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Supporting Information for

Improved malleability of miniemulsion-based vitrimers through in-situ generation of carboxylate surfactants.

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Contents

1. Materials

Reagents: The hydrogenated **dimer fatty acid** (COOH eq. 282.3 mol g^{-1}), 2,4,6,8–tetramethyl–2,4,6,8–tetrakis (propyl glycidyl ether) cyclotetra siloxane (**CS697**, *contains also other epoxy-functional cyclosiloxane coumpounds*, epoxy eq. 169.3 g mol^{-1}), poly dimethyl siloxane diglycidyl ether terminated (**PDMS-diepoxy**, epoxy eq. 477.5 g mol^{-1}), xylene and were purchased from Aldrich and used as received. NB: The molar equivalents were measured by ^{1}H NMR from solutions with known concentrations of reagents and ethylene carbonate as reference compound.

Deionized (DI) water (Purelab Classic UV, ElgaLabWater) was used for all experiments. $CDCl_3$ was purchased from Eurisotop. Aqueous NaOH solution (1N, Acros Chemicals) was used quickly after opening

2. Instrumentation

DLS analysis was carried out using a Malvern Zetasizer Nano ZS instrument, using the back-scattered signal at 173° angle from highly diluted samples (1 drop latex in 2 mL DI-water). The cumulant analysis method was used to compute the average particle size Zav.

^{1}H NMR characterization was performed on a Bruker Avance II Spectrometer operating at 400 MHz.

All rheological characterizations (e.g. sintering and temperature-dependent creep tests) were realized sequentially using a MARS 60 rotational rheometer from Thermo Fischer Scientific using an 8 mm plate-plate geometry. Thoroughly dried latex samples (liquids) were deposed at in the rheometer preheated at 150°C and inerted by a nitrogen flow, and the gaps were adjusted to 0.8 – 1 mm. Sintering at 150°C was monitored using small amplitude oscillations (2% strain, then successively, 3, 50 and 1000 Pa during the crosslinking process) over a minimum of 9h. Subsequently, creep tests (3 kPa shear stress) were run from 170 to 110°C for 2000 to 3600s. The viscosity was measured once a constant strain rate is reached: $\eta_{creep} = \frac{\sigma}{\dot{\gamma}}$

FTIR spectra were realized on a Nicolet i550 FT-IR apparatus. Aliquots of latexes cured for various times at 120°C were cast on a ZnSe window, left to dry a few minutes at 90°C, then analyzed at room temperature in transmission.

pH was measured using a SevenEasy pH-meter from Mettler Toledo, equipped with an InLab Expert Pro-ISM electrode.

Sonication of miniemulsions was performed with a 750 W VibraCell 75043 apparatus (Bioblock Scientific) equipped with a 13 mm probe. The optimized sonication profile consists in 10 sec ON / 10 sec OFF periods for an effective sonication duration of 10 min, at 66% amplitude. The miniemulsions were maintained in an ice bath during the sonication.

DSC analysis was realized on pierced 40 µL aluminium pans on a DSC 3+ apparatus from Mettler Toledo. The latex were first dried by a 10 min isotherm at 150°C, then analyzed by several cooling/heating cycles at 10K/min.

DMA analysis was realized in tension film mode on a DMA 1 apparatus from Mettler Toledo. Films with were equilibrated at temperatures ranging from -130°C to -90°C and heated up to 200°C at 3K/min while applying a 20 µm amplitude deformation at 1 Hz.

3. Synthesis of vitrimer latexes

The organic phase, i.e. mixture of dimer fatty acids, PDMS-diepoxy, CS697 and xylene, was prepared as previously described (See Table S1 for weights). NB: samples containing zinc salts are synthesized using a specific batch of dimer fatty acids containing pre-dissolved Zinc acetate. [1]

	Dimer fatty acids		Epoxy			Xylene	TOTAL OIL	**Xyl Fraction**	**ratio epoxy/COOH**
	w(g)	n(mmol)	PDMS-diepoxy w(g)	CS697 w(g)	TOTAL n(mmol)	w(g)	w(g)		
Organic Phase	7.58	26.85	7.72	1.89	27.33	16	33.19	**0.482**	**1.018**

Table S1. Weights of epoxy-acid precursors using for the preparation of the organic phase.

In 150 mL vials are added the organic phase (4 g), DI-water (16 g). NaOH (1N, from 40mg to 600 mg) is added dropwise to the mixture under fast stirring. The emulsion formed was sonicated, transferred into pressure-resistant vials, and cured in an oven for 24h at 120°C.

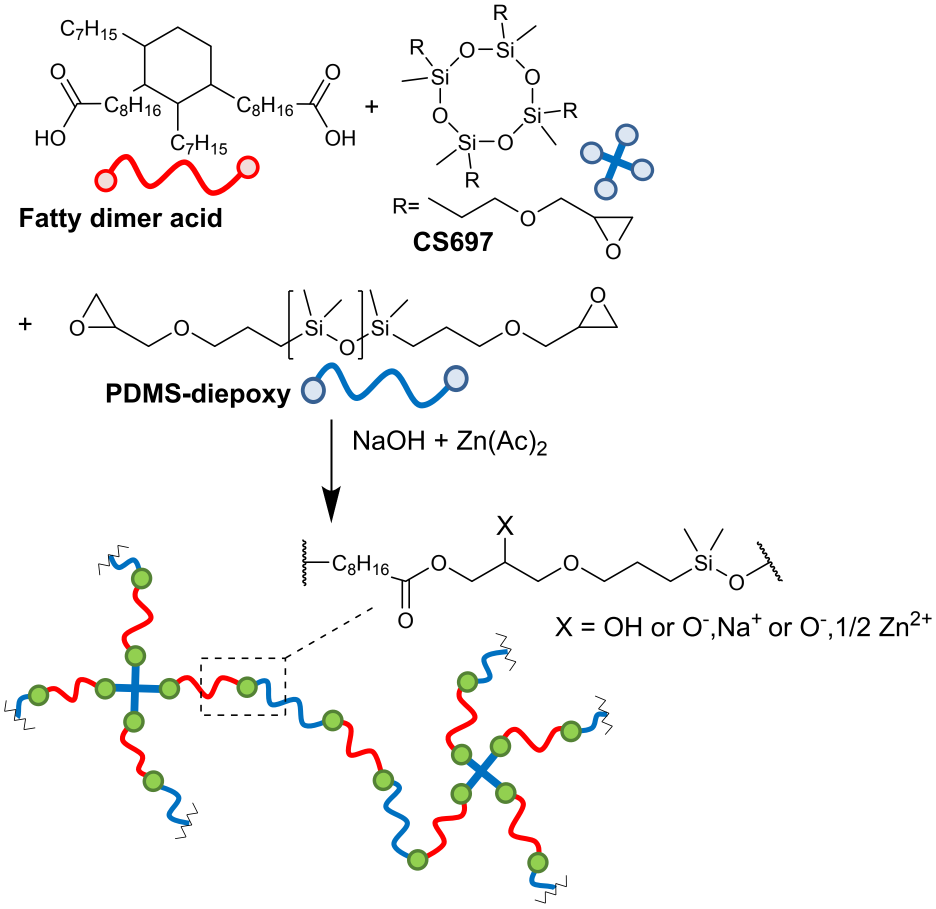


Figure S1– Schematic representation of monomers used and final network expected after complete, stoichiometric reaction of epoxydes with carboxylic acids.

4. Size distribution of vitrimer latexes

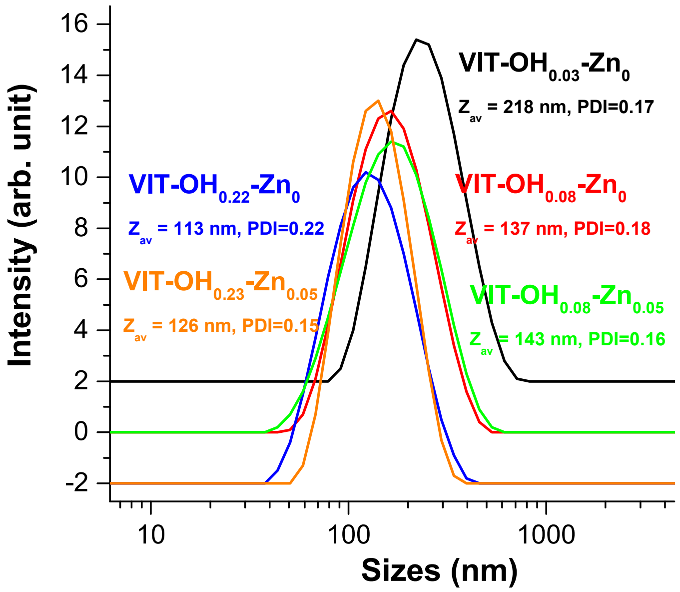


Figure S2 – Size distribution measured by DLS after sonication for the different samples

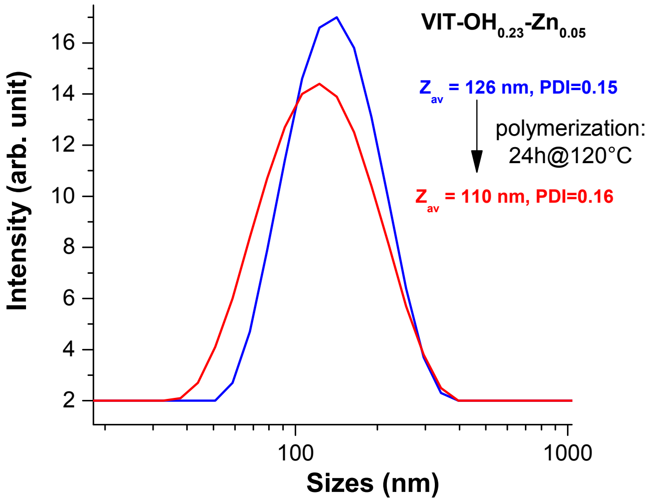


Figure S3- Size distribution measured by DLS for sample **VIT-0H$_{0.23}$-Zn$_{0.05}$** before and after polymerization (24h at 120°C)

5. ^{1}H NMR analysis of cured latexes

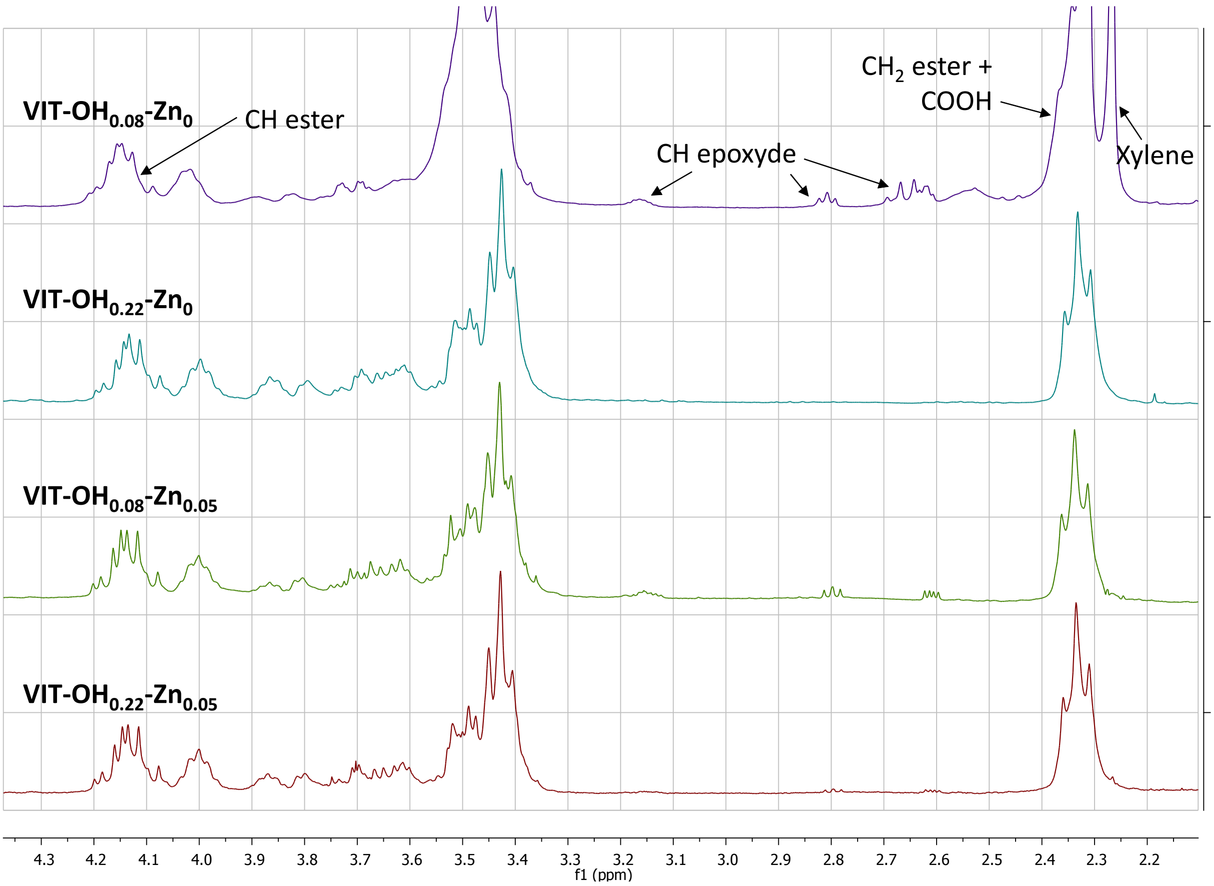
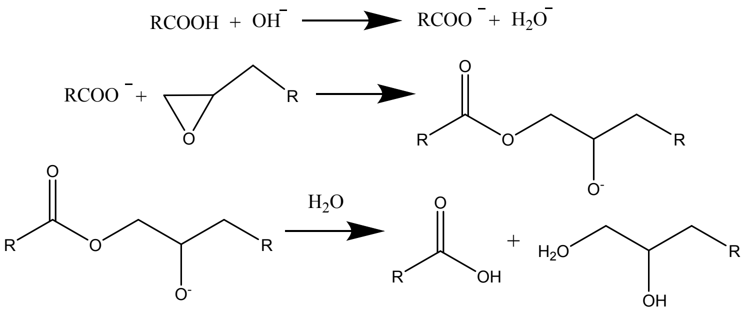


Figure S4 – ^{1}H NMR Spectrum (300 MHz) of vitrimer latexes cured at 120°C for 24h (49h for **VIT-OH$_{0.08}$-Zn$_0$**) and neutralized with TFA. Details of the signal attribution signals can be found in the previous paper.[1]

After curing the latex **VIT-OH$_{0.08}$-Zn$_0$** for 49h at 120°C, a few drops of trifluoroacetic acid (TFA) were added which caused immediate cracking of the emulsion. The organic phase was extracted with $CDCl_3$, evaporated to dryness, then redissolved in $CDCl_3$ and analyzed with ^{1}H NMR (300 MHz). It must be noted that an important amount of xylene is still present in sample **VIT-OH$_{0.08}$-Zn$_0$**, and was accounted for when comparing the integrals. The integral normalization was set so I(R-CH$_2$-COOR') = 200 (esters + carboxylic acids), which gives directly the molar fraction of epoxydes (CH at 3.15 and 2.8 ppm) and of β-hydroxyl esters (CH at 4.2 ppm). These integrals enable to calculate i) the epoxyde consumption: $x_{ep} = 1 - \frac{n_{ep}}{n_{ester} + n_{COOH}}$ and ii) the final ratio of carboxylic acids: $x_{COOH} = \frac{n_{COOH}}{n_{ester} + n_{COOH}}$ which are reported in **Table S1**. It must be noted that the final ratio of carboxylic acids is expected to depend i) on the epoxy/acid reaction and ii) on the potential hydrolysis of hydroxylesters.



In all cases, the final ratio of carboxylic acids was found to be lower than 10%, thus demonstrating very limited hydrolysis and excellent control of the epoxy-acid reaction.

Sample	x_{ep}	x_{COOH}
VIT-OH$_{0.08}$-Zn$_0$	0.94	0.03
VIT-OH$_{0.22}$-Zn$_0$	>0.99	0.09
VIT-OH$_{0.08}$-Zn$_{0.05}$	0.96	0.03
VIT-OH$_{0.22}$-Zn$_{0.05}$	0.99	0.10

Table S2 – Epoxyde consumption and final ratio of carboxylic acids of different vitrimer samples after curing, as defined above.

6. Sintering monitoring

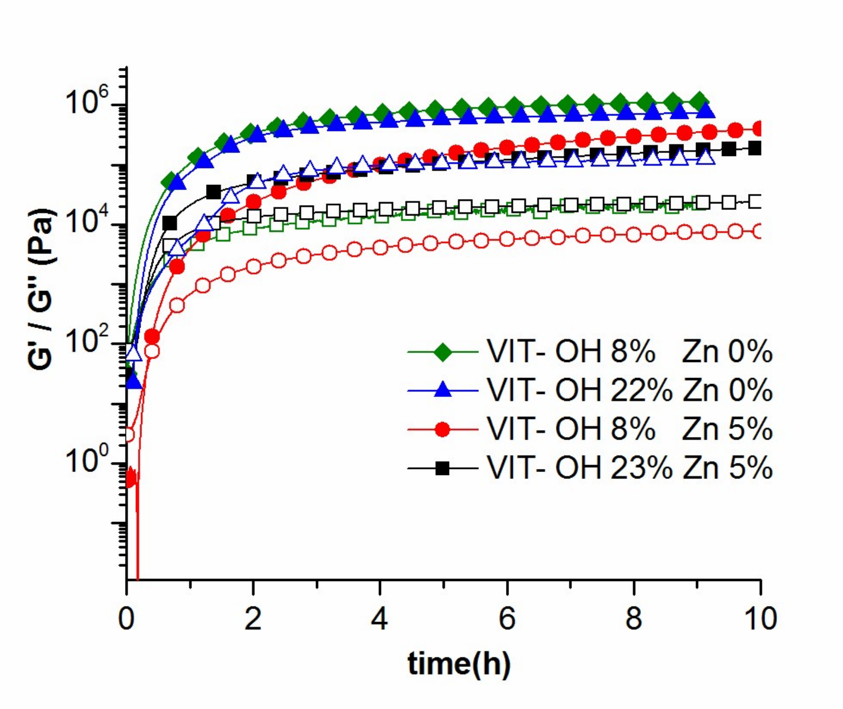


Figure S5 – Sintering of vitrimer particles at 150°C monitored by small amplitude oscillatory shear. G’ and G’’ are represented in full and open symbols, respectively.

7. DSC analysis

The vitrimers were analyzed by DSC at different stages: i) after curing in miniemulsion for 24h at 120°C and subsequent drying of volatiles (10 min at 150°C), ii) following step i) and 2h curing at 150°C and iii) following step i) and 24h at 150°C. Figure S6 displays the heating thermograms for sample **VIT-OH$_{0.08}$-Zn$_{0.05}$**, the T_gs measured for the other samples are reported in Table S2.

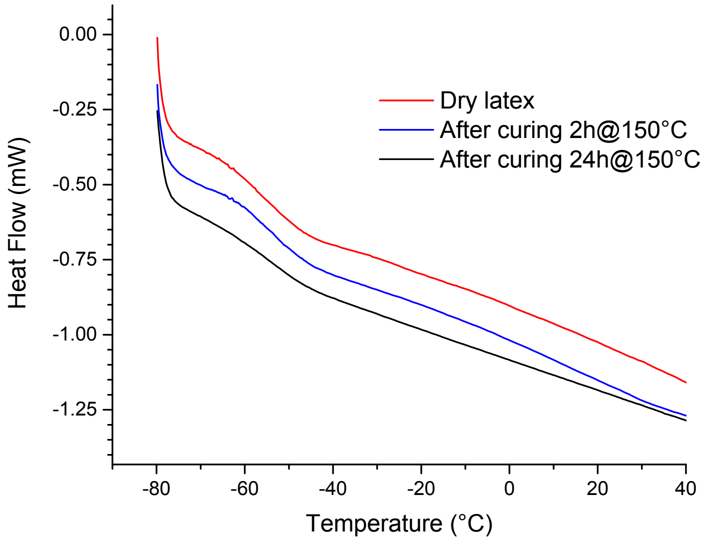


Figure S6 – DSC thermograms (heating curves) of sample **VIT-OH$_{0.08}$-Zn$_{0.05}$** after different heating treatments.

Sample	T_g (latex)	T_g (2h@150°C)	T_g(24h@150°C)
VIT-OH$_{0.08}$-Zn$_0$	-54.2	-49.6	-52.9
VIT-OH$_{0.22}$-Zn$_0$	-47	-46	-52
VIT-OH$_{0.08}$-Zn$_{0.05}$	-52.4	-52.6	-52.2
VIT-OH$_{0.22}$-Zn$_{0.05}$	-30.3	-25.2	-23.1

Table S3 – Values of glass transition of vitrimer samples after different heating treatments.

8. Dynamical Mechanical Analysis of vitrimer films

Vitrimer films were obtained by casting the corresponding latexes in Teflon moulds, slowly drying the films (a few hours at 100°C), then sintering the films in a vacuum oven for 24h at 150°C.

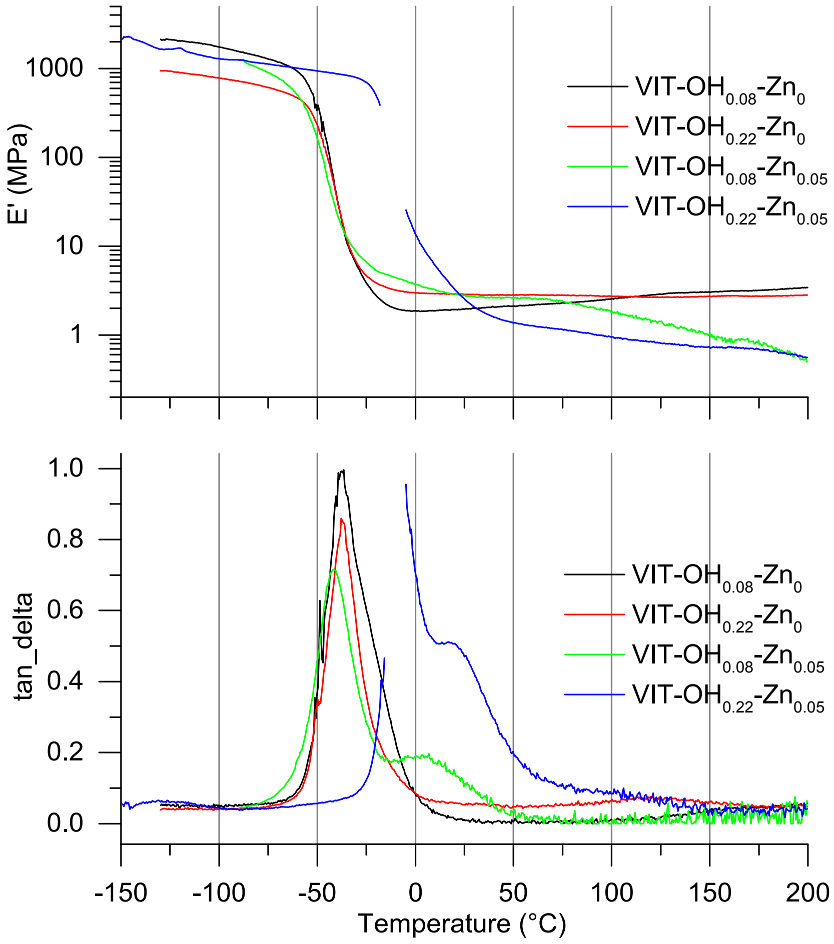


Figure S7– Dynamical Mechanical Analysis of fully sintered samples (1Hz, 3K/min).

[1] T. N. Tran, E. Rawstron, E. Bourgeat-Lami, D. Montarnal, *ACS Macro Letters* **2018**, *7*, 376.