Supporting Information

Adhesion and stiffness matching in epoxyvitrimers/strain sensor fiber laminates

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S1. Experimental methods

Supramolecular Prepolymer liquid precursor (SP50) preparation (1.2)

The liquid precursor, SP50 with a target conversion of 50 mol % of acid into amide, was synthesized as already reported ¹ by reacting Pripol 1040 (100 g, 338 mmol of COOH) and UDETA (21.8 g, 169 mmol of NH₂) in a 500 mL thermostated reactor equipped with a nitrogen inlet, a stirring system, and a bottom valve. The reactions were carried out for 3 h at 160 °C under nitrogen flow. The resulting material was collected as viscous oil through the bottom valve at 160 °C. After each synthesis, the actual conversion (close to 50 %) of carboxylic acids into amides was measured using the CH₂–CONH and CH₂–COOH signals from ¹H NMR spectra at 2.15 and 2.30 ppm, respectively.

Hybrid network synthesis (1.3)

The hybrid networks *x*D-(100-*x*)T_*n*epoxy were synthesized in the form of flat sheets. Desired quantities of DGEBA, TGMDA and supramolecular polymer precursor SP50 were introduced in a PTFE beaker, that was heated to 100 °C while mixing with a metallic stirrer until phase miscibility took place. 2-Methylimidazole (2-MI) was then added, and the mixture was stirred for two minutes before casting into a rectangular PTFE mold (an aliquot of the reactive mixture is taken at this point for IR monitoring). After degassing under vacuum, the mold was put in an oven and flushed with an inert atmosphere during curing at 130 °C for 3 h. Table S1 summarizes the hybrid network samples synthesized, with the different molar ratios and total quantities of di-(DGEBA) and tetra-(TGMDA) epoxide introduced. The molar quantity of the total epoxides in the network is shown in the right column. The crosslinking accelerator 2-MI was used at 6 mol %/COOH group for all formulations.

Name	SP50	DGEBA	TGMDA	COOH	Ероху	Ероху	Ероху
	[g]	[g]	[g]	[mmol]	(DGEBA)	(TGMDA)	[mmol]
					[mmol]	[mmol]	
0D-100T	15.00	0	2.358	22.3	0	22.3	22.3
75D-25T_0epoxy	15.00	2.85	0.589	22.3	16.7	5.6	22.3
75D-25T_5epoxy	15.00	2.99	0.619	22.3	17.6	5.9	23.5
75D-25T_10epoxy	15.00	3.13	0.648	22.3	18.4	6.1	24.5
75D-25T_50epoxy	15.00	4.27	0.884	22.3	25.1	8.4	33.5

Table S1. Quantities of reactants for the preparation of hybrid network sheets.

Chemical analysis (1.6)

¹H NMR was performed on a Bruker Avance 400 spectrometer (400 MHz, 298K) using CDCl₃ as solvent. IR measurements were recorded with a Bruker TENSOR 37 spectrometer equipped with a Specac golden gate ATR heating cell at 130 °C under inert atmosphere. During epoxy curing, a spectrum was recorded each minute during 90 min and the peaks were integrated with the intervals (*i*) 1758–1726 cm⁻¹ (ester peak at the C=O stretching peak 1735 cm⁻¹), (*ii*) 1726–1701 cm⁻¹ (carboxylic acid at the C=O stretching peak 1705 cm⁻¹), (*iii*) 1262–1225 cm⁻¹ (ether peak in the region of the alkyl-aryl ether functions) and (*iv*) 930–895 cm⁻¹ (asymptotic epoxy ring deformation at 914 cm⁻¹).

Solubility tests were realized with 15 mm \times 3 mm \times 2 mm samples, swollen in trichlorobenzene (TCB) for 24 h at 150 °C. After swelling, the samples were wiped, left to equilibrate, and weighed. The solvent uptake and swelling were measured using:

solvent uptake [mass %] =
$$\frac{W_s - W_I}{W_I} \times 100$$
 (S1)

where W_I and W_S are the weights before and after swelling, respectively. The samples were then dried under vacuum at 70 °C for 48 h, and the gel content was calculated as follows:

% gel [mass %] =
$$\frac{W_F}{W_I} \times 100$$
 (S2)

where W_I is the initial weight of the samples, while W_F is the one after swelling and drying.

Thermomechanical analyses (1.7)

Differential scanning calorimetry (DSC) was performed at a heating rate of 10 °C.min⁻¹ under helium using a TA DSC Q1000 analyser. Two heating ramps were performed from –50 to 200 °C. The glass transition temperature T_g was determined from the second heating cycle. Dynamic mechanical analysis (DMA) experiments were conducted on Q800 DMA, TA Instruments, in the film tension geometry at a frequency of 1 Hz. Heating ramps from –50 to 200 °C were applied at 3 °C.min⁻¹ to rectangular samples of 6 mm × 5 mm × 2 mm size.

S2. Results and discussion.



Figure S1. a) ATR-FTIR spectrum of 75D-25T_10epoxy before (black curve) and after (red curve) curing. b) Zoom-in on ester (1758-1726 cm⁻¹), carboxylic acid (1726-1701 cm⁻¹), alkyl-aryl ether (1262-1225 cm⁻¹) and epoxy peaks (930-895 cm⁻¹). c) Integration of IR peaks during curing of 75D-25T_10epoxy. d) Integration of alkyl-aryl ether peak (1262-1225 cm⁻¹) for 0D-100T, 75D-25T_0epoxy, 75D-25T_5epoxy, 75D-25T_10epoxy and 75D-25T_50epoxy.

Table S2. Solvent uptake and gel content values after immersion in trichlorobenzene for 24 h at 150 °C.

	Solvent uptake	% gel
	[mass %]	[mass %]
75D-25T_0epoxy	230	70
75D-25T_5epoxy	230	80
75D-25T_10epoxy	230	80
0D-100T	130	85



Figure S2. Swollen samples (from left to right: 75D-25T_0epoxy, 75D-25T_5epoxy, 75D-25T_10epoxy, 0D-100T) after 24 h in trichlorobenzene at 150 °C.



Figure S3. Glass transition temperature T_g of all compositions measured by the second heating cycle in DSC.



Figure S4. a) Storage modulus E' and b) $tan(\delta)$ from -50 to 200 °C for the four matrix compositions.



Figure S5. Creep measurements (applied stress of 0.01 MPa for 45 min, relaxation for 15 min) at 110 °C-160 °C for a) 0D-100T, b) 75D-25T_0epoxy, c) 75D-25T_5epoxy and d) 75D-25T_10epoxy.



Figure S6. Arrhenius plots of the viscosities (data of Figure S5) for the four matrix compositions.



Figure S7. Tensile test until rupture for three samples per composition from different curing sheets.







Figure S9. 75D-25T_0epoxy rectangular sensor fiber sample after rupture of one sheet before delamination.



Figure S10. Representative image of 75D-25T_0epoxy sample after cyclic loading at room temperature with no delamination of matrix sheets.

Variation of α with matrix modulus E_2 (Figure 8b).

The shear stress τ generated all along the interface S_T between fiber and matrix in the shoulder region may be written as the difference of forces Δf applied on the fiber in the narrow (f_1) and large (f_1) parts divided by the interfacial surface S_T in the shoulder region (Figure 9g):

$$\tau = \frac{\Delta f}{S_T} \tag{S3}$$

The overall force *f* applied to the dog-bone bar may be decomposed into partial forces f_1 and f_2 , f_1 and f_2 , applied to the fiber and to the matrix, in both extremities of the shoulder:

$$f = f_1 + f_2 = f'_1 + f'_2$$
(S4)

and the variation Δf expressed as:

$$\Delta f = f_1 - f'_1 = f_2 - f'_2 \tag{S5}$$

Introducing strains ε and ε' in narrow and large parts of the bar, (S5) may be written as:

$$f = S_1 E_1 \varepsilon + S_2 E_2 \varepsilon = S'_1 E_1 \varepsilon' + S'_2 E_2 \varepsilon'$$
(S6)

Assuming the fiber cross-section remains constant during stretching, $S_1 = S'_1$ implies:

$$f = (S_1 E_1 + S_2 E_2)\varepsilon = (S_1 E_1 + S'_2 E_2)\varepsilon'$$
(S7)

and:

$$\Delta f = f_1 - f'_1 = S_1 E_1 \varepsilon - S_1 E_1 \varepsilon' = S_1 E_1 (\varepsilon - \varepsilon')$$
(S8)

Combining (S7) and (S8) leads to:

$$\frac{\Delta f}{f} = S_1 E_1 \left(\frac{1}{S_1 E_1 + S_2 E_2} - \frac{1}{S_1 E_1 + S'_2 E_2} \right) = \alpha$$
(S9)

where α describes the relative variation of the force when the composite sensor is under strain.

References

 Sordo, F.; Mougnier, S.-J.; Loureiro, N.; Tournilhac, F.; Michaud, V. Design of Self-Healing Supramolecular Rubbers with a Tunable Number of Chemical Cross-Links, *Macromolecules* 2015, *48*, 4394–4402. DOI: <u>10.1021/acs.macromol.5b00747</u>