Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Multiple Welding of Long Fiber Epoxy Vitrimer Composites

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1— Welding at constant applied stress

To ensure the most repeatable process and reach better control of the applied pressure on the joint surface, a homemade lever structure that is drawn in Figure S1 was built. It consists in a crane made out of aluminum bars, with a lever factor of l/l_0 = 13.5, i.e. a 10 kg load actually applies a 1350 N force under the lever axis. Two masses have been used: 3.8 kg and 10 kg. The whole setup was dimensioned in order to fit inside a laboratory oven.

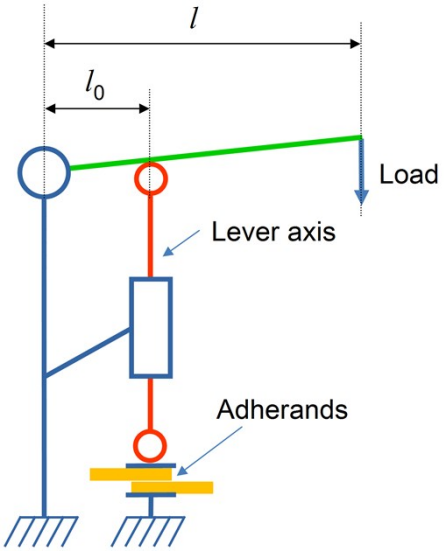

Figure S1. Schematic of the home built lever setup

2— Surface roughness

The surface of composite plates was analyzed using a Veeco Dektak 6M Surface Profiler. Figure S2 uses the Henry graphic method that makes a Gaussian distribution fall on a straight line. The normit is the inverse function of the standard Gaussian distribution law applied to the cumulative frequency count of the asperities heights. The normit is plotted against the asperities height in Figure S2. A straight line is found which indicates a Gaussian distribution as predicted by Greenwood [1] and confirmed by Leibler.[2]

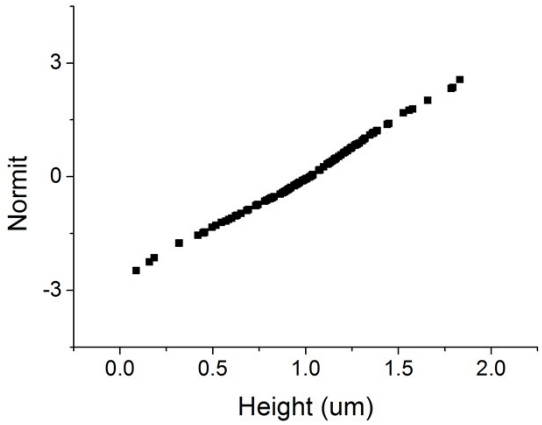

Figure S2. Henry line of the cumulative frequency count of the asperities height of polished joint sample before adhesion.

3 — Composite plates formulations and physical properties

Table S1 presents the formulation of the reference 2:2 and the epoxy vitrimer 2:1-Zn matrices used to prepare composite plates. The epoxy index from the analysis certificate (in $Eq.kg^{-1}$) was used to calculate the weight of Araldite in the formulation according to the chosen monomer feed ratio of Table S1.

Table S1. Formulation of the control 2:2 and vitrimer 2:1-Zn matrices; viscosity before cure; glass fiber content and thickness of the composite plates after cure.

Composition & properties		**Control 2:2**	**Vitrimer 2:1-Zn**
Araldite LY564	(epoxy resin)	2 mol	2 mol
Aradur 917CH	(anhydride crosslinker)	2 mol	1 mol
Accelerator 960-1	(amine accelerator)	3 wt%	3 wt%
$Zn(acac)_2 .x H_2O$	(transesterification catalyst)	0 mol	0.2 mol
Viscosity at 50°C		0.11 Pa.s	0.37 Pa.s
Glass Fibers		53 wt%	53 wt%
Thickness		3 mm	3 mm

Before cure, the viscosity was measured at 50°C in the whole 0.1 to 100 s^{-1} shear range using an Anton-Paar MCR 501 rheometer in the 25 mm diameter parallel plane geometry. In this isothermal conditions, the viscosity of both formulated resins was less than 0.5 Pa.s for more than 15 minutes whereas the time necessary for injection into the RTM mold is about 3 minutes. Once heated to the curing temperature of 120°C, the viscosity first decreases, then

increases due to crosslinking reactions. The time dependance of the complex viscosity (at 1 rad/s) in such conditions is plotted in figure S3.

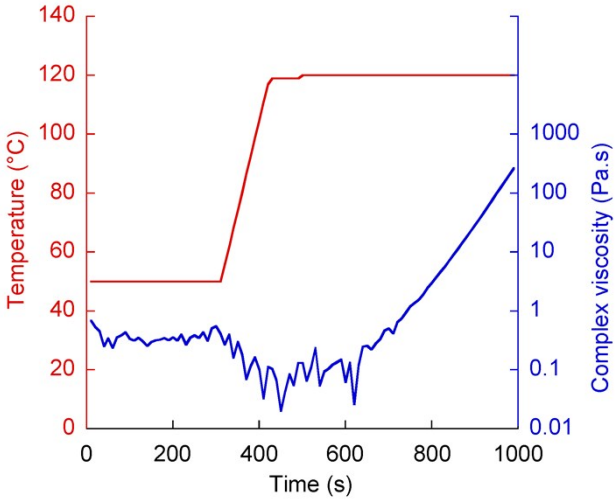

Figure S3. Time dependance of the complex viscosity (at 1 s^{-1}) of the **2:1-Zn** reactive formulation. during application of a heating ramp up to 120°C.

Composite plates were prepared with an inclusion of 53 vol.% glass fiber plies and a light cloth (30g/m²) of poly(ethylene terephthalate) at the upper surface. The RTM technique ensured a constant thickness of 3 mm.

4 — DSC measurements

Table S2 presents the glass transition temperature of the control 2:2 and vitrimer 2:1-Zn matrices. Measurements are performed by DSC (Tg was determined as the midpoint of the change in specific heat on the second heating cycle) after 4h curing at 120°C and various postcuring times at 160°C.

Table S2. Measured glass transition temperatures by DSC (from 0 to 230°C with a 10°C/min heating rate) as a function of the post-cure time.

Curing	Postcuring	Glass transition temperature	
at 120 °C	at 160°C	**Control 2:2**	**Vitrimer 2:1-Zn**
4 h	0 h	121 °C	90 °C
4 h	3 h	124 °C	100 °C
4 h	6 h	124 °C	103 °C
4 h	12 h	121 °C	95 °C

5 — Swelling experiments

Swelling experiments have been performed on cured 2:1-Zn and 2:2 samples taken from the edge of the plates in the fibre-free marginal area. Small pieces were immersed in

trichlorobenzene (TCB) at 180°C overnight in an autoclave. It was checked that the material swelled (solvent uptake about 60 wt%) and did not dissolve.

6 — DMA measurements

Stress relaxation (SR) tests and DMA traces under a 3°C/min temperature ramp were carried out using a TA Instruments 2980 dynamic mechanical analyzer (DMA) in the three bending points geometry. Figure S4 presents the DMA traces (E' and tan δ) of 2:2 and 2:1-Zn compounds. Figure S5 presents the results of stress relaxation at 210°C for an applied strain of 1% for an epoxy vitrimer sample 2:1-Zn and for a control 2:2 sample. The vitrimer sample fully relaxes stresses.

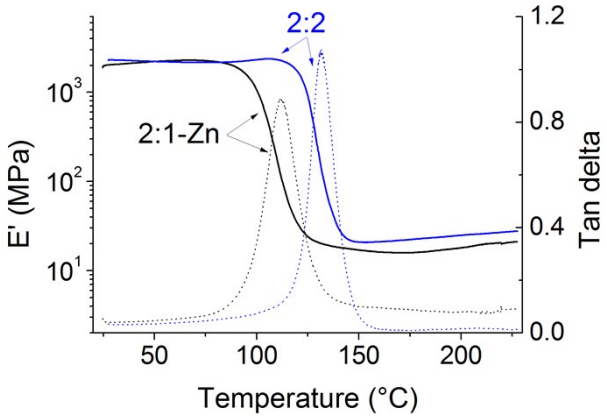

Figure S4. DMA traces (1Hz, 3°C/min, 20µm) of an epoxy vitrimer sample 2:1-Zn and a control sample 2:1. (Solid line:E'; dotted line: tanδ)

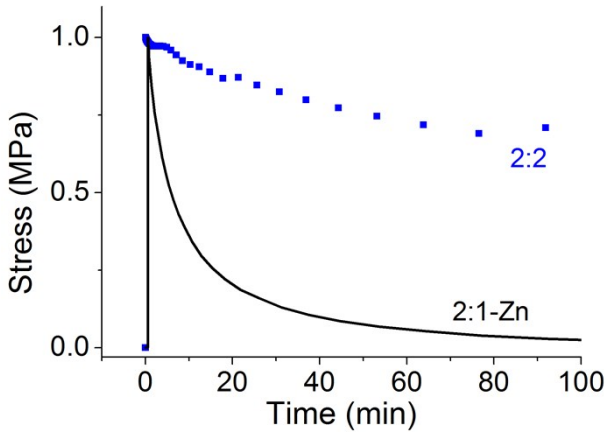

Figure S5. DMA stress relaxation (1%, 210°C) in the three point bending geometry on an epoxy vitrimer sample 2:1-Zn and a control sample 2:2 (normalized stress)

7 —Fracture of an epoxy vitrimer joint made at 180°C

Figure S6 shows the aspect after rupture of an epoxy vitrimer joint welded in a heating press at 210°C under 10 MPa and tested in the lapshear geometry according to ISO 4587.[3] The temperature of the joint area during the welding was 180°C. For this sample, measured force at break was 2800N; fracture surfaces show important roughness and transfer of matter from one face to the other, typical of a cohesive failure.

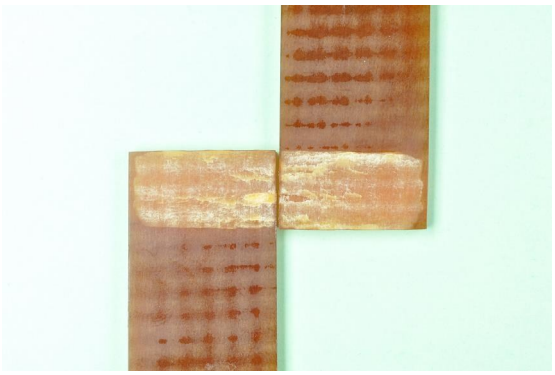

Figure S6. Lapshear sample profile after tensile test of a 2:1-Zn joint welded under heating press at 210°C, during 25 min under 10MPa

8 —Force at break as a function of three different factors

A full 2^3 factorial design with 3 factors denoted A, B and C of two levels each (low and high levels) has been chosen. Factors A and B are of chemical nature.

- Factor A designates the absence (lower level) or the presence (higher level) of the zinc catalyst in the reactive formulation.
- Factor B designate the stoichiometry (epoxide:anhydride ratio) of the reactive formulation: '2:2' (lower level) or '2:1' (higher level).
- Factor C designate the load : 500 N (lower level) or 1320 N (upper level) applied to welding.

Main factor effects (β_i) and first and second order interactions (β_{ij} and β_{123} respectively) are evaluated through a least square model based on linear regression equation written as (1).

$$\eta(X_{i,1\leq i\leq 3}) = \sum_{i=1}^{3} \beta_i X_i + \sum_{i\neq j} \beta_{ij} X_i X_j + \beta_{123} X_1 X_2 X_3 \qquad (1)$$

Where η is the predicted response β_i the effects, β_{ij} and β_{123} the interactions. As a result of least square adjustement, $\eta(X_i)$ differs from the experimental response, $Y(X_i)$ by a gaussian variable K of standard deviation σ and centered on zero.

The effect (or estimated value) of a factor is half of how much the response value varies when the lower level is changed into the upper level. Significance of factors or interaction was evaluated by mean of a test of hypothesis as described for instance by Massart et al. [4]. The t-ratio is essentially the ratio of the estimate β with respect to its standard deviation. A factor or an interaction was judged significant if its t-ratio is more than the limit tabulated value for a given risk of first kind α. For α equal to 5% and in the case the standard deviations are estimated from a large number of repeated measurements, the limit tabulated value is close to 2.

Significant effects (in N) are plotted in the form of an histogram in Figure 6.

Table S3. Raw data results used in the 2^3 full factorial design for the identification of the significant factors influencing the force at break at first and second sticking, F1 and F2 respectively. The welding was performed at 160°C during 1h30 on a 20mm long and 15mm wide joint surface

# sample	Cata.	Stoich.	P [N]	F1 [N]	F2 [N]	# sample	Cata.	Stoich.	P [N]	F1 [N]	F2 [N]
1	0	2:2	500	0	0	22	0	2:1	500	374	257
2	0	2:2	500	0	0	23	0	2:1	500	157	0
3	0	2:2	500	0	0	24	0	2:1	500	297	0
4	0	2:2	500	0	0	25	0	2:1	500	257	0
5	0	2:2	500	0	0	26	0	2:1	500	97	0
6	0	2:2	1320	261	47	27	0	2:1	1320	731	259
7	0	2:2	1320	210	94	28	0	2:1	1320	588	278
8	0	2:2	1320	235	0	29	0	2:1	1320	298	0
9	0	2:2	1320	395	188	30	0	2:1	1320	40	0
10	0	2:2	1320	122	0	31	0	2:1	1320	311	0
11	Z	2:1	500	440	516	32	Z	2:2	1320	0	0
12	Z	2:1	500	441	556	33	Z	2:2	1320	0	0
13	Z	2:1	500	363	478	34	Z	2:2	1320	0	0
14	Z	2:1	500	821	581	35	Z	2:2	1320	0	0
15	Z	2:1	500	248	391	36	Z	2:2	1320	231	0
16	Z	2:1	1320	763	496	37	Z	2:2	500	0	0
17	Z	2:1	1320	861	353	38	Z	2:2	500	0	0
18	Z	2:1	1320	517	556	39	Z	2:2	500	0	0
19	Z	2:1	1320	620	532	40	Z	2:2	500	0	0
20	Z	2:1	1320	667	605	41	Z	2:2	500	0	0
21	Z	2:1	1320	572	477						

8 —References

1. Greenwood, J. and Williamson J., *Contact of nominally flat surfaces.* Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 1966. **295**(1442): p. 300-319.
2. Creton, C. and Leibler L., *How does tack depend on contact time and contact pressure.* J Polymer Sci B Polymer Phys, 1996. **34**: p. 545-554.
3 ISO 4587:2003 Adhesives -- Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies
4 Massart, D.L., Vandeginste B.G.M., Buydens L.M.C., De Jong S., Lewi P.J., and Smeyers-Verbeke J., *Handbook of Chemometrics and Qualimetrics: Part A*, in *Data Handling in Science and Technology*. 1998, Elsevier.