VITRIMERS BASED ON EPOXIDIZED CARDANOL RESIN AND CYSTAMINE FOR 3D PRINTING APPLICATIONS

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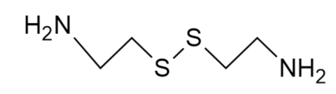
INTRODUCTION

With the aim of finding alternatives to fossil-based epoxies for 3D printing, a reprocessable bio-based vitrimer based on a bio epoxy resin (Cardolite® Lite 514HP) and cystamine was investigated. Cystamine was chosen as cross-linker due to its dynamic disulfide bonds, bio-based nature and the presence of highly reactive aliphatic amine groups, enabling rapid network formation. Microfibrillated cellulose (MFC) and ultrafine cellulose (UFC) were used as fillers and rheology modifiers to formulate printable pastes via Liquid Deposition Modeling. The bio-based pastes were printed into various structures by two consecutive steps: printing of the paste at RT followed by cross-linking in oven. Finally, a preliminary Life Cycle Assessment was performed to evaluate the environmental impact of the chemicals used.

MATERIALS

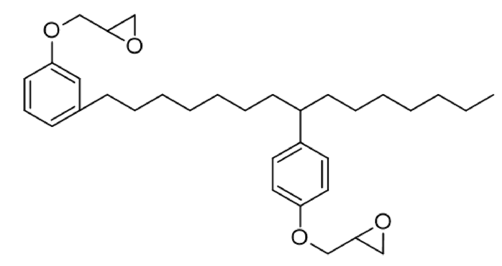
- Cystamine

  Desalination of cystamine needed to have a pure liquid cross-linker

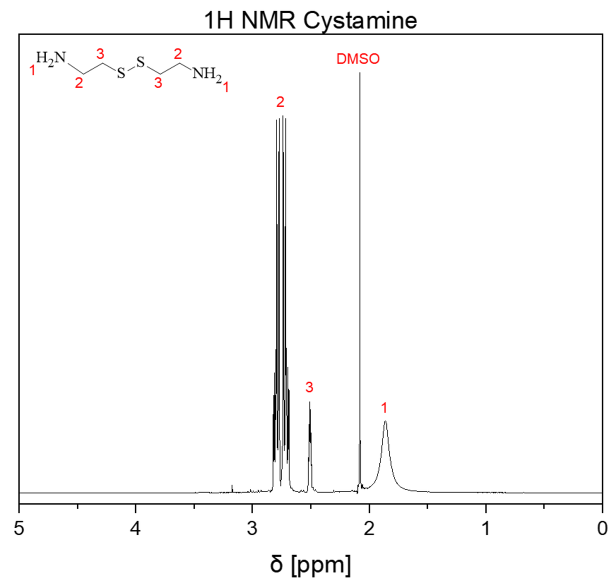


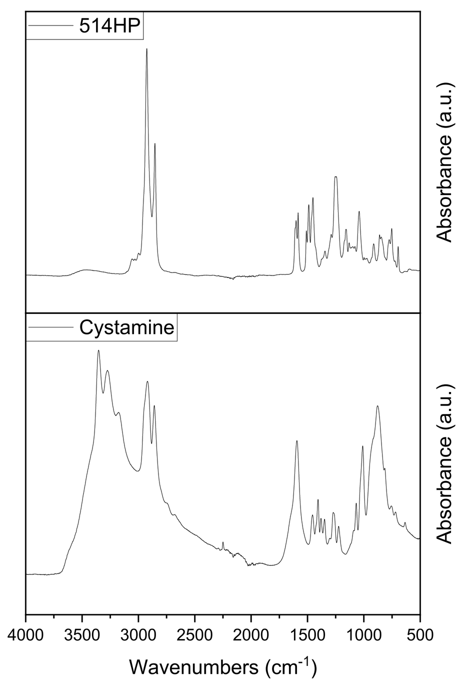
- Cardolite LITE 514HP

  Bio-based epoxy resin from cardanol oil extracted from chestnut shells

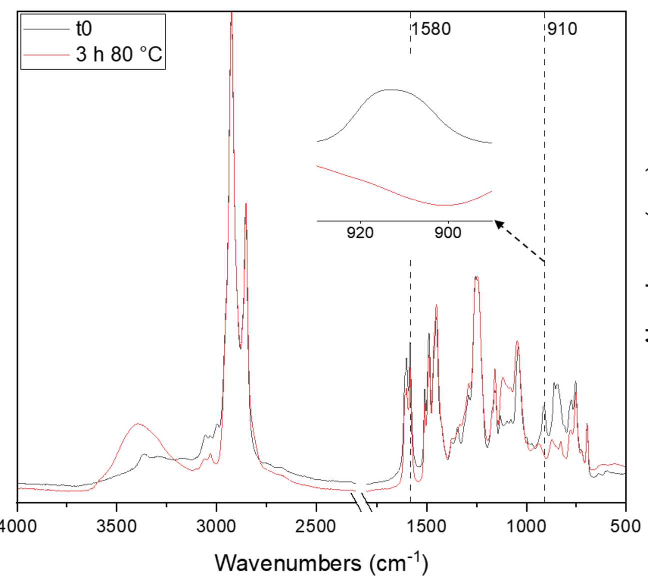


- Cellulose (Celova MFC 45 %, Technocel FM8 UFC)

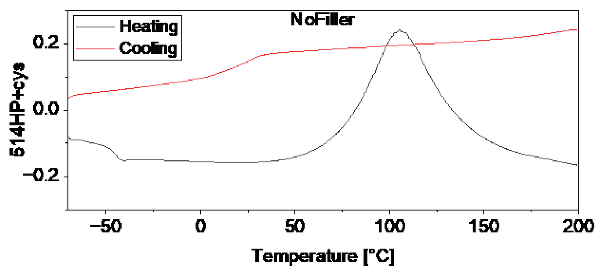




OPTIMIZATION OF THE CURING CYCLE

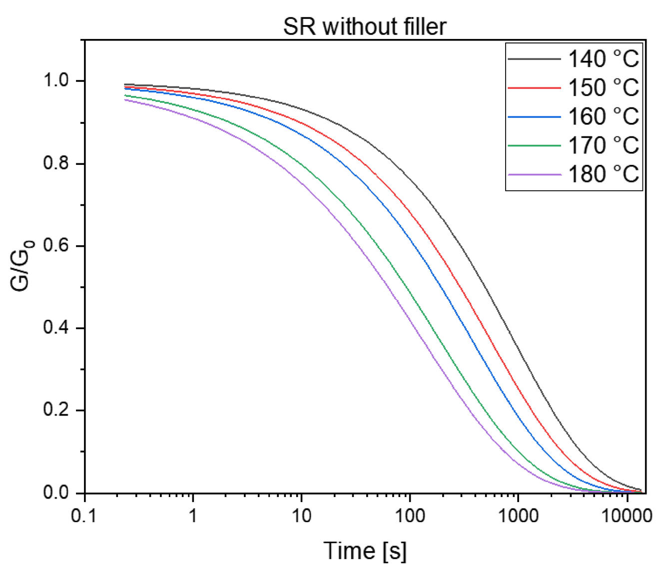


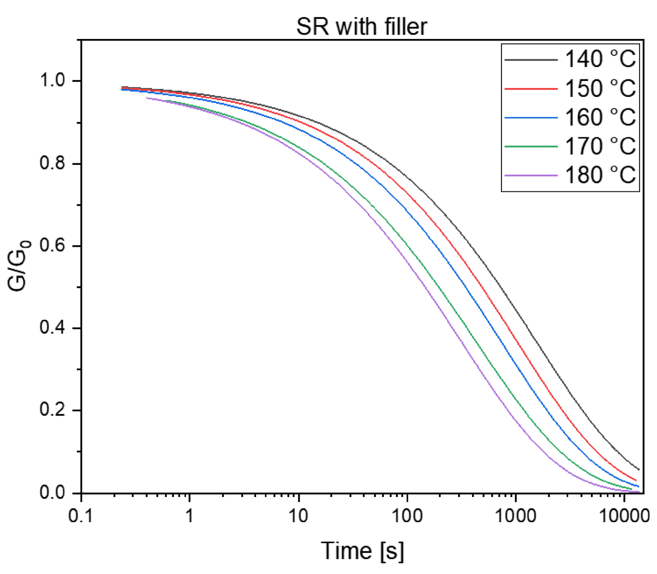
	Conversion [%]	% gel [%]	Swelling [%]
NoFiller	100	98.9 ± 0.1	1.8 ± 0.0
13UFC	94	99.9 ± 0.0	5.7 ± 0.3
13MFC	95 – 83	80.8 ± 0.2	24.8 ± 1.0
13MFC+9UFC	95	82.1 ± 0.4	27.2 ± 0.1
13MFC+11UFC	92	83.2 ± 0.0	29.5 ± 0.3
13MFC+13UFC	94	82.8 ± 0.0	28.9 ± 0.1



Optimization of the cross-linking cycle was done to maximize the conversion of epoxy groups: 3 h 80 °C.
MFC and UFC caused a general reduction of conversion and % gel with an increase of swelling in water.

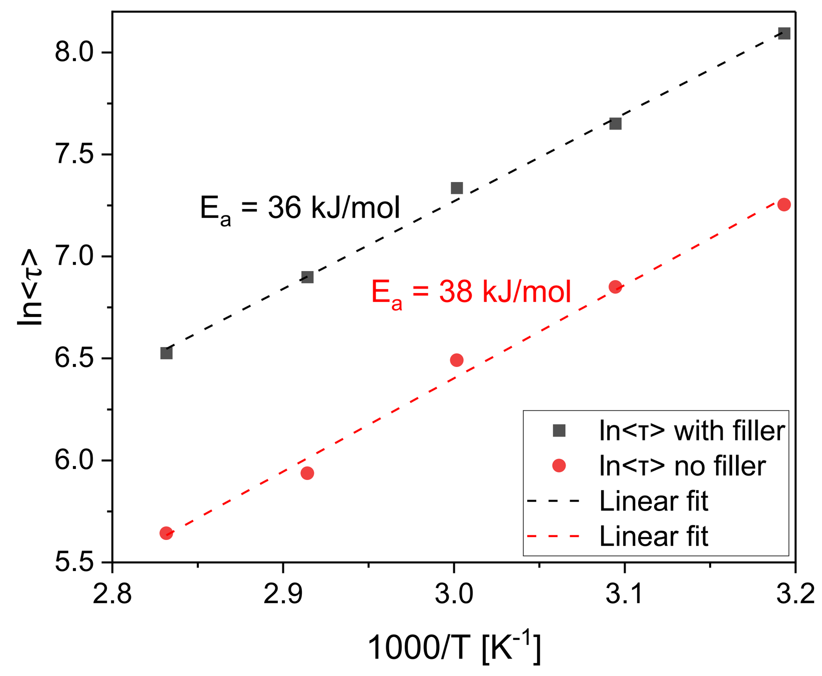
STRESS RELAXATION





	NoFiller		13MFC+13 UFC	
T [°C]	β	<τ> [s]	β	<τ> [s]
140	0.59	1414	0.48	3272
160	0.54	659	0.49	1533
180	0.48	282	0.48	682

Increase of stress relaxation time with consequent slowing effect on exchange kinetics for sample with cellulosic filler due to restricted mobility.



Logaritmic form of Arrhenius equation

$$lnK = lnA - \frac{E_a}{RT}$$

$$E_a = slope \times 8.314$$

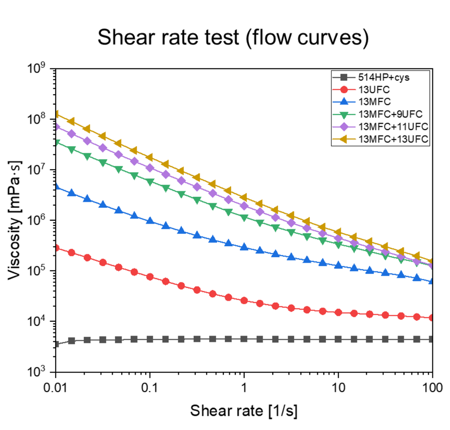
Comparable activation energies with same relaxation trend means **no difference in the relaxation mechanism**. Effect of the filler can be noticed only from the increase of the relaxation time <τ>.

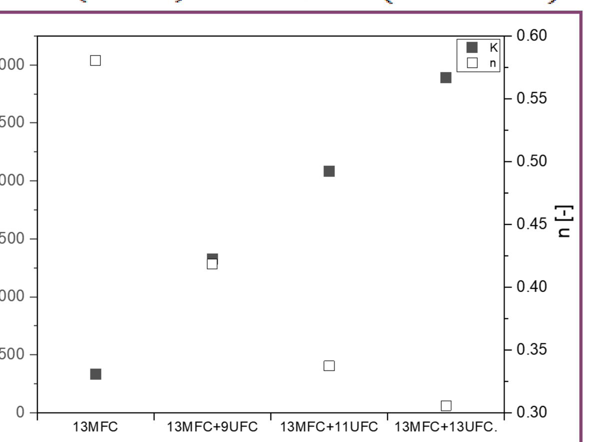
KWW = Kohlrausch–Williams–Watts: $G(t)/G_0 = G_{res}/G_0 + (1 - G_{res}/G_0)\exp(-t/\tau^*)^{\beta}$ ⟶ $<\tau> = (\tau^*\Gamma(1/\beta))/\beta$

$G(t)/G_0$ = normalized stress at time t, G_{res}/G_0 = fraction of residual relaxation modulus, τ* = characteristic relaxation time, β (0 < β ≤ 1) = stretching exponent, <τ> = characteristic average relaxation time

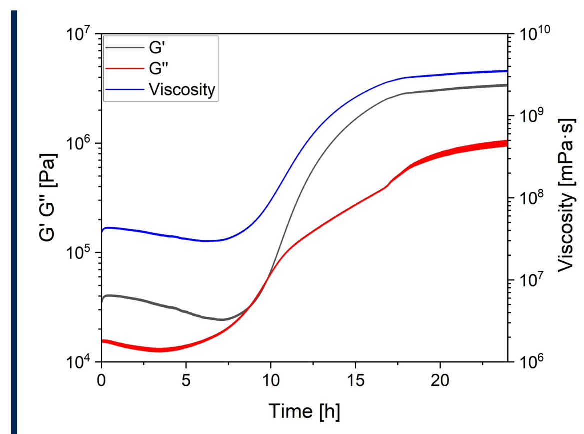
RHEOLOGY FOR 3D PRINTING

Herschel-Bulkley model: $ln(\tau - \tau 0) = lnK + n\,ln(shear\ rate)$

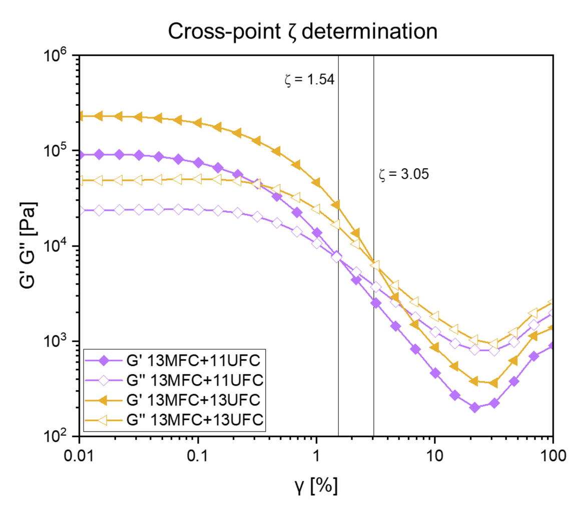


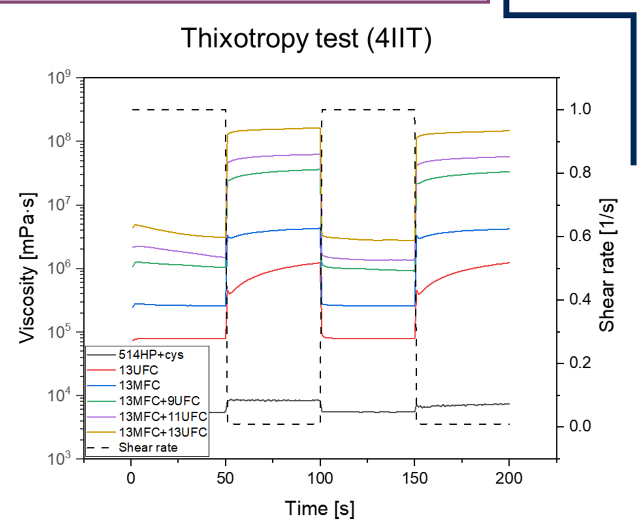


n = flow behavior index K = flow consistency index



Study of the rheology of the 13MFC+13UFC paste at 35 °C for determining the **gelification time**. The increase of G' and G'' after 12 h means gelification is reached.

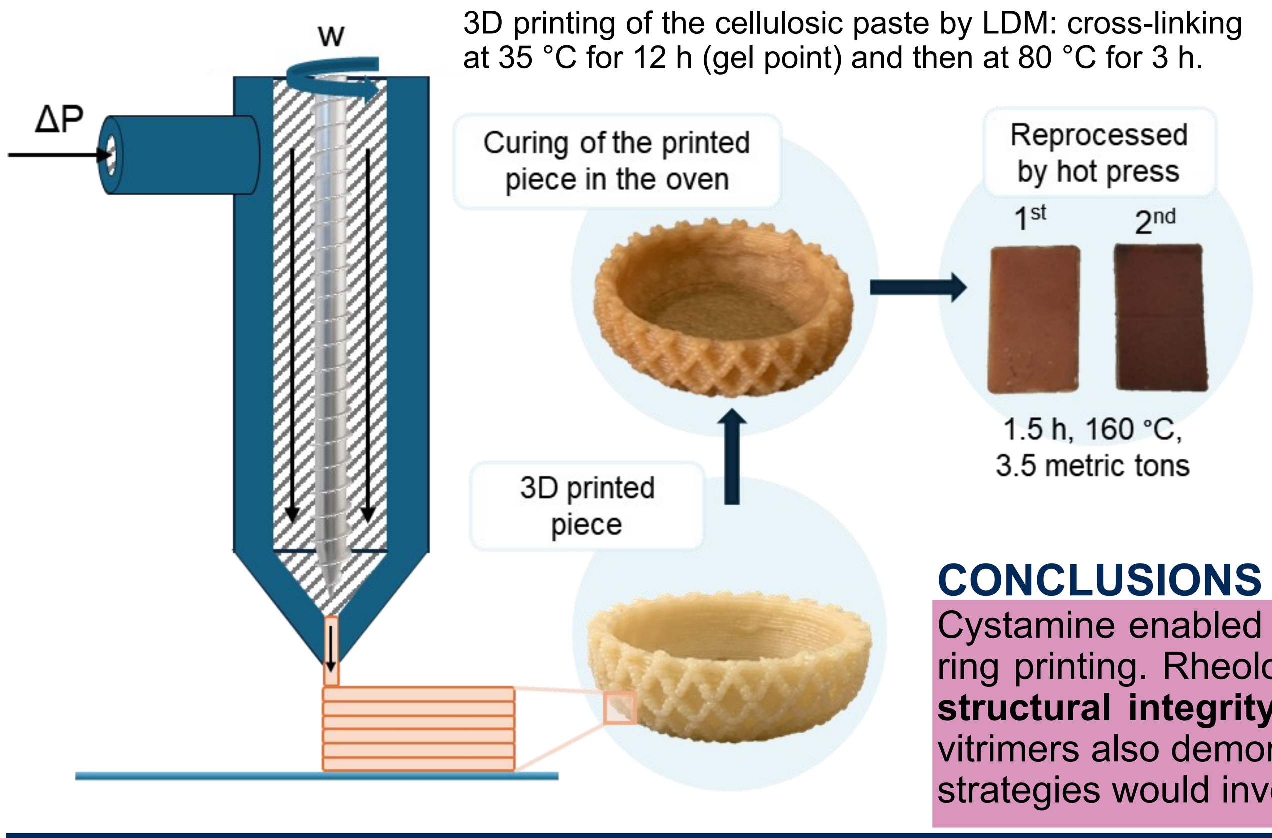




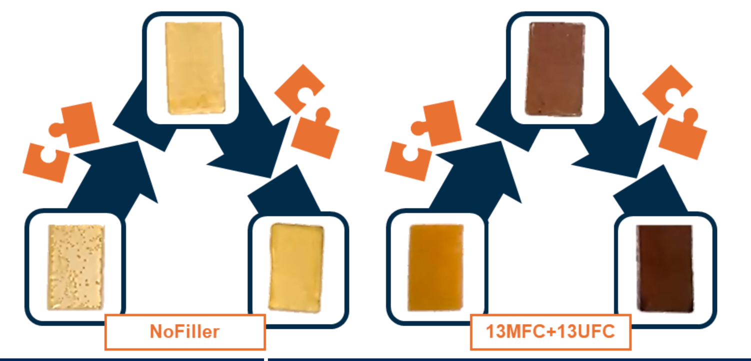
Cross-point between G' and G'' and thixotropy fundamental for a correct LDM printing.

LIQUID DEPOSITION MODELING

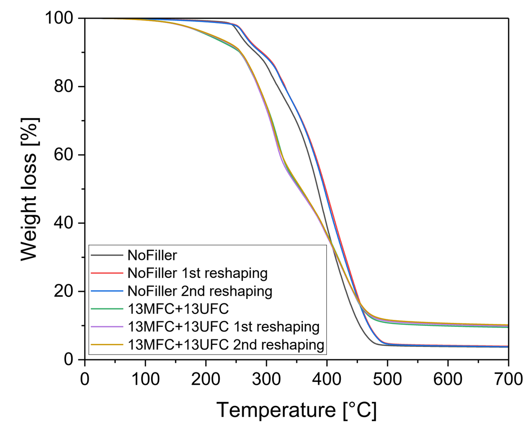
3D printing of the cellulosic paste by LDM: cross-linking at 35 °C for 12 h (gel point) and then at 80 °C for 3 h.

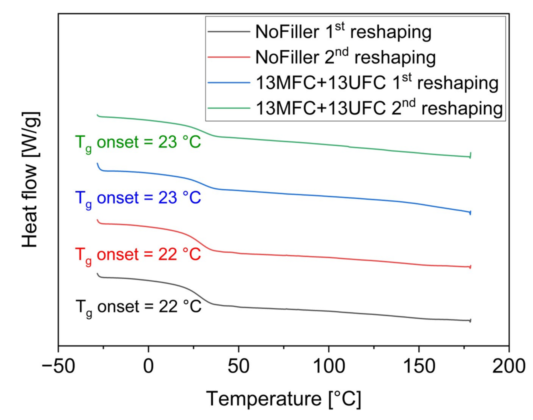


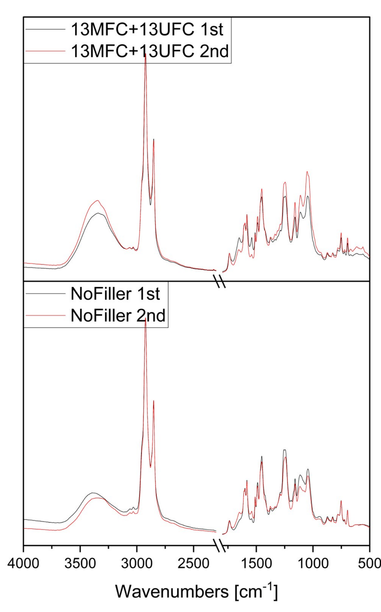
REPROCESSING



	NoFiller	13MFC+13UFC
Conversion 1st [%]	100 ± 0.0	100 ± 0.0
Conversion 2nd [%]	100 ± 0.0	100 ± 0.0
% gel 1st [%]	99.7 ± 0.3	83.0 ± 1.2
% gel 2nd [%]	99.3 ± 0.0	83.4 ± 2.1
T_g 1st [°C]	22	23
T_g 2nd [°C]	22	23
$T_{5\%}$ 1st [°C]	265	204
$T_{5\%}$ 2nd [°C]	264	204





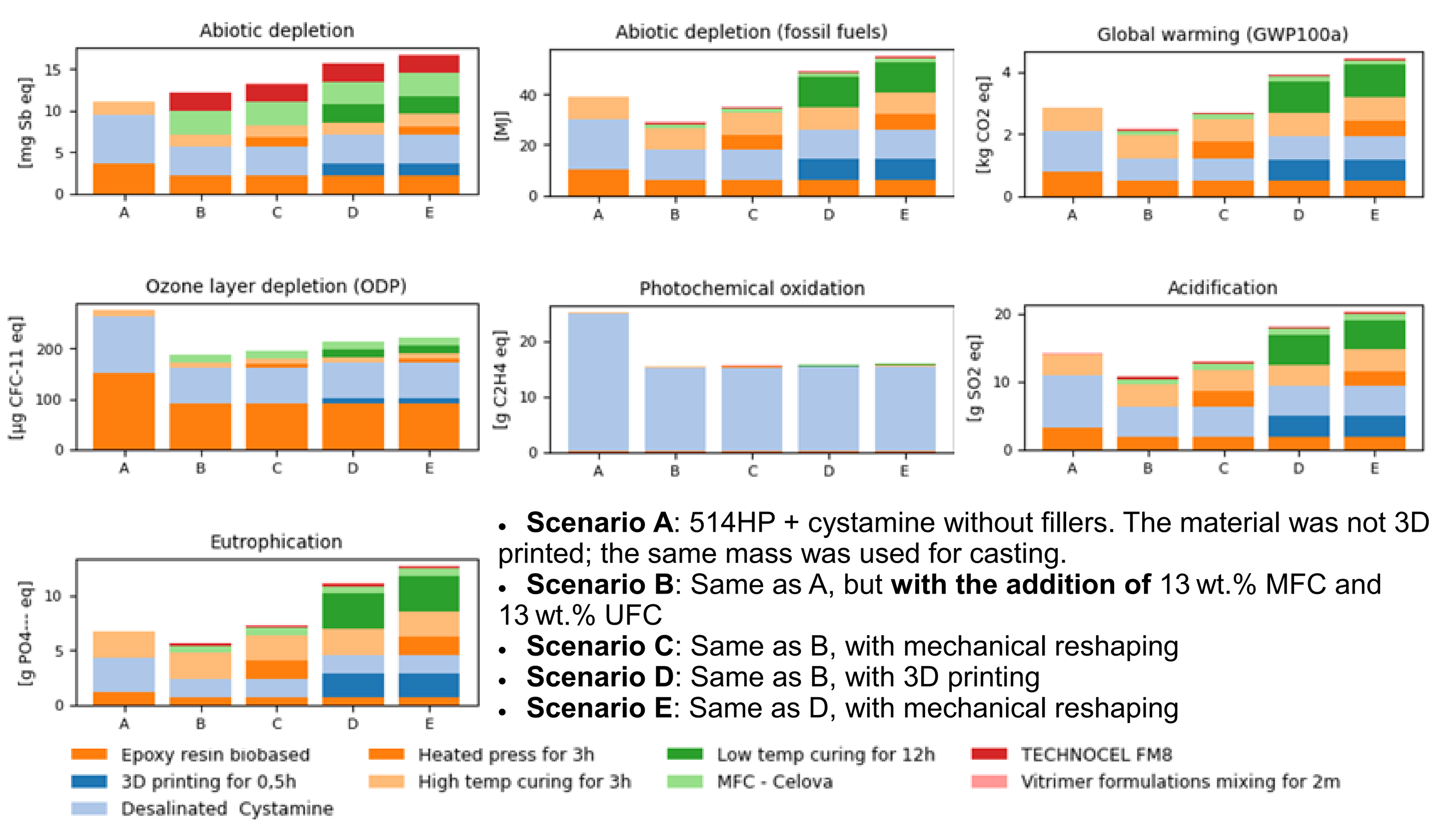


No difference between the reprocessing steps and good repeatability.

LIFE CYCLE ASSESSMENT

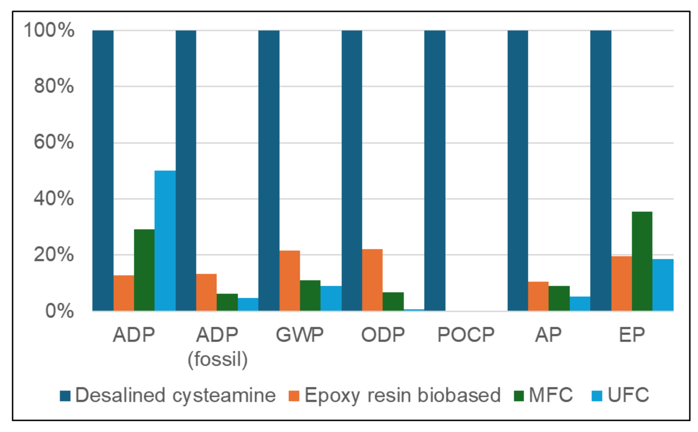
Preliminary Life Cycle Assessment (LCA) was carried out to evaluate the environmental performance of vitrimer production at laboratory scale by analyzing the contributions of individual components and process steps to the overall environmental footprint.

The functional unit = batch of 50 cylindrical samples measuring 3 cm in height and 2 cm in radius, weighing 5 g each (total batch weight of 250 g).



- **Scenario A**: 514HP + cystamine without fillers. The material was not 3D printed; the same mass was used for casting.
- **Scenario B**: Same as A, but **with the addition of** 13 wt.% MFC and 13 wt.% UFC
- **Scenario C**: Same as B, with mechanical reshaping
- **Scenario D**: Same as B, with 3D printing
- **Scenario E**: Same as D, with mechanical reshaping

Relative environmental impact of key materials in Scenario B:



Incorporation of fillers mitigates climate- and fossil-related impacts, but it introduces a trade-off in terms of non-fossil mineral resource use. **Scenario B** achieves an overall reduction in environmental impacts, but also a 10 % impact in the abiotic depletion category higher than **Scenario A**.

CONCLUSIONS

Cystamine enabled curing of printed structures at T low enough to prevent deformation in the oven, yet high enough to avoid premature curing during printing. Rheological tests identified a concentration of **13 wt.% MFC and UFC** as the optimal compromise between shear-flow behavior and **structural integrity**. The vitrimer behavior of the formulations with and without cellulose was confirmed by stress-relaxation measurements and the vitrimers also demonstrated **successful mechanical recyclability** (1.5 h, 160 °C, 3.5 metric tons). LCA suggested that the most effective mitigation strategies would involve improving the synthetic route for cystamine·HCl and implementing closed-loop solvent recovery to minimize emissions.

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