ELECTRONIC SUPPLEMENTARY INFORMATION

Transient mechanochromism in epoxy vitrimer composites containing aromatic disulfide crosslinks

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1. Materials

4-Aminophenyl disulfide (4-AFD) 98% and 2-aminophenyl disulfide (2-AFD) 97% were purchased from sigma Aldrich and used as received. ARALDITE LY1564 (DGEBA based epoxy resin) was purchased from Huntsman Advanced Materials. HexForce 1103 PLAIN glass fiber (basis weight 290 gm^{-2}), release film and breather cloth were purchased from Gazechim.

2. Methods

Thermogravimetric analyses (TGA) were performed on a TA Instruments Q500 equipment under nitrogen atmosphere at a heating rate of 20 C min^{-1} from 25 to 60 ºC. Differential scanning calorimetry (DSC) experiments were performed using a Perkin Elmer Pyris Diamond DSC over a temperature range from 25 to 220 ºC under nitrogen. Glass transition temperatures were obtained as the inflection point of the heat flow step recorded at 20 C min^{-1} scan rate. Tensile tests of cured epoxy resins were carried out according to UNE-EN-ISO 527 standard using type 5 dumbbell-type specimens using an INSTRON 3365 Long travel Elastomeric Extensometer controlled by Bluehill Lite software.

3. Synthesis

Synthesis of p-EPO resin: Araldite LY1564 and 4-AFD were mixed by heating the mixture at 80 ºC and degassed under vacuum. The degassed mixture was poured into a metallic mould and cured in an oven at 120 ºC for 2.5 h and postured at 150 ºC for 2 h. The cured resin was cooled down to room temperature and 2 mm thick plaque was obtained.

Synthesis of o-EPO resin: Araldite LY1564 and 2-AFD were mixed by heating the mixture at 100 ºC and degassed under vacuum. The degassed mixture was poured into a metallic mould and cured in an oven at 130 ºC for 2 h and postured at 150 ºC for 2 h. The cured resin was cooled down to room temperature and 2 mm thick plaque was obtained.

4. Mechanochromic behavior of o-EPO resin

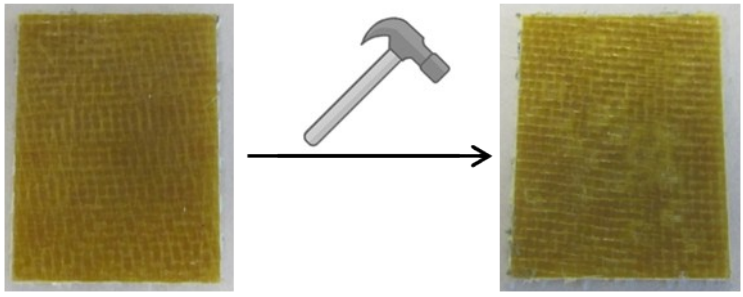

Figure S1. Photographic sequence showing how a glass-fiber composite made of **o-EPO** is hit with a hammer and no coloration was observed.

5. Differential Scanning Calorimetry (DSC)

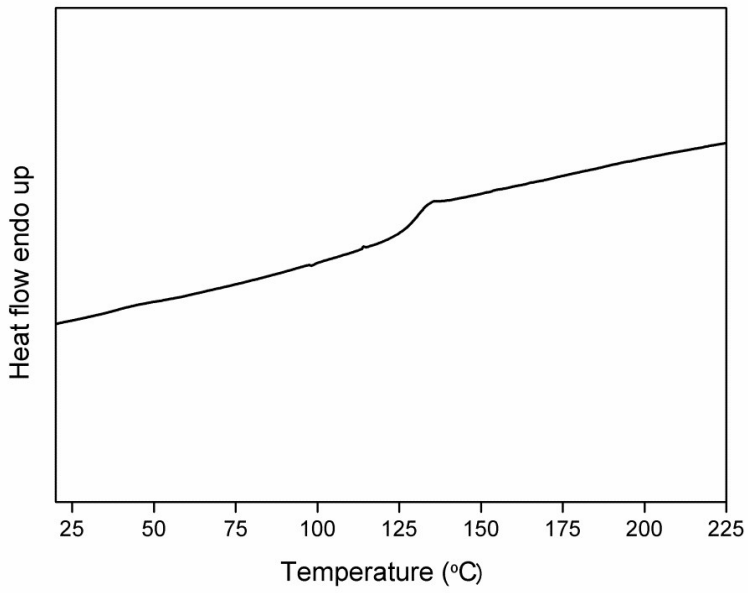

Figure S2. DSC thermogram for **p-EPO** resin, from where a T_g value of 130 ºC was determined.

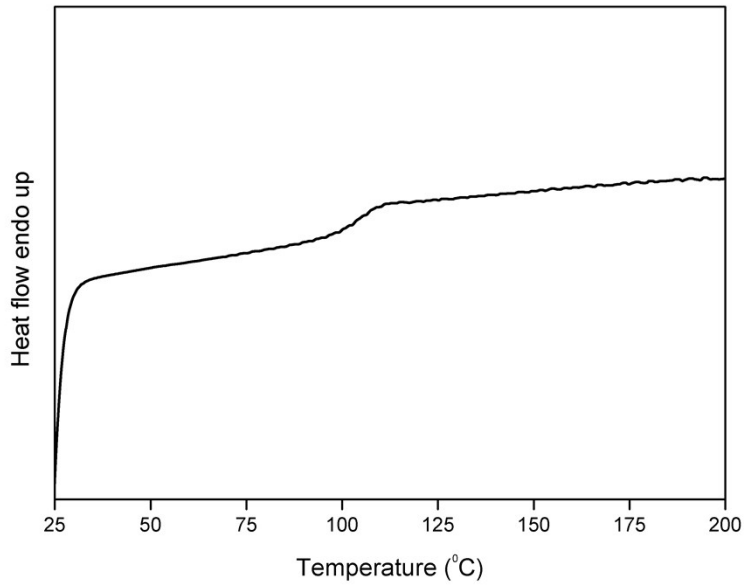

Figure S3. DSC thermogram for **o-EPO** resin, from where a T_g value of 105 ºC was determined.

6. Thermogravimetric analysis (TGA)

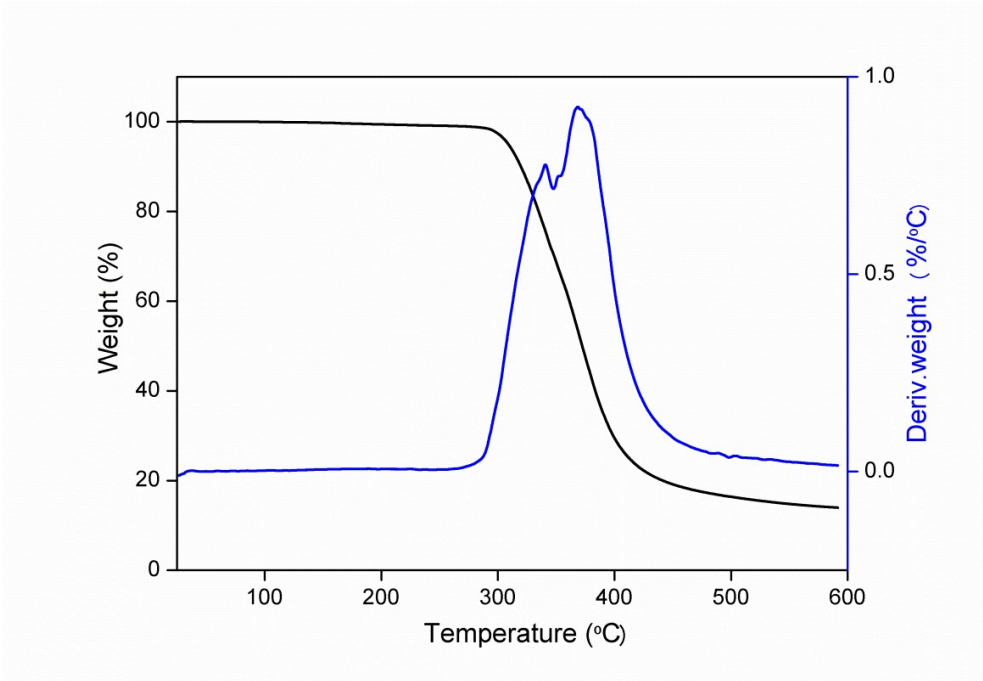

Figure S4. TGA thermogram of **p-EPO** resin, representing weight loss (black trace) and derivative weight loss (blue trace) versus temperature.

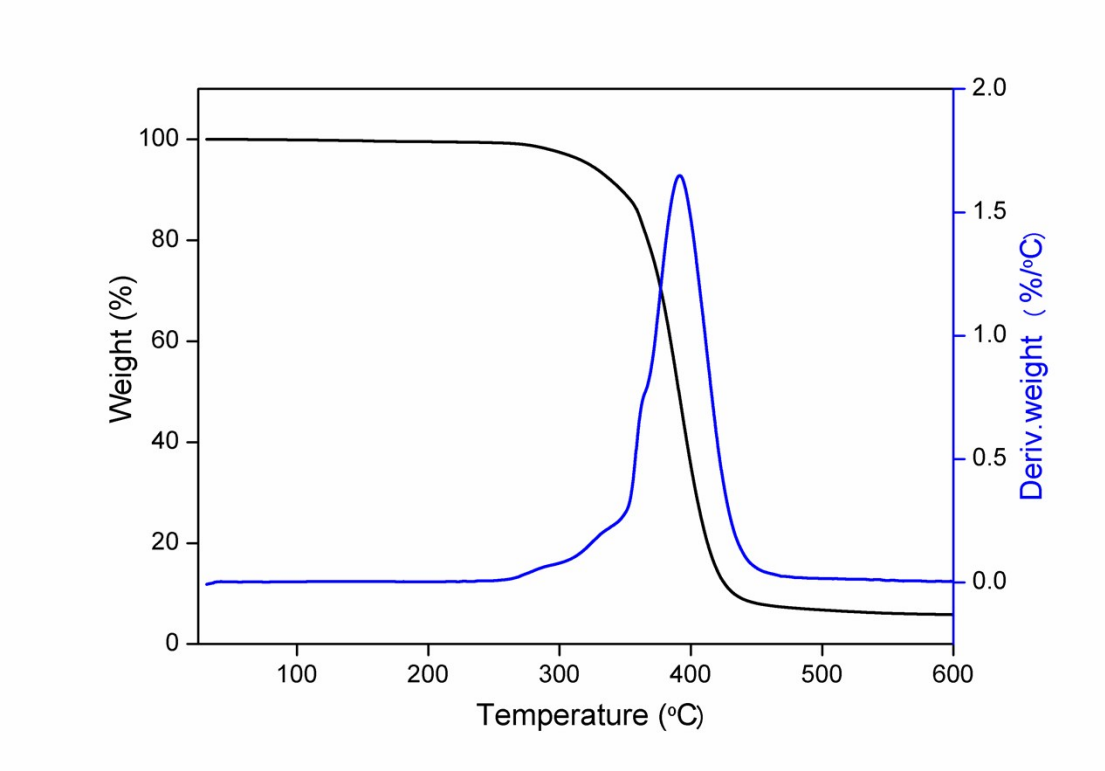

Figure S5. TGA thermogram of **o-EPO** resin, representing weight loss (black trace) and derivative weight loss (blue trace) versus temperature.

7. Mechanical tests

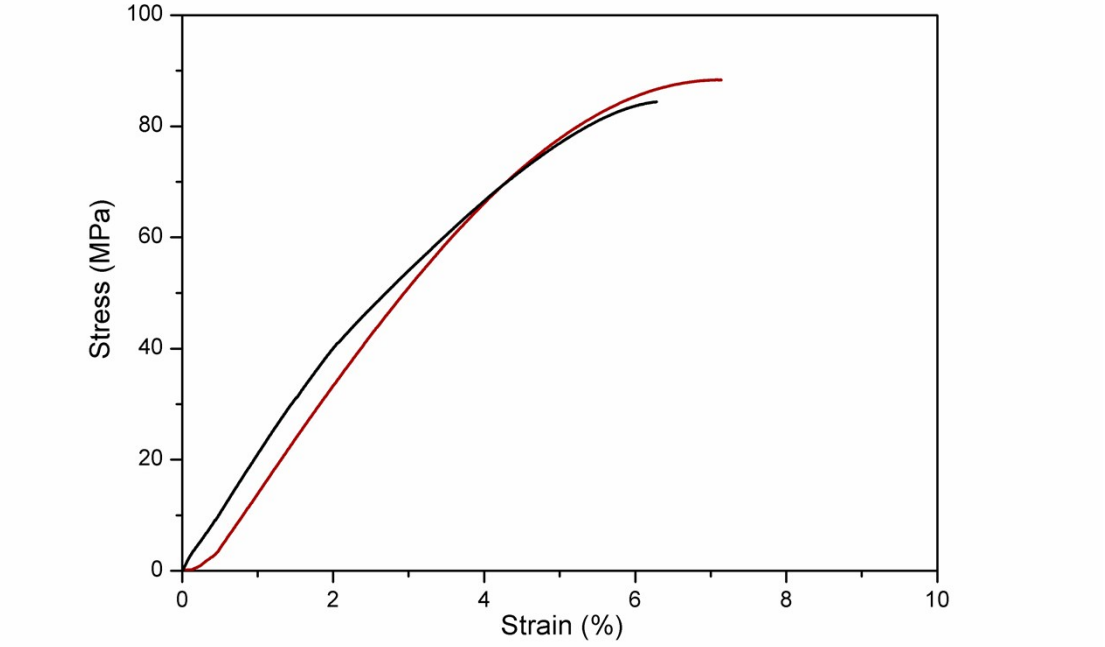

Figure S6. Stress-strain curves for **p-EPO** resin (red trace) and **o-EPO** resin (black trace).

8. Thermoplastic blends

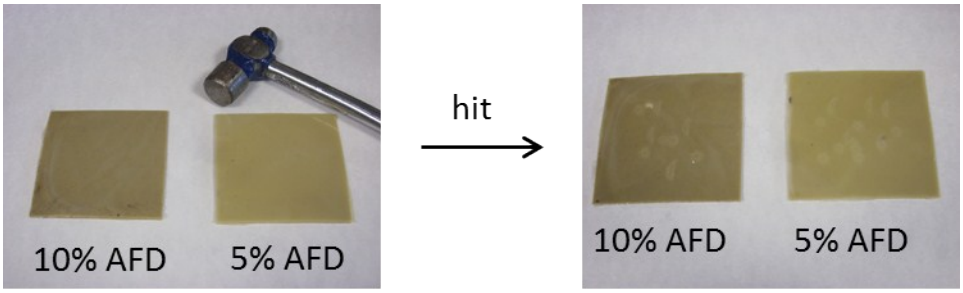

Figure S7. Blends of polyethylene with 4-AFD before (left) and after (right) being hit with a hammer.

9. Calculation details

Geometry optimizations have been performed with the Gaussian 09[1] suite of programs using the ωB97XD functional[2] together with the 6-31+G(d,p) basis set.[3] In order to confirm that the optimized structures were minima on the potential energy surfaces, frequency calculations were performed at the same level of theory. All the structures showed real frequencies for all the normal modes of vibration. In order to calculate the absorption spectra, Time-Dependent Density Functional Theory (TDDFT)[4] was used at the same level of theory used in the structural characterization, namely: ωB97XD/6-31+G(d,p). This level of theory has been previosuly shown to be suitable for this kind of species.[5] TDDFT calculations have been carried out using the Q-Chem package.[6]

Table S1. Mulliken atomic charges (q) and spin densities (ρ) on sulfur and nitrogen atoms of the ·S-Ph-N($C_2H_4OH)_2$ *ortho* and *para* radical species in the ground (G. S.) and excited (E. S.) states.

	q_S		q_N		ρ_S		ρ_N	
	G. S.	E. S	G. S	E. S.	G. S.	E. S.	G. S.	E. S.
ortho	-0.13	-0.52	-0.46	-0.23	0.65	0.25	0.11	0.33
para	-0.14	-0.39	-0.57	-0.41	0.67	0.37	0.09	0.23

Cartesian coordinates

1. *Ortho* ·S-Ph-N($C_2H_4OH)_2$ radical:

C	1.092471	-1.202675	-1.207798
C	-0.635312	-0.243267	-0.277832
C	-1.619344	0.543799	0.425289
C	-2.995819	0.234502	0.218594
C	-3.408390	-0.717199	-0.683504
C	-2.439347	-1.431762	-1.410066
N	0.719502	-0.059761	-0.090286
S	-1.234549	1.916798	1.368109
H	-2.746443	-2.199013	-2.114561
H	-4.464794	-0.911827	-0.835358
H	-0.370023	-1.821210	-1.727653
H	-3.719643	0.814735	0.781347

C	1.641778	-0.311295	-1.184212
C	1.288255	0.008732	1.249488
C	2.720131	0.757747	-1.307359
H	2.117382	-1.300006	-1.095699
H	1.081043	-0.293410	-2.120214
H	3.444412	0.417075	-2.062336
O	2.101369	1.964120	-1.701310
H	3.261710	0.881681	-0.359684
H	2.708484	2.697145	-1.578994
H	1.811789	0.958865	1.412787
C	2.234493	-1.146890	1.558962
H	0.469836	-0.022176	1.967013
H	2.539221	-1.046020	2.610188
O	1.545377	-2.361728	1.330419
H	3.146209	-1.096832	0.944921
H	2.099286	-3.098747	1.598249

1. *Para* ·S-Ph-N($C_2H_4OH)_2$ radical:

C	-1.211388	1.073206	0.000000
C	-1.204605	2.451004	0.000000
C	-0.000988	3.200987	0.000000
C	1.203175	2.451840	0.000000
C	1.210945	1.074067	0.000000
C	0.000000	0.326622	0.000000
S	-0.001526	4.907956	0.000000
N	0.000429	-1.054157	0.000000
H	2.172243	0.579635	0.000000
H	-2.172300	0.577997	0.000000
H	-2.148123	2.987709	0.000000
H	2.146284	2.989256	0.000000
C	-1.321780	-1.686113	0.000000
C	1.322920	-1.685466	0.000000
C	-1.466445	-3.202337	0.000000
H	-1.875863	-1.340811	0.881490
H	-1.875863	-1.340811	-0.881490
O	-2.869157	-3.403377	0.000000
H	-1.018338	-3.650637	-0.893941
H	-1.018338	-3.650637	0.893941
H	-3.055120	-4.345201	0.000000
C	1.468219	-3.201634	0.000000
H	1.876852	-1.339924	-0.881493
H	1.876852	-1.339924	0.881493
O	2.871015	-3.402100	0.000000
H	1.020294	-3.650115	0.893943
H	1.020294	-3.650115	-0.893943
H	3.057344	-4.343851	0.000000

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