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Functional composite materials with bio-based epoxy vitrimer matrix

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FuncMat Functional and Smart Materials

UNIVERSITAT ROVIRA i VIRGILI

SUSMATx
Sustainable matrices for structural composites: processing and mechanical performance
5-6 September 2024
Girona - Spain
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- Catalan R&I Smart Specialisation Strategy

We promote alliances with universities and research centers to bring the sources of knowledge closer to companies.

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7. Batteries
8. Climate change

Our standout value:

Our interdisciplinary capabilities enable us to address complex challenges.

Introduction

Background and objective

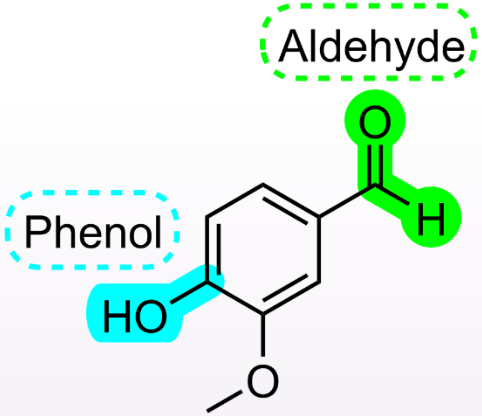
- Non-renewable
- Causes CO_2 emissions
- Not accessible worldwide

- Renewable
- Minimize CO_2 emissions
- Accessible worldwide

Lignocellulose

Lignin

Vanillin



Thermoplastics

- Poor mechanical performance ✗
- Low chemical resistance ✗
- Good reprocessing ✓
- Recyclable ✓

Thermosets

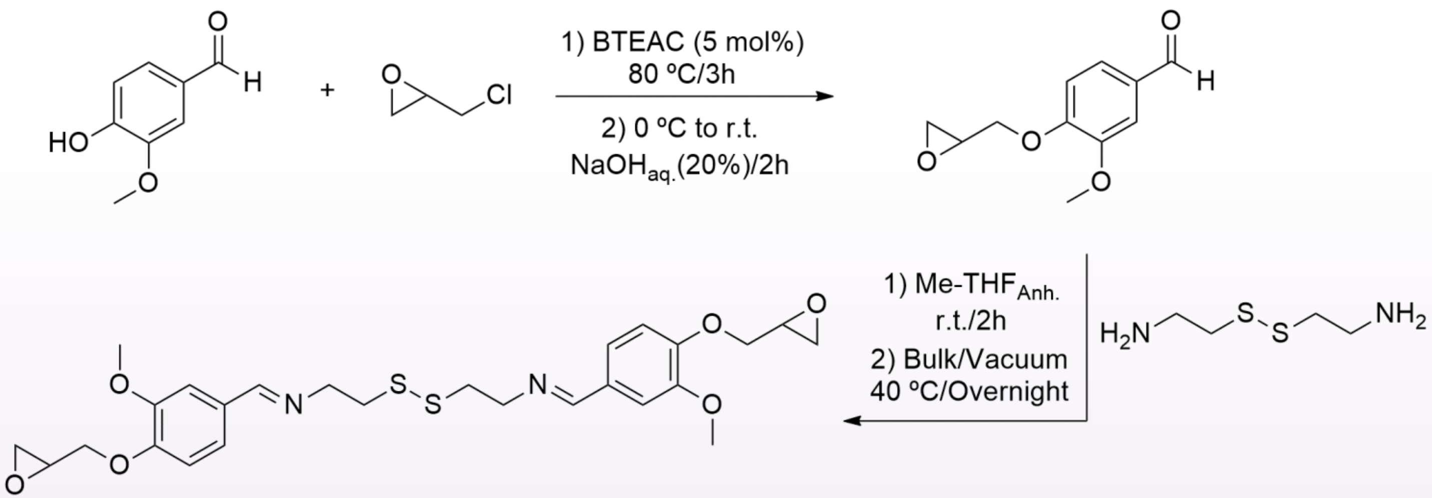
- Good mechanical performance ✓
- High chemical resistance ✓
- Not reprocessing ✗
- Not recyclable ✗

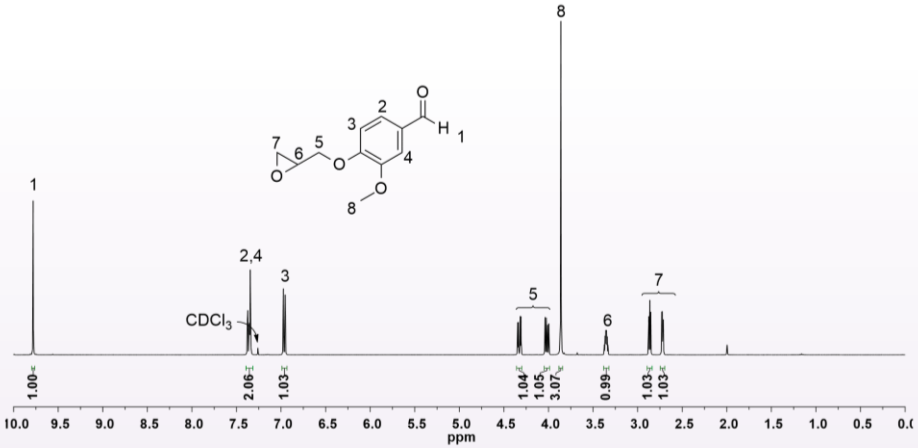
Vitrimers

Objective:
Synthesize an epoxy monomer, derived from renewable sources, used it to prepare epoxy-based vitrimers, and demonstrate that it can be used for functional adhesives and composites

Introduction

Synthesis of monomer from vanillin and cystamine (Cyst-BVGE)





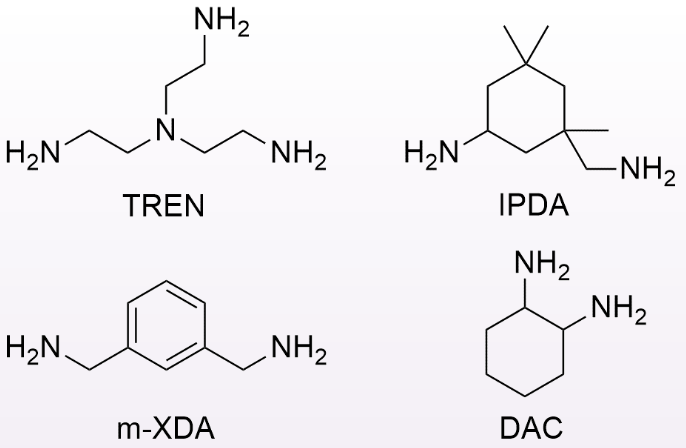
- Easy procedure and purification.
- High yield obtained, 78% in the first step and quantitative in the second step.
- The whole process is sustainable (use of Me-THF as solvent).
- No epoxide ring opening was observed during the imine condensation reaction.
- The monomer is a viscous oil at 40-50 ºC.

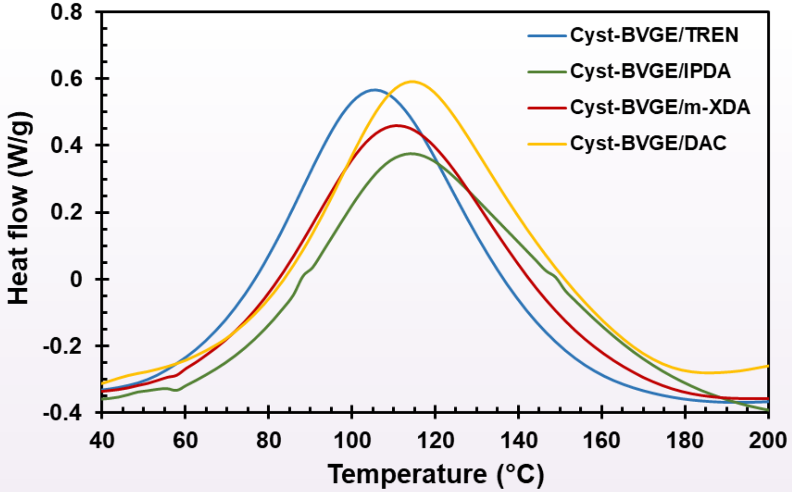
The incorporation of aliphatic imine and disulfide groups, involved in the exchange reactions, are part of the epoxy monomer. Theoretically, any curing agent suitable for epoxy resins to obtain a vitrimer.

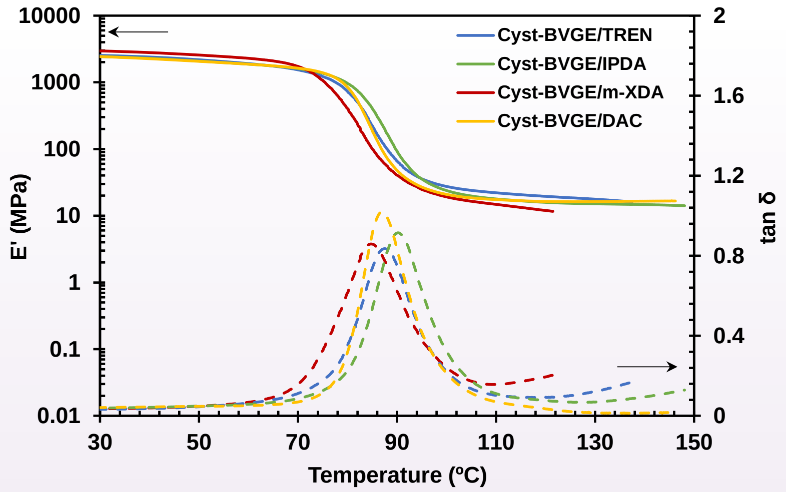
Results

Formulations and thermal characterization

Curing of Cyst-BVGE with different amines







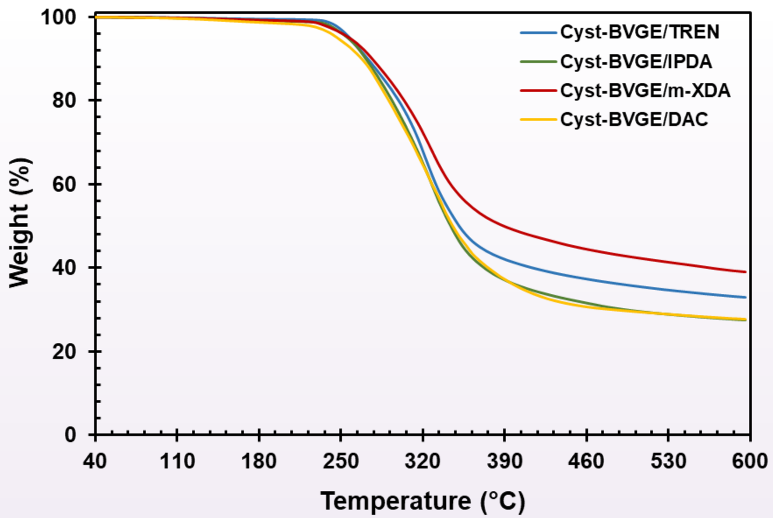
- The formulations were prepared between 40 and 50 ºC.
- All formulations present a single broad curing peak, with no significant differences between the amines.
- The heat of reaction corresponds with that reported in the literature.
- The curing was performed 2 h at 120 ºC, 2 h at 140 ºC and 1 h at 160 ºC.
- All formulations present high T_gs, around 90 ºC.

Formulation	T_{peak} (ºC)	ΔH (kJ/ee)	$T_{tan\delta}$ (ºC)	FWHM (ºC)	E'_g (MPa)	E'_r (MPa)
Cyst-BVGE/TREN	105	87	88	14	2570	16
Cyst-BVGE/IPDA	114	93	90	13	2467	15
Cyst-BVGE/m-XDA	112	86	85	17	3015	12
Cyst-BVGE/DAC	117	84	87	12	2510	16

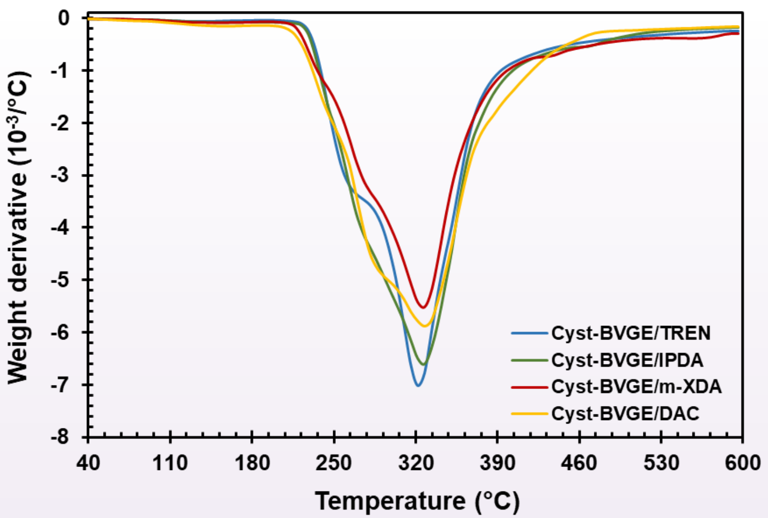
Results

Thermal stability

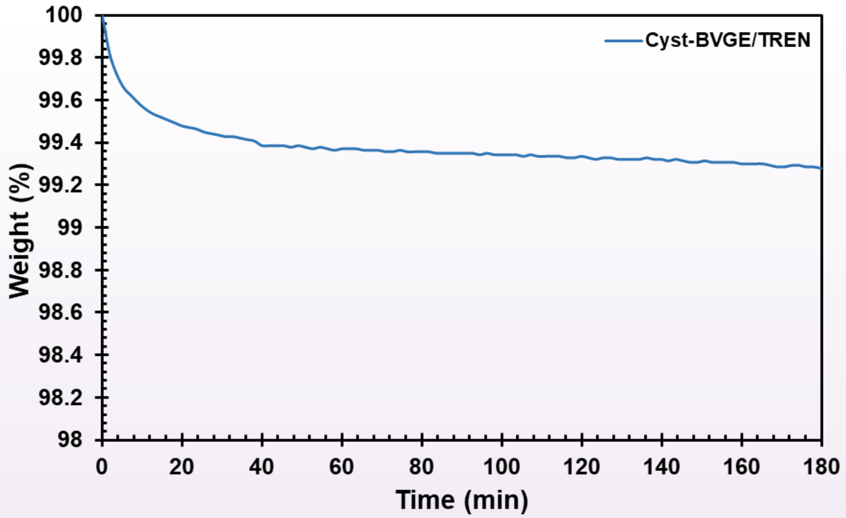
TGA curves



TGA 1st derivative curves



TGA isotherm at 160 ºC (3h)

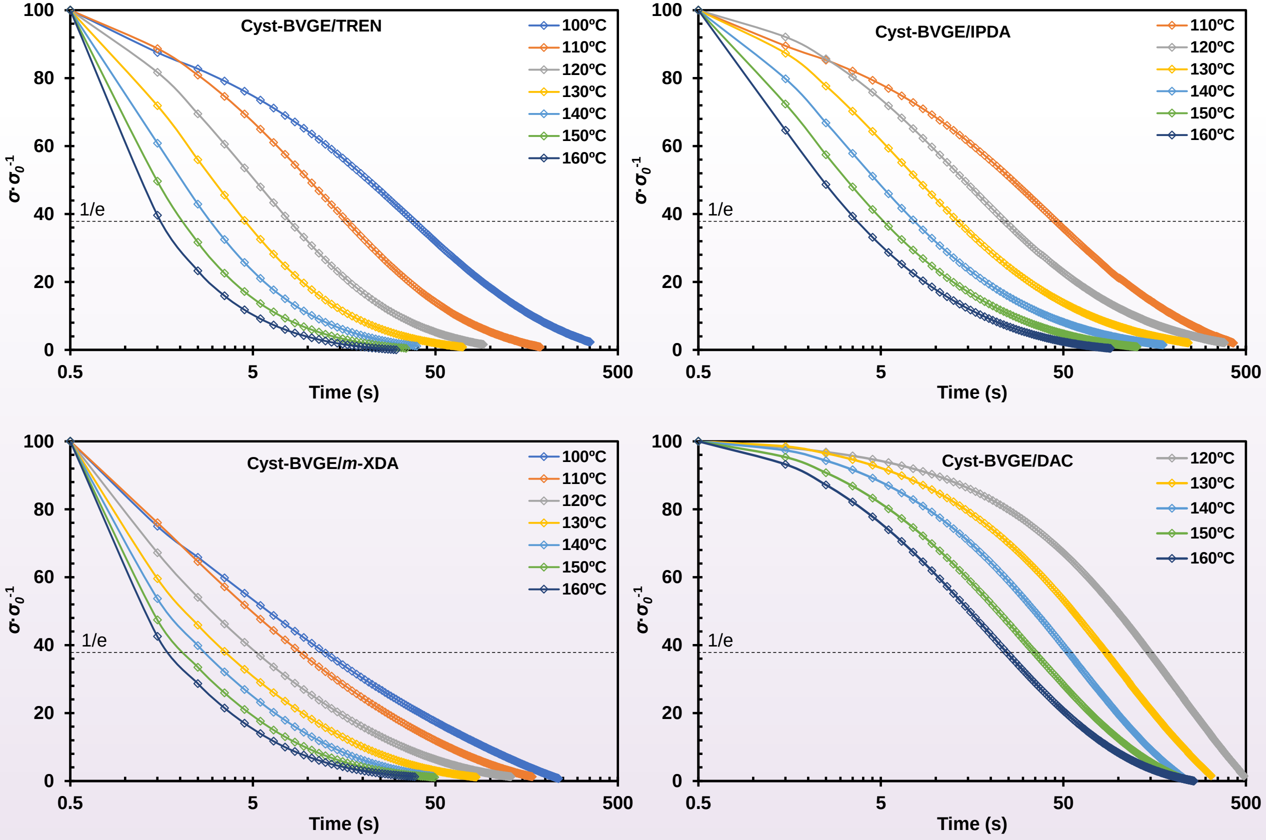


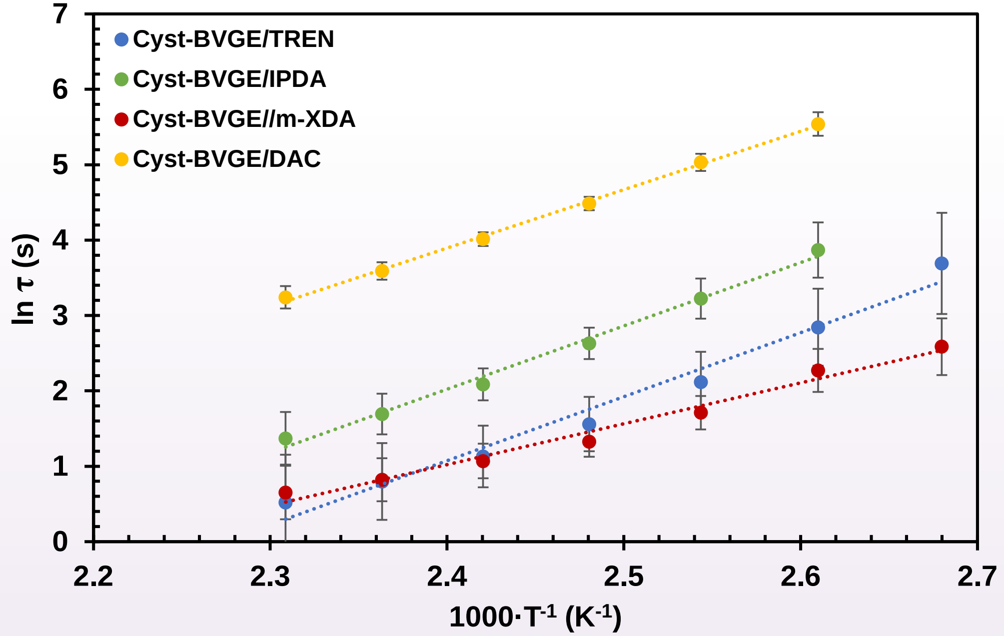
Formulation	$T_{2\%}$ (°C)	T_{max} (°C)	Char yield (%)
Cyst-BVGE/TREN	245	323	32.8
Cyst-BVGE/IPDA	240	326	27.5
Cyst-BVGE/*m*-XDA	236	326	38.9
Cyst-BVGE/DAC	222	328	27.7

- Very similar degradation rate in all the formulations.
- A shoulder can be observed in all formulations, which can correspond to more labile bonds (imine and disulfide).
- Only ≈ 0.7 % weight loss after 3 h at 160 ºC.

Results

Vitrimer characterization





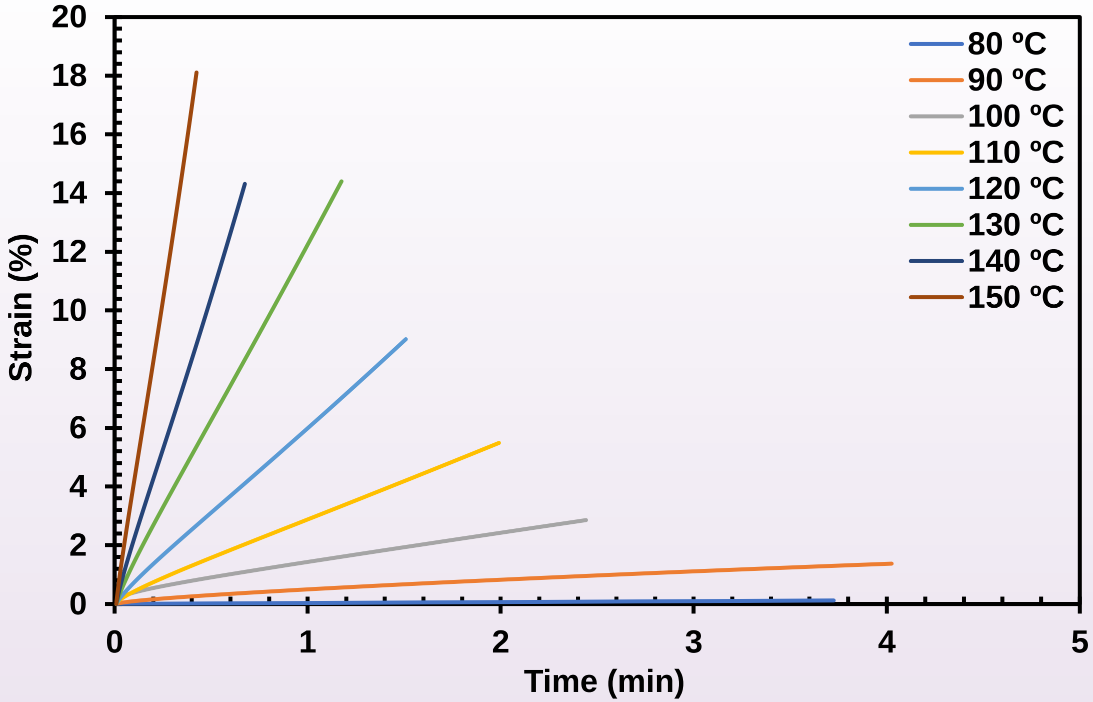
Sample	τ (s)	T_v (°C)	E_a (kJ/mol)	Ln A (s)	R^2
Cyst-BVGE/TREN	1.7	26	71	19.30	0.98
Cyst-BVGE/IPDA	3.9	29	70	18.12	0.99
Cyst-BVGE/m-XDA	1.9	46	45	12.01	0.98
Cyst-BVGE/DAC	25.6	-38	64	14.68	0.99

- Most formulations achieve complete relaxation in less than 1 min at 160 ºC.
- The topology freezing temperature (T_v) is far below the T_g of the material, then the relaxation temperature will be fixed by the T_g.

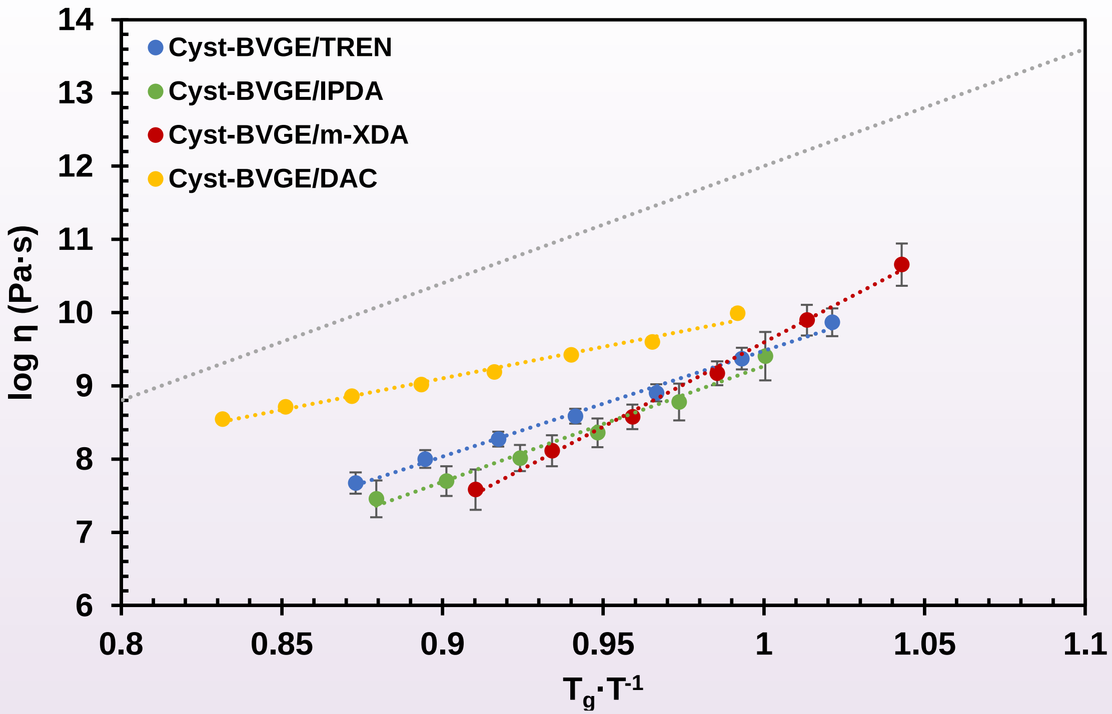
Results

Vitrimer characterization

Creep (Cyst-BVGE/IPDA)



Angell fragility plot



- The materials do not present significant creep below the T_g (T > 90 ºC).
- The Angell fragility plot shows lower viscosity than the reference (grey line) corresponding to an ideal strong liquid.

Results

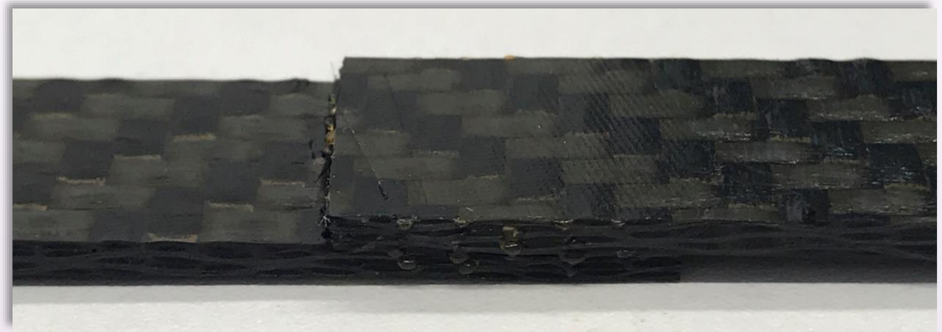
Functional adhesives and composites

Shear stress (MPa)				
	First adhesion	Re-adhesion after break	Re-adhesion after self-welding	Re-adhesion after debonding
Cyst-BVGE/IPDA	7.3±0.6	6.3±1.6 (86.2%)	7.2±3.1 (97.5%)	6.7±1.2 (90.9%)

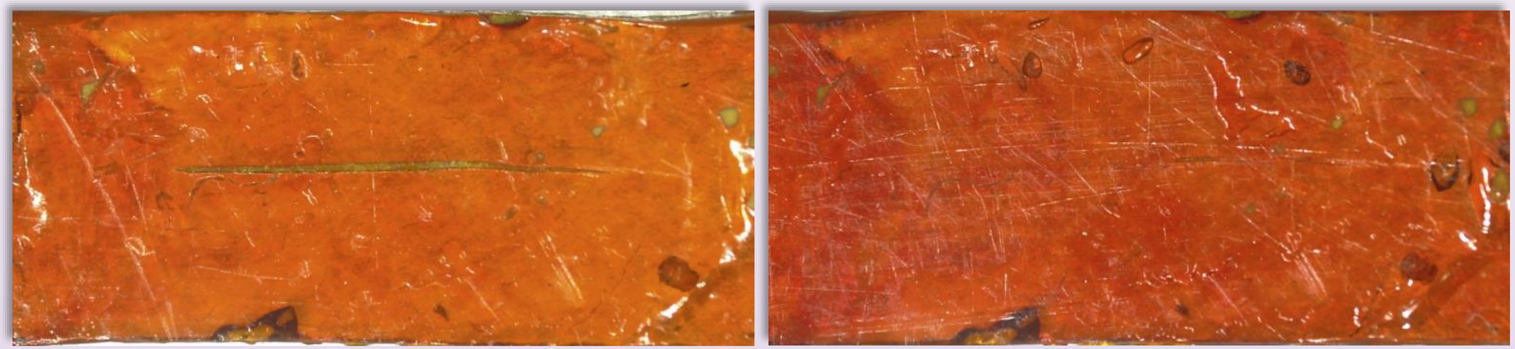
Set-up for re-adhesion

Self-welding assembly before making the adhesive bond.

Re-shaping of carbon-fiber composites through hot-pressing



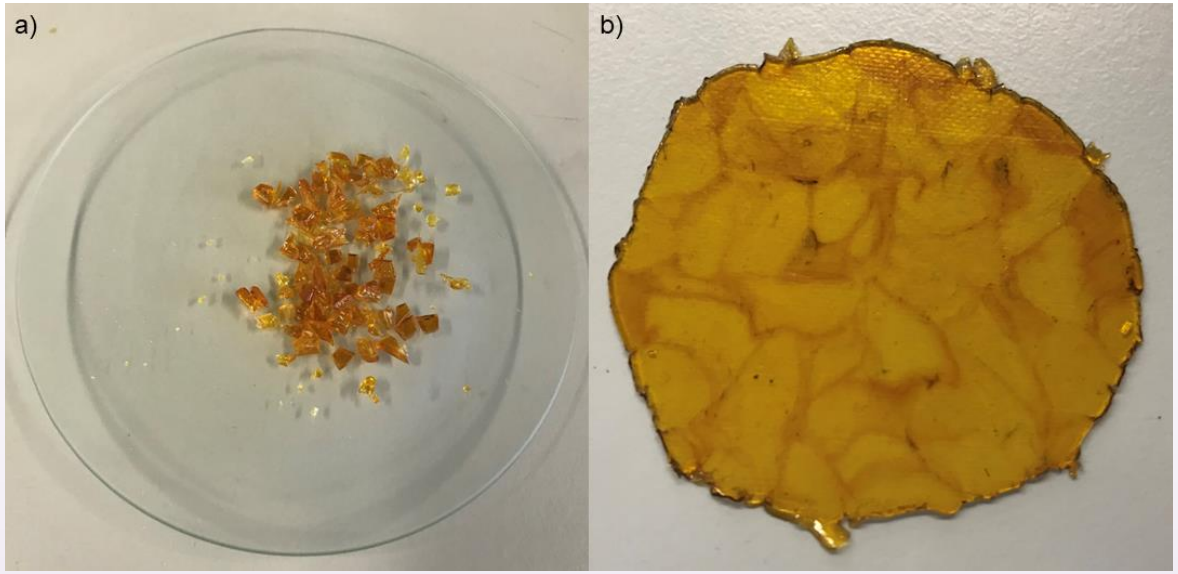
Self adhesion of composite pieces



Self-healing process after 1 h, 160 ºC, and no external pressure

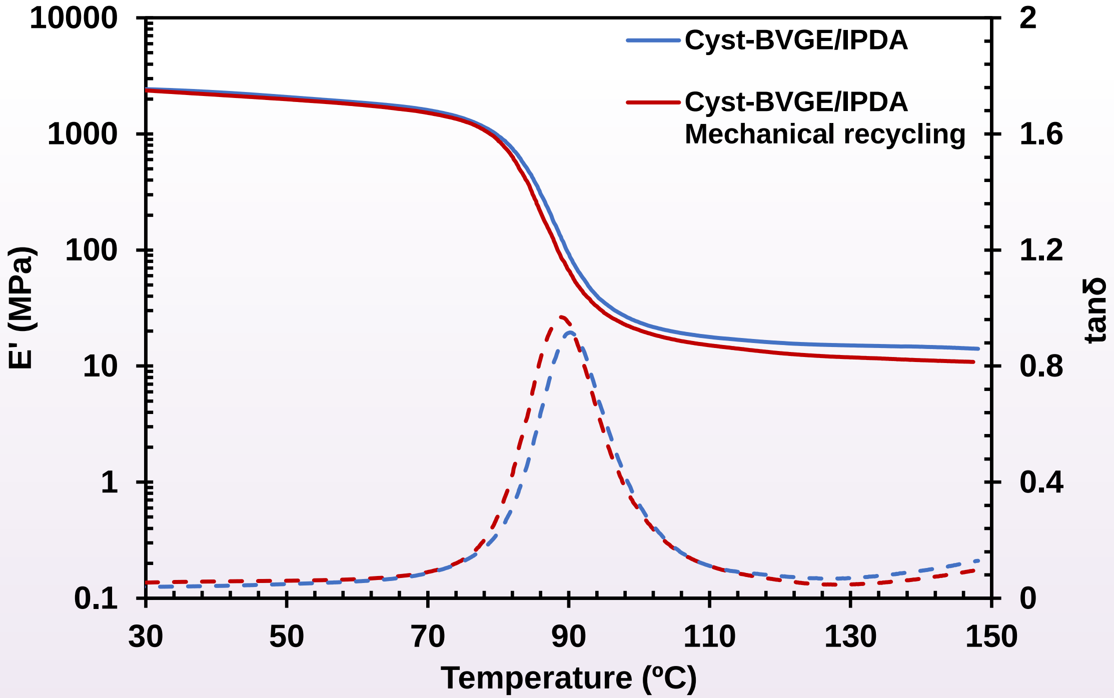
Results

Mechanical recycling



(a) Virgin grinded Cyst-BVGE/IPDA sample

(b) Sample after mechanical recycling at 140 °C and 0.4 MPa for 1 h.

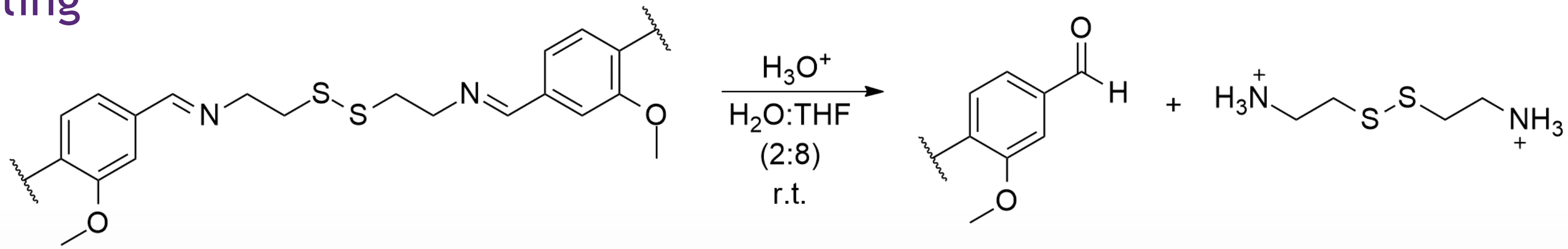


No remarkable differences were found in the thermomechanical properties of the recycled material.

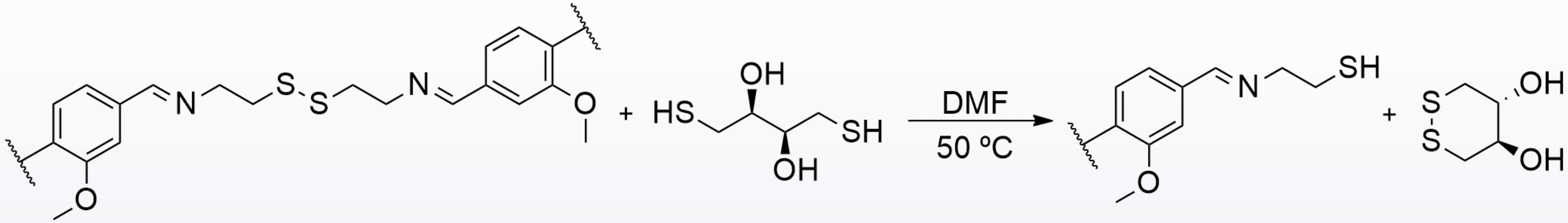
Results

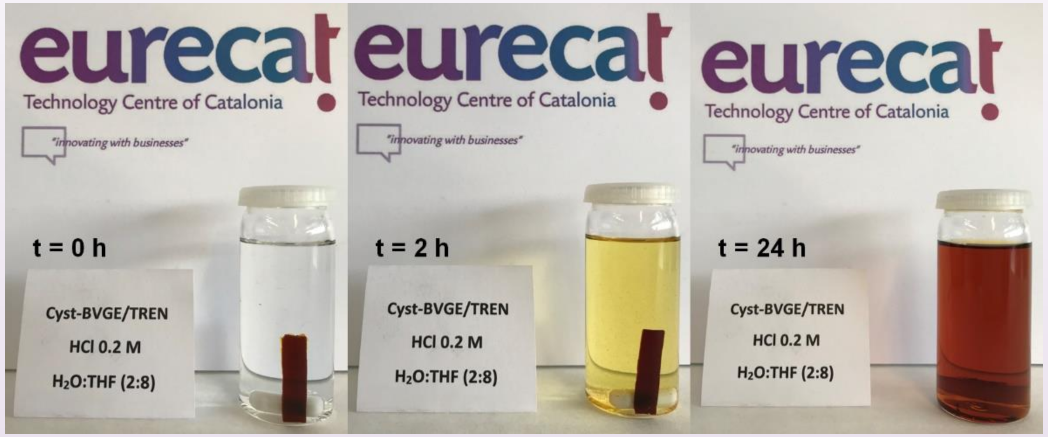
Chemical recycling

Acid hydrolysis

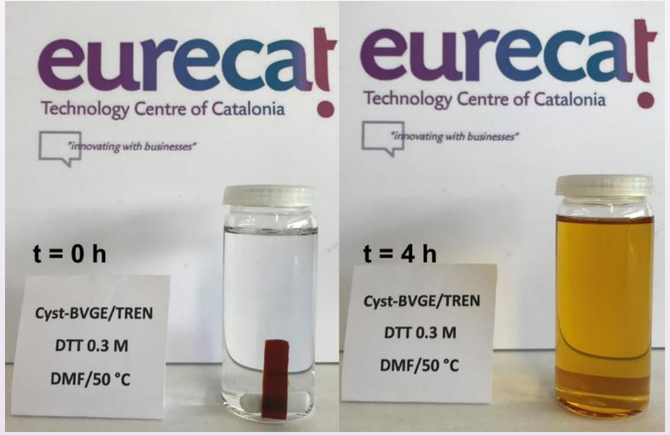


Thiol-disulfide exchange





Sample of Cyst-BVGE completely solubilized after 24 h in a 0.2 M HCl solution in H_2O:THF (2:8) at room temperature.

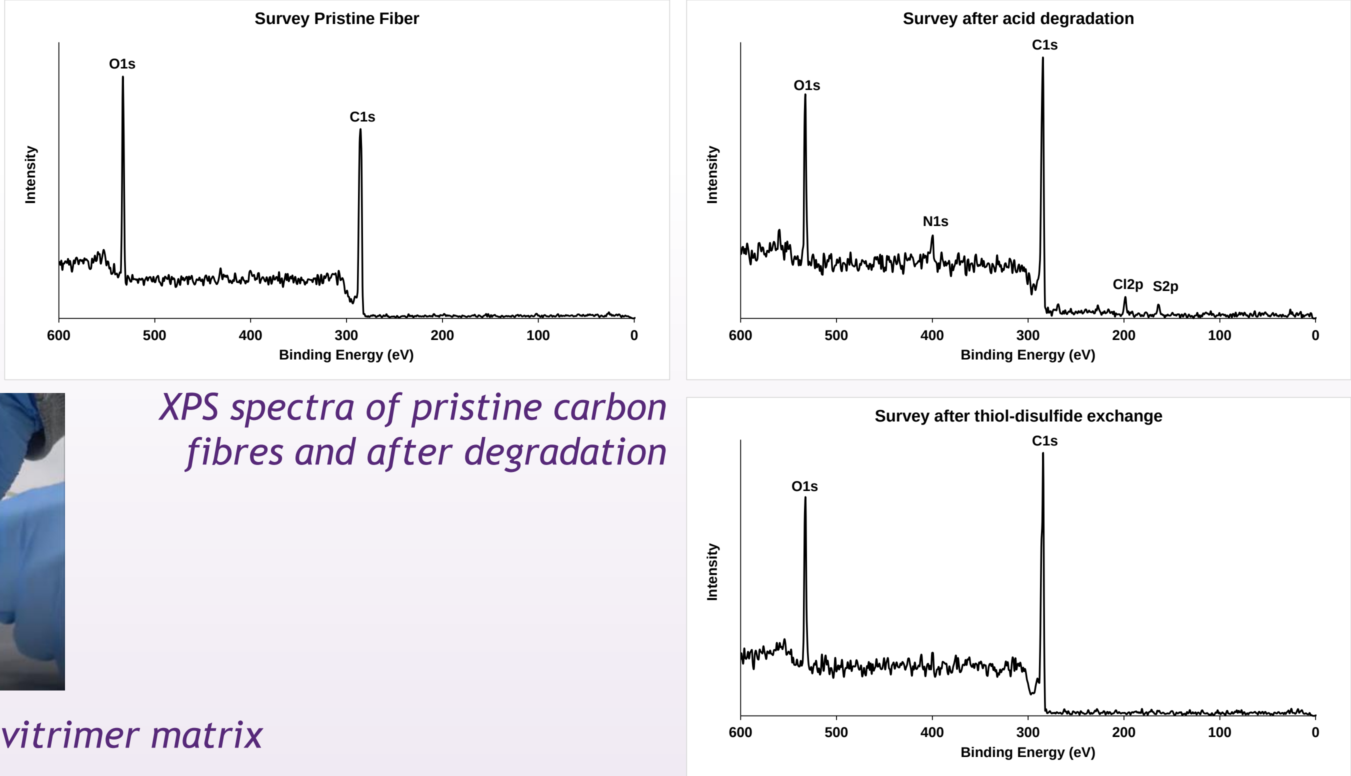


Sample of Cyst-BVGE completely solubilized after 4 h in a 0.3 M DTT solution in DMF at 50 ºC.

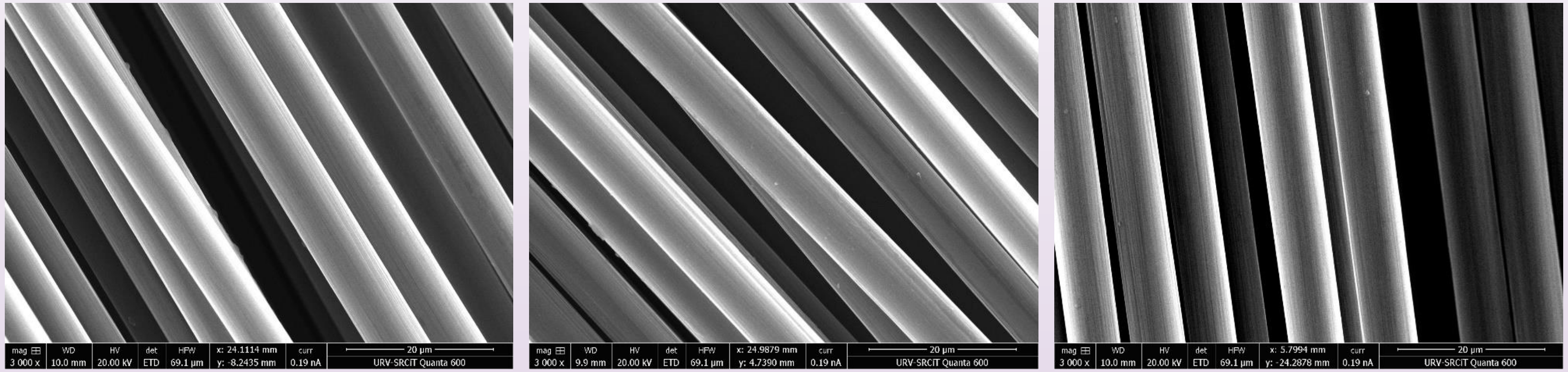
Results

Recycling of composites

Recycling process of carbon-fibre composite materials with vitrimer matrix



XPS spectra of pristine carbon fibres and after degradation



SEM images of carbon fibres after thiol-disulfide exchange degradation

Conclusions

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- Procedure for preparing an epoxy monomer containing 2 imine and 1 disulfide moieties as dynamic exchangeable groups.
- The process for synthesizing the monomer was completely renewable, from the starting materials to the procedure using renewable solvents.
- The materials obtained present a relatively high T_g
- The presence of imine and disulfide moieties allows for an extremely fast relaxation (<1min) at a relatively low temperature (160 ºC).
- The mechanical recycling of the materials allows the preparation of a new material with very similar properties.
- The easy chemical recycling allows the recovery of fibres of composite materials.
- The vitrimeric behavior of the material allows the preparation of functional adhesives and composite materials.

The results of this work are part of a European patent application (Ref. EP23383089.2, “Epoxy Vitrimer Formulations”, requested October 24th, 2023) and were published in ACS Sustainable Chem. Eng., 2024, 12, 15, 5965–5978 (DOI: 10.1021/acssuschemeng.4c00205).

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Thank you

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