Supporting Information

Closed-loop recycling of bio-based disulfide vitrimer via a solvent- and waste-free strategy

Solène Guggari,[a,b] Fiona Magliozzi,[b] Samuel Malburet,[b] Alain Graillot,[b] Mathias Destarac [a] and Marc Guerre[a]*

[a] Laboratoire SOFTMAT, Université de Toulouse, CNRS UMR 5623, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 9, France
E-mail: marc.guerre@cnrs.fr

[b] SPECIFIC POLYMERS, Zac Via Domitia, 150 Avenue des Cocardières, 34160 Castries, France

Keywords: recycling, vitrimers, cystamine, closed-loop

EXPERIMENTAL SECTION

1.1.Materials

Diglycidyl ether of vanillyl alcohol (DGEVA, SP-9S-5-005, EEW (Epoxy equivalent weight) = 139 g/eq) and cystamine (SP-2-4-001, AHEW (Amine equivalent weight = 38 g/eq) were synthetized and provided by SPECIFIC POLYMERS. DGEVA building block was synthesized through a two-step procedure from vanillin and epychlorohydrin following and already reported protocol[30]. Cystamine was purchased as cystamine dihydrochloride and desalinated following the procedure by Khalafi et al.[31]

1.2. Preparation of epoxy vitrimer DGEVA/cyst

In a typical procedure, the epoxy resin (DGEVA, 1 g) was first melted at 100°C for 10 min to afford a viscous resin, easier to handle. Then, 0.334 g of cystamine was added in a molar epoxy/amine ratio of 1/1.2 and stirred mechanically with a speedmixer for 40 seconds at 2000 rpm at room temperature to afford a homogeneous viscous liquid. The mixture was then cured at 60°C for 1h and at 90 °C for 2h.

1.3. Preparation of fiber reinforced epoxy composites

In the PTFE mold, one layer of a carbon fiber fabric covered with peel ply and sealed in a vacuum bag then the epoxy mixture of DGEVA/cyst was infused into the fibers under vacuum at room temperature. Then, additional epoxy mixture was used to fill the mold completely. The average infusion time for was about 10 mins and after infusion, the composite was placed at 60 ◦C in a vacuum oven for 1h, the composites were then post cured at 90 ◦C for 2h.

1.4. Characterization

FTIR was performed on Thermo Nicolet NEXUS spectrophotometer equipped with an ATR diamond. All samples were analyzed through 16 scans and within a range of 400–4000 cm^{-1} for both cured and uncured states.

DSC was performed on a Mettler Toledo Differential Scanning Calorimeter under a constant nitrogen flow rate (50 ml min^{-1}). The samples of about 6-10 mg were heated from 0 °C to 150 °C at the rate of 10 °C min^{-1} under nitrogen as a purged gas. Tg was determined at the inflection point of the curves measured at a scan rate of 10 ◦ C/min.

DMA experiments were conducted on a METTLER TOLEDO DMA1 in three-point bending. Heating ramps of 3°C/min were applied in air from 25 to 120°C. The samples (20 × 10 ±0.5 × 1.5 ± 0.1 mm^3) were tested at 1 Hz with an applied strain of 5 or 10 µm, depending on their linearity range, and an adapted prestress force of 800 or 950% of the force applied to deform.

Stress-relaxation was conducted on an Anton Paar rheometer using a 8 mm plate-plate geometry on epoxy resin samples with thicknesses of 0.8-0.4 mm. After a 10min temperature equilibration (from 100 to 160◦C), a 1% strain step was applied and the stress was monitored over time. To ensure a good contact of the material with the geometries, a constant normal force of 5 N was applied. According to a previous strain sweep experiment, 1% deformation were within the linear range.

1.5. Chemical recycling procedure

1.5.1. Vitrimer resin

100 mg of the sample was immersed in 10 weight equivalents of cystamine (1 g). The mixture was stirred for 24h at 60°C to finally afford a limpid yellow solution. Then, to reform a new crosslinking network, DGEVA (3 g) was added to the yellow mixture and the recipient was speed mixed at room

temperature for 40 seconds to afford a homogeneous final mixture. The mixture was then cured at 60 °C for 1h and at 90 °C for 2h to obtained the desired fully cured resin DGEVA/cyst10 (R).

For the procedure with 5 equivalents of cystamine, the quantities were adjusted: 100 mg of the sample was immersed in 0.5 g of cystamine. Following this, 1.63 g of DGEVA was added to the mixture. The process followed the same curing protocol as described above.

1.5.1. Carbon fiber composites

The preparation of the carbon fiber composites was carried out according to the vitrimer resin protocol outlined in section 1.5.1. The carbon fiber reinforced epoxy composites were immersed in cystamine (at a 10 weight equivalent ratio) at 60°C. This step served to dissolve the epoxy resin and facilitate the recycling of the carbon fiber. Then, the carbon was manually extracted and washed with ethanol to remove the excess of cystamine.

Table S1. DMA data of DGEVA/cyst, DGEVA/cyst5 (R) and DGEVA/cyst10 (R)

Sample	E' (25°C)	T_{onset} E' Log scale	T_{peak} E''	T_{peak} Tan δ
	MPa	°C	°C	°C
DGEVA/cyst	2980	46	47	55
DGEVA/cyst10 (R)	3709	43	44	55
DGEVA/cyst5 (R)	3457	48	47	56

Table S2. Fitting parameters for stretched exponential decay of DGEVA/cyst10 (R) et DGEVA/cyst5 (R)

T	DGEVA/cyst10 (R)					DGEVA/cyst5 (R)				
	G_{res}/G_0	τ *	β	< τ>	R^2	G_{res}/G_0	τ*	β	< τ>	R^2
(°C)		(s)		(s)			(s)		(s)	
110	-	-	-	-	-	0.215	595.6	0.47	1343	0.99
120	0.212	454	0.58	714	0.99	0.172	369.7	0.47	835	0.99
130	0.162	292.1	0.56	484	0.99	0.127	230.6	0.46	543	0.99
140	0.124	200.6	0.55	341	0.99	0.094	162.9	0.47	367	0.99
150	0.09	147	0.53	265	0.99	0.007	124.7	0.47	282	0.99

Table S3. Comparison of thermomechanical properties of DGEVA/cyst and composites

Sample	E' (à 25°C)	T_{onset} E' Log scale	T_{peak} E''	T_{peak} Tan δ
	MPa	°C	°C	°C
DGEVA/cyst/CF (MO)	12370	41	50	53
DGEVA/cyst/CF (MU)	54670	40	48	51

Table S4. Fitting parameters for stretched exponential decay of DGEVA/cyst/CF (MO) ®

T	DGEVA/cyst/CF (MO) ®				
	G_{res}/G_0	τ *	β	<τ >	R^2
(°C)		(s)			
110	0.11	398	0.60	599	0.99
120	0.08	246	0.58	387	0.99
130	0.06	157	0.57	253	0.99
140	0.04	103	0.56	170	0.99
150	0.04	74	0.54	130	0.99

Equation $(S1)$ $$\frac{G(t)}{G_0} = \frac{G_{res}}{G_0} + (1 - \frac{G_{res}}{G_0}) exp^{(-\frac{t}{\tau *})^{\beta}}$$

$Equation\ (S2)$ $$< \tau >= \frac{\tau^* \Gamma(1/\beta)}{\beta}$$

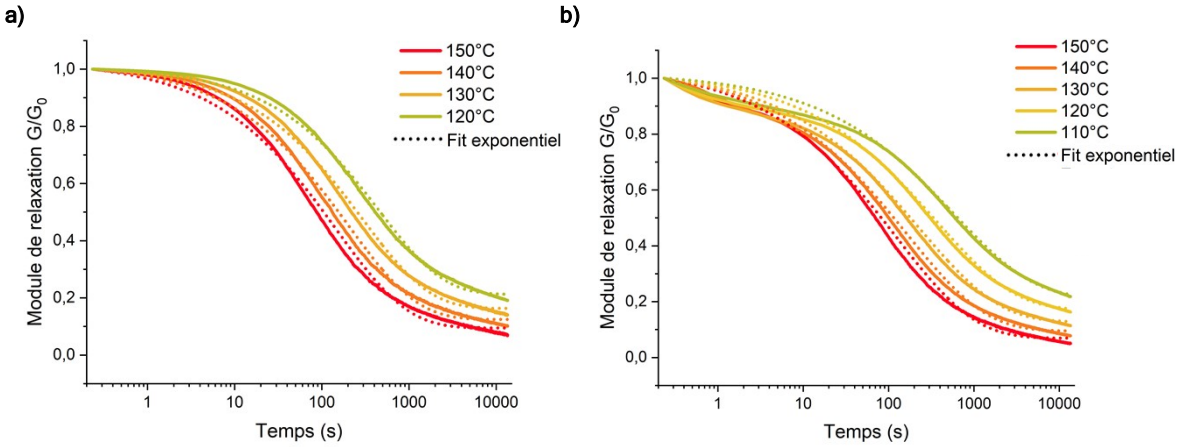

Figure S1. Normalized relaxation curves fitted by KWW model of materials a) DGEVA/cyst10 (R) et b) DGEVA/cyst5 (R)

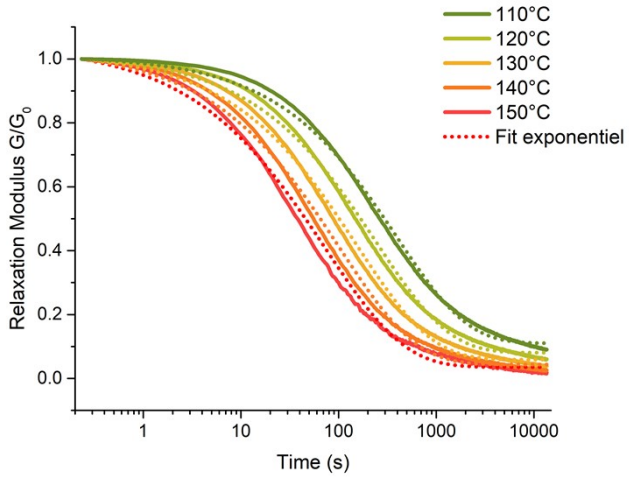

Figure S2. Normalized relaxation curves fitted by KWW model of recycled DGEVA/cyst/CF (MO) (R)

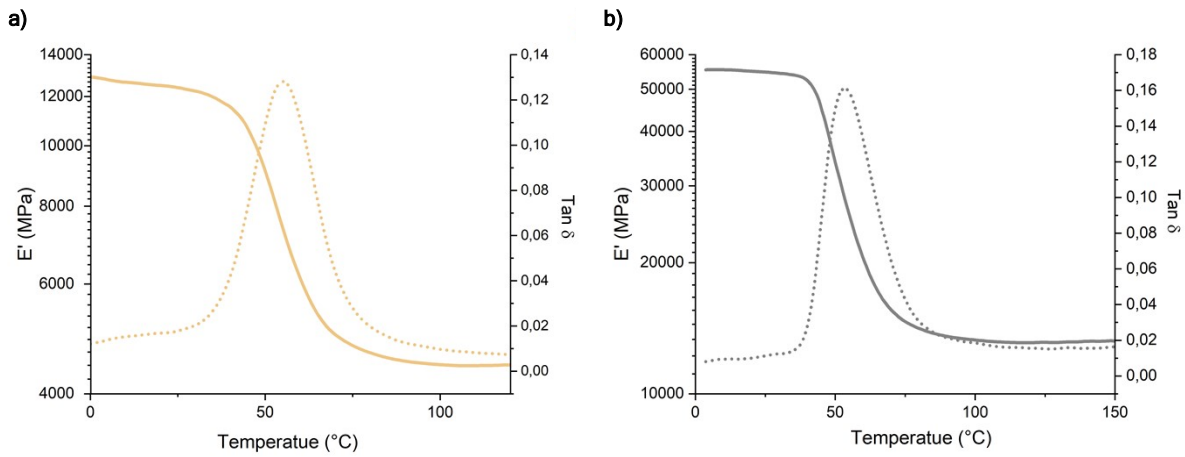

Figure S3. Storage modulus E' and Tan delta of a) monolayered composite DGEVA/cyst/CF (MO) and b) trilayered composite DGEVA/cyst/CF (MU)