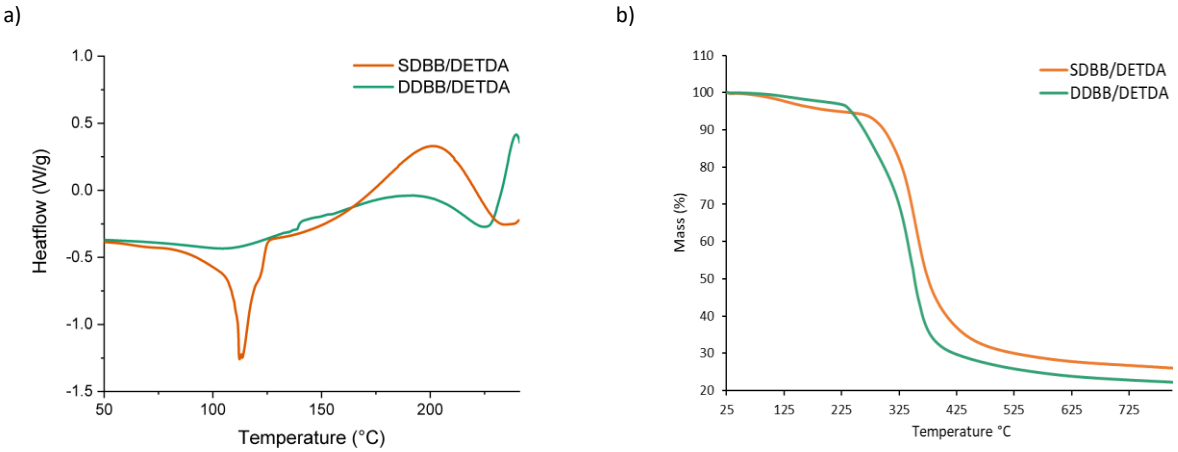

Figure S7. a) DSC thermograms obtained at a heating rate of 10 °C min^{-1} for SDBB/DETDA and DDBB/DETDA formulations (b) Thermogravimetric experiments of both materials

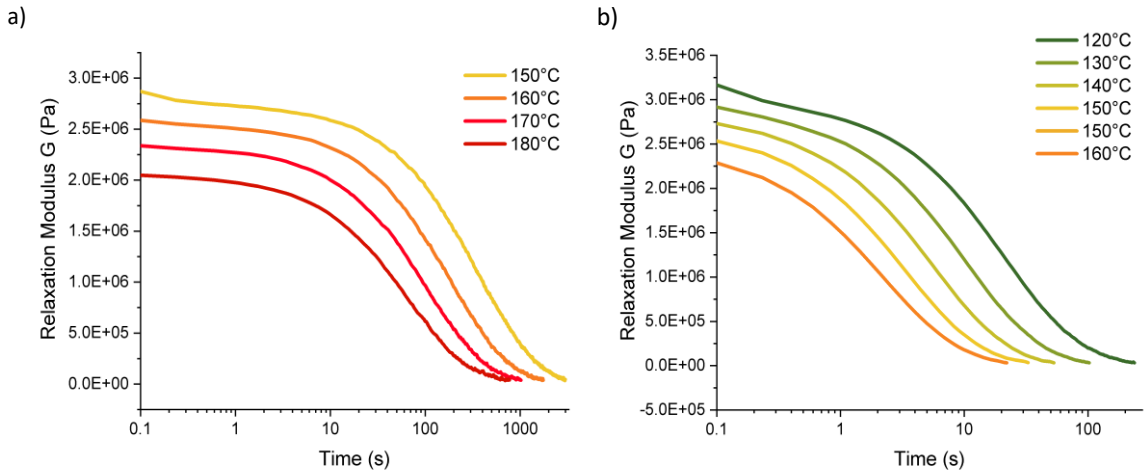

Figure S8. Non-normalized stress relaxation experiments of (a) SDBB/DETDA at different temperatures above T_g in a range of 150°C to 180°C and (b) DDBB/DETDA in a range of 120°C to 160°C.

Table S1. Stretched exponential fitting of a) DDBB/DETDA stress relaxation curves and b) SDBB/DETDA curves at different temperatures above the T_g in a range of 120°C to 180°C.

	DDBB/DETDA					SDBB/DETDA				
T	G_{res}/G_0	τ*	< τ>	β	R^2	G_{res}/G_0	τ*	< τ>	β	R^2
(°C)		(s)	(s)				(s)	(s)		
120	0.002	22.29	27.84	0.71	0.99	-	-	-	-	-
130	0.014	11.44	13.22	0.78	0.99	-	-	-	-	-
140	0.016	6.42	7.23	0.81	0.99	-	-	-	-	-
150	0.022	3.94	4.28	0.85	0.99	0.002	379	486.5	0.69	0.99
160	0.025	2.72	2.94	0.86	0.99	0.012	197	237.2	0.74	0.99
170	-	-	-	-	-	0.017	115	136.9	0.75	0.99
180	-	-	-	-	-	0.023	73	86	0.76	0.99

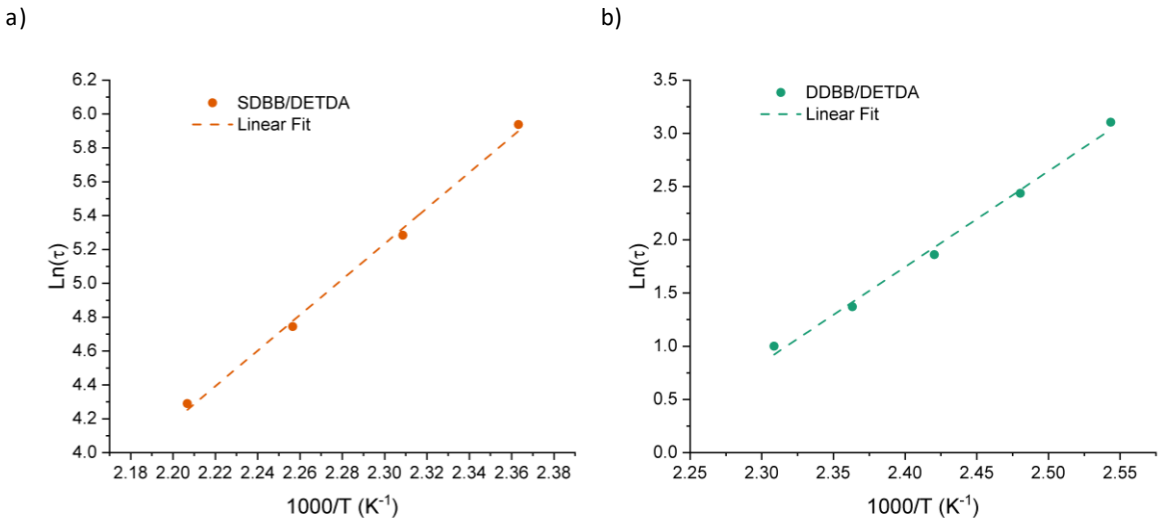

Figure S9. Arrhenius dependency of a) SDBB/DETDA (orange) and b) DDBB/DETDA (green).

Table S2. Thermomechanical properties of SDBB/DETDA and DDBB/DETDA formulations

Name	Cristalline free	T_{onset}	T_g (DSC)	T_d[a]	$<\tau>$ [b]	slope[c]	E_a
	-	°C	°C	°C	s		kJ/mol
SDBB/DETDA	No	120	129	215	237.2	10.52	87.4
DDBB/DETDA	No	107	78	241	2.94	9.00	74.8

[a] T_d determined at 5w/w% of loss

[b] $<\tau>$ determined at 160°C

[c] Slope calculated from Arrhenius linear fitting of Fig. S9

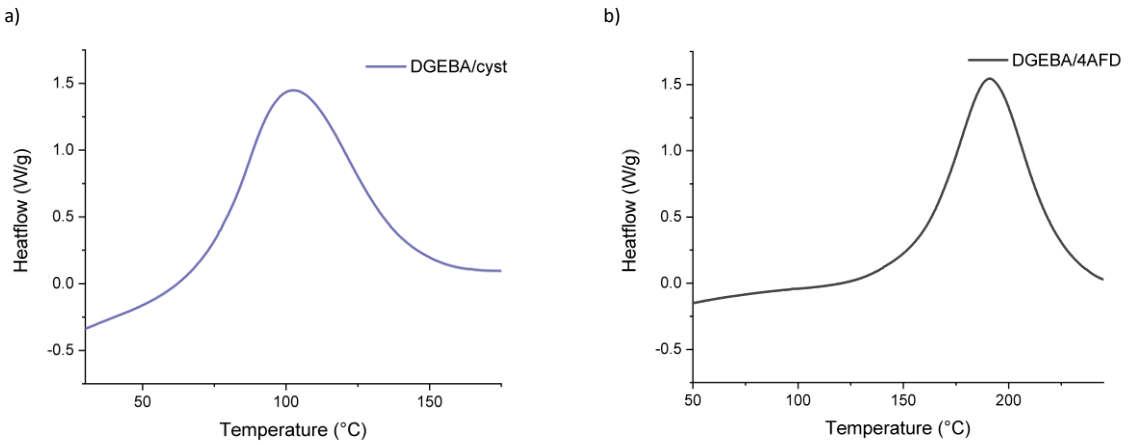

Figure S10. a) DSC thermograms of the first heating cycle obtained at heating rate of 10°C min^{-1} for DGEBA/cystamine and b) DGEBA/4AFD

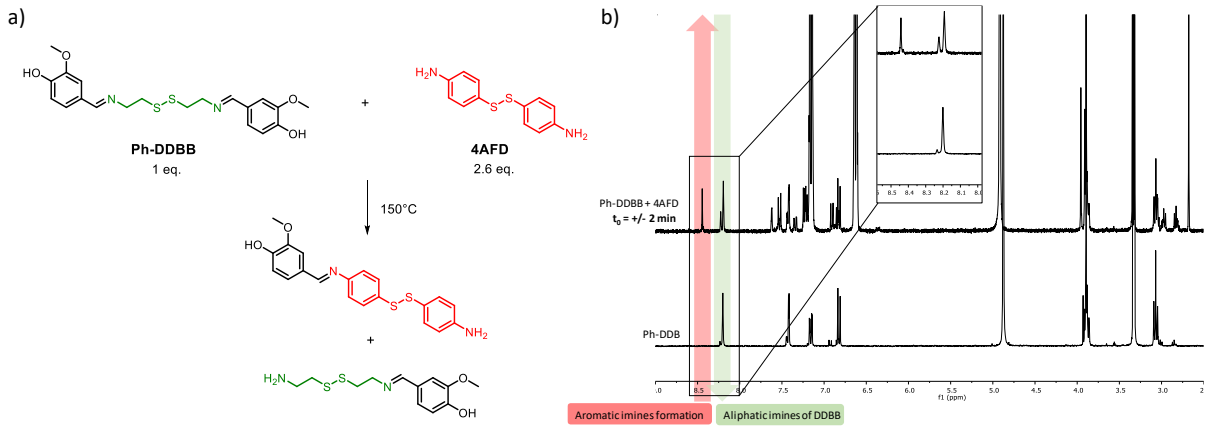

Figure S11. a) Model reaction describing the exchange between the imine of ph-DDBB and 4AFD. b) Comparison between ^{1}H NMR of the model reaction at t=t_0 at 150°C and ^{1}H NMR spectra of Ph-DDBB

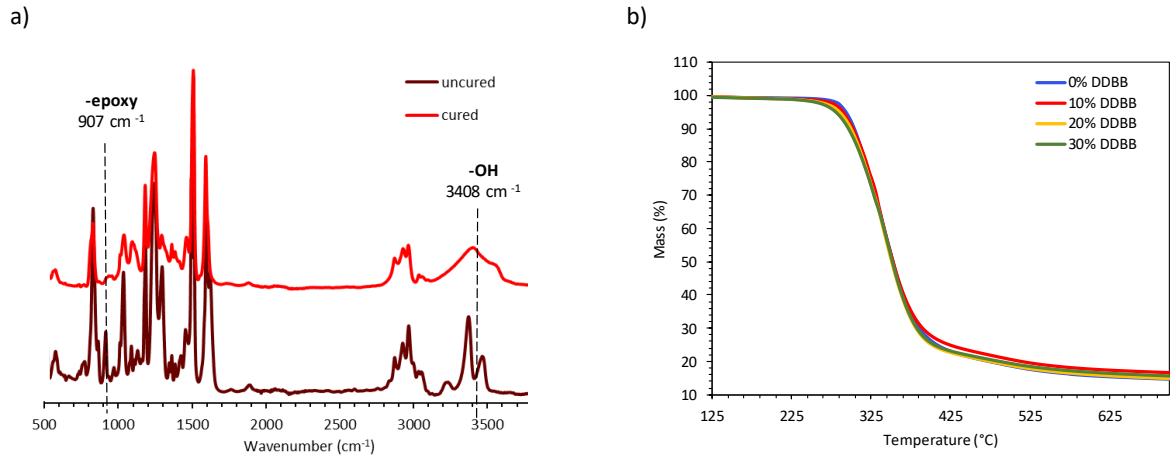

Figure S12. a) Full view FTIR analysis of $DDBB_{0.10}DGEBA_{0.90}$/4AFD and b) thermogravimetric analysis of $DDBB_xDGEBA_y$/4AFD

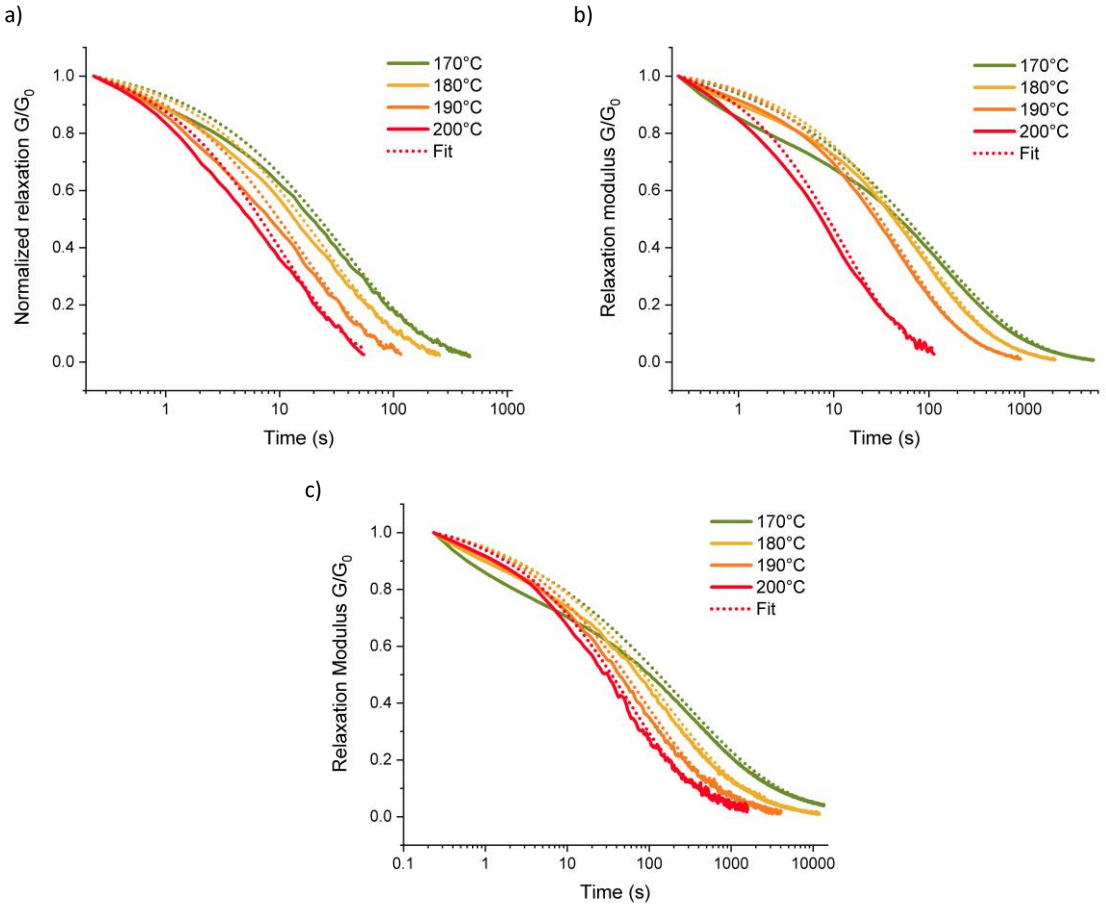

Figure S13. Normalized stress relaxation curves of $DDBB_xDGEBA_y$/4AFD formulations a) $DDBB_{0.30}DGEBA_{0.70}$/4AFD b) $DDBB_{0.20}DGEBA_{0.80}$/4AFD c) $DDBB_{0.10}DGEBA_{0.90}$/4AFD

Table S3. Table of experimental results after fitting with the KWW model

T	$DDBB_{0.10}DGEBA_{0.90}$/4AFD					$DDBB_{0.20}DGEBA_{0.80}$/4AFD					$DDBB_{0.30}DGEBA_{0.70}$/4AFD				
	G_{res}/G_0	τ*	< τ>	β	R^2	G_{res}/G_0	τ*	< τ>	β	R^2	G_{res}/G_0	τ*	< τ>	β	R^2
(°C)		(s)	(s)				(s)	(s)				(s)	(s)		
170	0.02	243	1354.8	0.34	0.99	0.0004	109	318.4	0.42	0.99	0.01	40	64.6	0.57	0.99
180	0.02	159	464.5	0.42	0.99	0.001	83	149.9	0.53	0.99	0.02	24	34.6	0.62	0.99
190	0.02	88	198.6	0.47	0.99	0.002	50	76.9	0.59	0.99	0.02	15	21.2	0.63	0.99
200	0.03	54	100.7	0.52	0.99	0.034	22	29.6	0.66	0.99	0.03	11	15.3	0.64	0.99

Table S4. Swelling experiments for $DDBB_xDGEBA_y$/4AFD formulations

Resin	Ratios		Swelling ratio % (Sf)				Soluble fraction % (Sr)			
	DDBB	DGEBA	$CHCl_3$	DMF	DMSO	THF	$CHCl_3$	DMF	DMSO	THF
1	10	90	79	114	139	125	5,5	4,3	0,8	0,2
2	20	80	27	290	240	50	4,2	4,5	0,03	0,05
3	30	70	61	337	328	62	2,3	3,7	0,002	0,007

The soluble fraction and swelling ratio were calculated according to the following equations:

$$Sf = \frac{mi - md}{mi} \, x \, 100$$

$$Sr = \frac{ms - mi}{mi} \, x \, 100$$

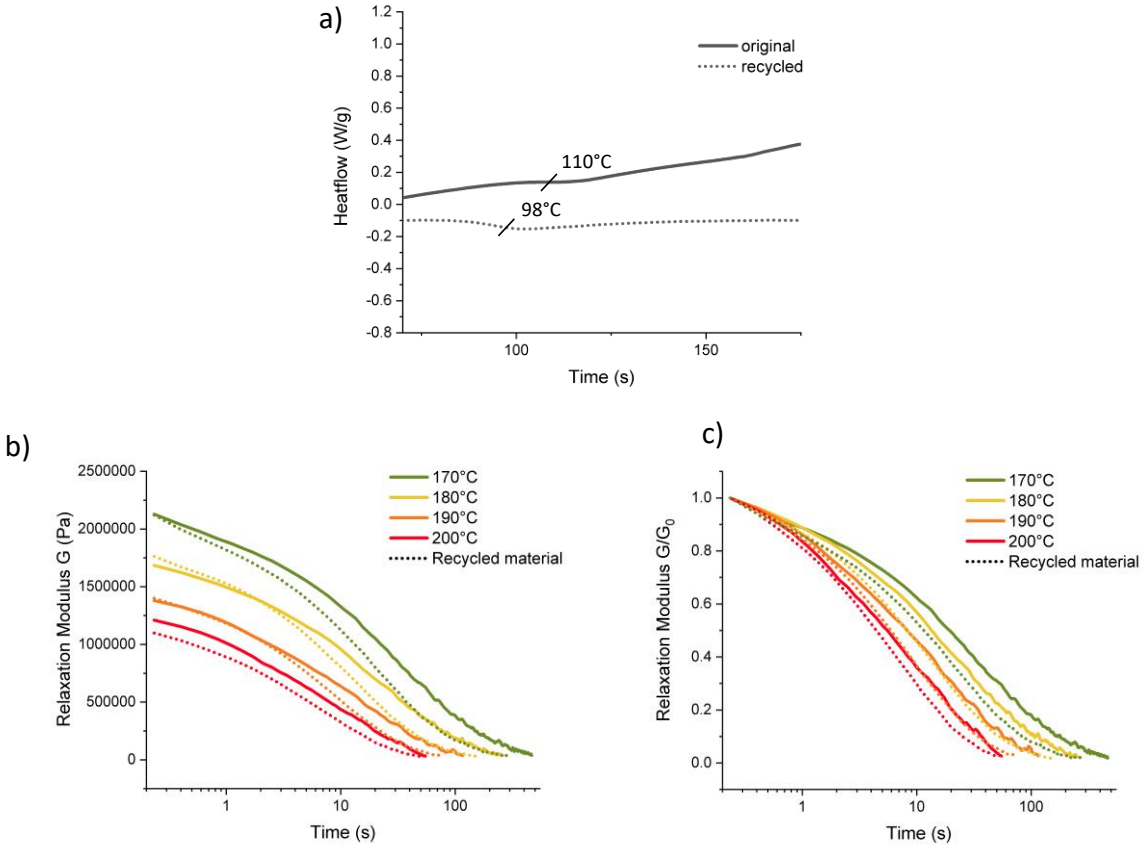

Figure S14. a) DSC thermograms obtained at heating rate of 10°C min^{-1} for reprocessed $DDBB_{0.30}DGEBA_{0.70}$/4AFD b) non-Normalized and c) normalized stress relaxation curves of $DDBB_{0.30}DGEBA_{0.70}$/4AFD