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Thi Nga Tran, Eleanor Rawstron, Elodie Bourgeat-Lami, Damien Montarnal. Formation of Cross-Linked Films from Immiscible Precursors through Sintering of Vitriemer Nanoparticles. *ACS Macro Letters*, 2018, 7 (3), pp.376 - 380. 10.1021/acsmacrolett.8b00173 . hal-01859495

HAL Id: hal-01859495

<https://hal.science/hal-01859495>

Submitted on 8 Oct 2021

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Formation of Crosslinked Films from Immiscible Precursors through Sintering of Vitrimer Nanoparticles.

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Supporting Information Placeholder

ABSTRACT: Colloidal dispersions of epoxy-acid vitrimers have been synthesized by miniemulsion polymerization. This versatile strategy enables to obtain stable crosslinked particles even from initially incompatible precursors, while minimizing hydrolysis of the ester bonds formed during the curing. After drying of the latexes, trans-esterification exchanges occurring at high temperatures through inter-particle interfaces induces an efficient sintering into homogeneous crosslinked polymer films.

Blending polymers of drastically different nature (e.g. high T_g / low T_g, polar / apolar, hydrophilic / hydrophobic, semi-crystalline / amorphous) offers a very versatile strategy to combine and/or create new properties. Often, such polymers are incompatible and tend to phase separate at a macroscopic scale. To overcome this inconvenience, various methods have been developed for over fifty years, including high-shear mixing, addition of compatibilizers or reactive copolymerization at polymer interfaces.^{1,2} The extent of phase separation can thus be limited to domain sizes ranging from a few microns to tens of nanometers, greatly improving the mechanical properties of these materials. Obtaining covalently crosslinked networks from incompatible precursors following these same methods is considerably more challenging, as intimate mixing is essential to promote efficient chemical reactions between the precursors. Reactive copolymerization under shear is a noteworthy strategy,³ yet the viscosity of the polymer gradually increases, eventually preventing further pro-

cessing such as injection molding or fiber impregnation, as well as proper homogeneity after gelation has occurred. It is possible to use non-specific solvents as compatibilizers in order to crosslink the incompatible precursors into gels. However, considerable stresses arise upon drying such gels; the crosslinked materials obtained can be brittle and show poor shape control due to extensive shrinking.⁴

Vitrimers, i.e. dynamic networks crosslinked by exchangeable covalent bonds, offer unique features in this context: these covalently crosslinked materials can relax stresses thanks to bond-exchange reactions between crosslinks and flow like thermoplastics.⁵⁻⁷ We present here for the first time the synthesis of vitrimer nanoparticles, and illustrate the usefulness of such materials by preparing homogeneous, crosslinked polymer films from incompatible epoxy – acid vitrimer precursors in four steps (Figure 1). First, the incompatible precursors are pre-compatible with a co-solvent (xylene) and emulsified with a surfactant into nanodroplets serving as individual reactors. Then the emulsion is cured, thus transforming each droplet of precursors into a vitrimer nanoparticle swollen with co-solvent. In a third step the water and co-solvent are dried, yielding solvent-free vitrimer nanoparticles. Finally the vitrimer nanoparticles can be sintered together to form a homogeneously crosslinked, bulk polymer network. Thanks to the reduced size of the nanoparticles (ca. 100 nm), inter-particle contact and effective exchange reactions at the interfaces can occur without external pressure.

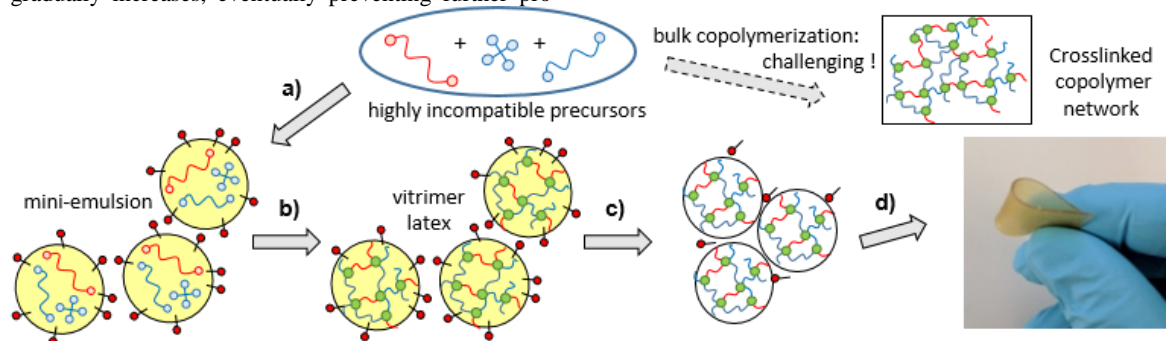
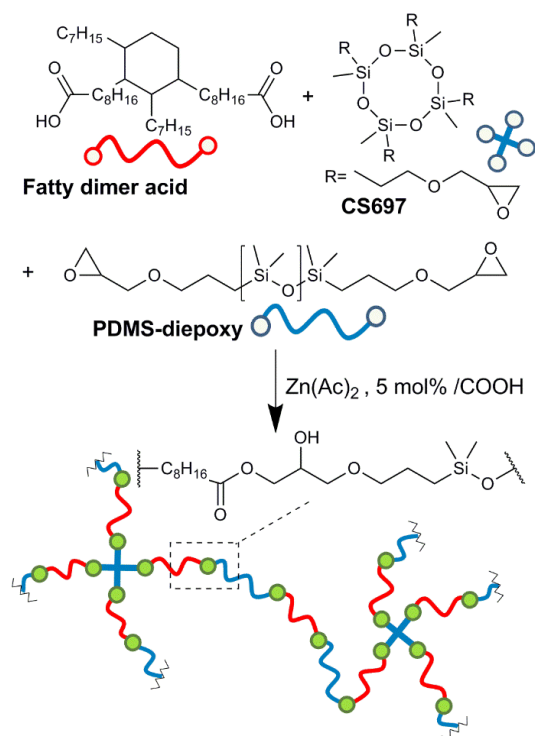


Figure 1. Schematic representation of our strategy to crosslink incompatible precursors by formation of vitrimer nanoparticles. a) Formation of an emulsion of precursors pre-compatible with an organic solvent (yellow); b) Crosslinking of the precursors in the nano-

droplets; c) Drying of water and the organic solvent, yielding solvent-free crosslinked nanoparticles and d) Sintering of the nanoparticles into a homogeneous crosslinked film through exchange reactions at the interfaces at high temperature.

Our choice of incompatible precursors is motivated by the strong interest of the paint industry for silicone-based protective coatings that combine greater resistance to water with increased thermal resistance.⁸ Such improvements are only significant at high levels of silicone incorporation, typically between 30% and 50%. In such conditions, silicones are strongly incompatible with most monomers or polymers, thus far needing to be chemically modified for compatibility and/or pre-reacted under shear. Notably, vitrimers obtained from epoxy-functional PDMS and trimer fatty acids have been obtained through pre-reactive mixing in bulk at high temperature followed by curing into moulds.⁹ Following this strategy, the compatibilized prepolymers have a considerably increased viscosity and meticulous control of the pre-reaction is critical to avoid gelation.

Epoxy-acid polyadditions, in combination with $\text{Zn}(\text{Ac})_2$ catalyst promoting i) β -hydroxyl ester formation and ii) subsequent transesterifications between hydroxyls and ester bonds, have been widely used to produce vitrimer materials.^{6,10–18} We chose to illustrate the versatility of our strategy by selecting a commercially-available diglycidyl ether-terminated poly (dimethyl siloxane) oligomer (**PDMS-diepoxy**, $M_n = 800 \text{ g mol}^{-1}$) and fatty hydrogenated dimer acid (see Figure 2 for the representation of our system). A poly-functional component is also required as a crosslinker, we chose a commercial tetrafunctional epoxy molecule: 2,4,6,8-tetramethyl-2,4,6,8-tetrakis(propyl glycidyl ether) cyclotetrasiloxane (**CS697**). A weight ratio between **CS697** and **PDMS-diepoxy** of 1:4 is maintained throughout this study. The three incompatible precursors are compatibilized by adding 50



wt% of xylene.

Figure 2. Formation of the crosslinked network from **PDMS-diepoxy**, **fatty dimer acids**, and crosslinker **CS697**. The amounts of reactants are adjusted to maintain a 1:1:0.05 molar ratio of carboxylic acids, epoxides and $\text{Zn}(\text{Ac})_2$.

Miniemulsion polymerization is our preferred method to obtain vitrimer particles from such incompatible precursors. This technique is particularly adapted to very hydrophobic reactants and

affords submicronic droplets with minimal mass transport of reactants during the polymerization time.^{19–21} Analogously to other polyaddition reactions,²² it is essential to maintain a stoichiometric epoxy:acid ratio within the droplets throughout the polymerization for efficient crosslinking, and also to minimize the contact of the reactants with water, which leads to hydrolysis of the esters and possible ring-opening of epoxides under basic/acidic conditions. Remarkably, Landfester and Barrère reported miniemulsion polymerization synthesis of polyesters from diacids and diols,²³ which pose even greater challenges as water is formed as a byproduct of the esterification reaction.

Depending on the composition of the system, destabilization of the miniemulsion and complete phase separation into aqueous and oil phases can occur after a few hours at 120°C. We investigated in detail the influence of the nature and concentration of surfactants in the aqueous phase, and of the amount of oil phase dispersed. Aliquots of the latex were taken after different curing times, and the size distribution of the droplets was analyzed with dynamic light scattering (DLS). It should be noted that in many cases the size distributions measured are relatively large; we used the Z_{av} value obtained by the technique of cumulants as an indicator of droplet diameters only for comparative purposes.

Figure S1 in Supplementary Information displays the comparison of droplet diameters at 25°C, immediately after sonication when different surfactants are used. A 10 mM concentration of surfactants is used (i.e. well above their critical micellar concentration in all cases, *abbreviations and full description of the different surfactants can be found in Table S1 in Supplementary Information*). Anionic surfactants such as sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) or Dowfax 2A1 perform much better than non-ionic or cationic surfactants. They lead to small miniemulsion droplets, stable for several months at room temperature.

At 120°C the stability of the miniemulsions is dramatically affected and only SDS-stabilized emulsions are stable after a few hours (see Figure S2 in Supplementary Information for time-dependent stabilities at 120°C, with various surfactant concentrations and oil phase contents). Notably, the stability significantly increases for high concentrations of SDS ($\geq 25 \text{ mM}$) or low amounts of oil phase ($\leq 20 \text{ wt\%}$). The curing reaction between the epoxide and acid precursors was monitored using separate miniemulsion polymerizations (30 mM SDS and 20 wt% oil phase) run at 120°C for different durations. The obtained latexes were dried and analyzed with ^1H NMR (see Figure S3a and S3b in Supporting Information). At first, the consumption of epoxide groups is concomitant with the formation of ester groups. After 16h, all epoxide groups are effectively consumed, yet the amount of esters starts to decay. We attributed this to the hydrolysis of the β -hydroxyl esters into mono-glycerols and carboxylic acids as confirmed by NMR (Figure 3). The latexes remain stable during the whole duration of the experiments up to 30h. Cryo-TEM analysis of a latex cured for 23h (Figure 4) confirms the formation of spherical particles with large polydispersity and diameters in accordance with DLS measurements.

The optimal curing time of about 10-12h at 120°C, yielding the highest content of esters, is also supported by measurements of gel fractions in the final latex (see Supporting Information for details). The latexes cured for 8h (VP8), 12h (VP12) and 18h (VP18) showed a gel fraction of 74 wt%, 86 wt% and 74 wt%, respectively. As expected, the evolution of the gel fraction follows the same trend than the amount of β -hydroxyl esters; the latter are indeed forming the bonds effectively maintaining the crosslinked polymer network. Further ^1H NMR analysis on the **VP12** sample

also confirms that the sol fraction contains a higher amount of hydrolyzed species (see Figure S4 in the Supplementary Information).

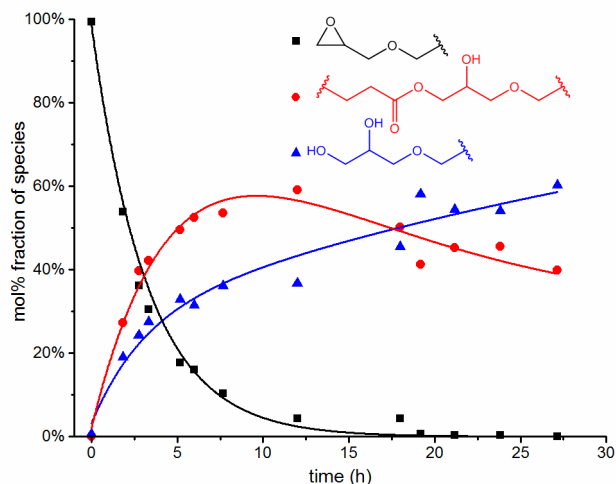


Figure 3. Monitoring of the reaction by ^1H NMR involving conversion of epoxide groups (black) by reaction with carboxylic acids into β -hydroxyl esters (red), and further hydrolysis into mono-glycerols (blue).

After evaporation to dryness, the latexes do not form films but rather viscous oils, since the crosslinked particles have a T_g significantly below room temperature. Rheological characterization of dried **VP12** at 25°C (Figure S5a and S5b in Supplementary Information) reveals a Newtonian behavior ($\eta = 17 \text{ Pa}\cdot\text{s}$) over the short range of shear rates tested ($0.1 - 20 \text{ s}^{-1}$).

The sintering of vitrimer nanoparticles was assessed by heating the samples at 150°C and monitoring their rheological behavior with oscillatory shear. Figure 5a shows the rheological profiles for the latexes **VP8**, **VP12** and **VP18**. The low-viscosity samples remain almost unchanged during an induction period, before crosslinking occurs very quickly (G^* increases by up to 5 orders of magnitude within 20 min). Eventually, the storage modulus reaches a plateau when the sample is fully crosslinked ($G' \gg G''$, independent of frequency). Homogeneous and flexible crosslinked films can be obtained thanks to this sintering process.

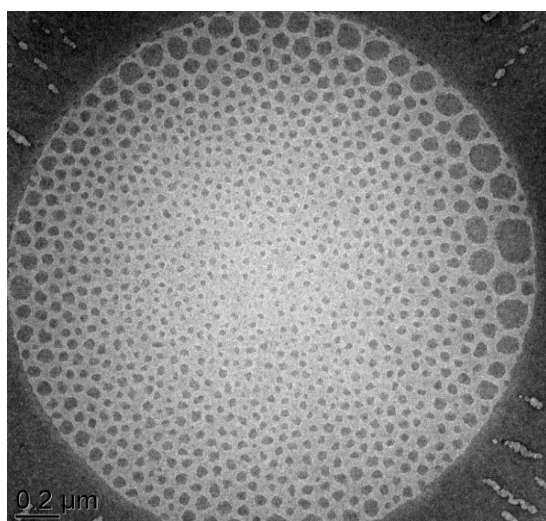


Figure 4. Cryo-TEM image of a vitrimer latex obtained crosslinking the precursors within the droplets (20 wt% oil content, 30 mM SDS, cured for 23h at 120°C).

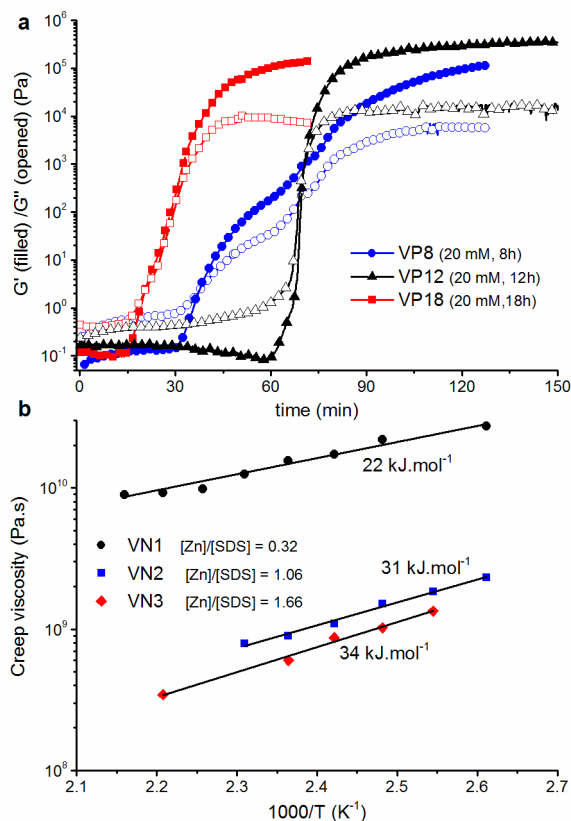


Figure 5. a) Rheological monitoring of sintering of the dried vitrimer particles at 150°C (1 to 3000 Pa stress-controlled oscillations, 1 Hz). b) Temperature-dependence of viscosities measured by creep experiments. The full lines show the Arrhenius fits for the different data sets

Although the three different samples, **VP8**, **VP12** and **VP18**, all reach a similar asymptotic crosslinking density ($G' \approx 200 \text{ kPa}$), the effective sintering kinetics are considerably different. In our opinion, this could be due to the combination of two effects. First, the presence of a sol fraction (oligomeric, unreacted or hydrolyzed species) with high diffusivity should help to accelerate covalent exchanges across inter-particle interfaces.²⁴ In this regard, samples **VP8** and **VP18** that have lower gel fractions should show faster sintering. Then, the reactivity and concentration of the different species present in the system might also influence the sintering. In comparison to **VP12**, **VP18** contains particles and a sol fraction with a higher number of hydroxyls, which is particularly desirable in order to form bond exchanges with ester groups. **VP8** contains fewer hydroxyls but also a small amount of unreacted epoxides and carboxylic acids. The first sintering at 30-40 min might therefore be due to epoxy-acid condensation while the second sintering at 60-90 min may be due to transesterification exchanges.

The dynamic character of these silicone-fatty acid networks was investigated by creep experiments at different temperatures on fully cured films (dried latexes cured for 15h at 150°C). Sample **VN1** is obtained from a latex stabilized with 30 mM SDS. The measured viscosities display an Arrhenius dependence with temperature in the 110 to 190°C range (Figure 5b). Yet, the relaxation time at 150°C (estimated by $\tau = \eta/E' = \eta/3G'$) is about 4 h, i.e. three times longer than previously reported zinc-catalyzed transesterifications with comparable catalyst loading.⁵ Moreover, the corresponding viscous flow activation energy ($E_a = 22 \text{ kJ mol}^{-1}$) is significantly lower than previously reported ($E_a(\text{Zn})$ ca. 80 kJ mol^{-1}).⁵ Such drastic changes suggest that the ability of zinc

salts to catalyze transesterifications is diminished, and lead us to conjecture competitive binding of SDS surfactants on zinc cations which would be unfavorable for hydroxyl / ester transesterifications. The **VN1** sample contains indeed an excess of SDS (216 mmol.kg⁻¹) with regard to zinc salts (69 mmol.kg⁻¹). Two other vitrimer networks were synthesized for comparison: **VN2** is obtained by adding to the vitrimer latex used for **VN1** (stabilized with 30 mM SDS) an excess of Zn(ac)₂; **VN3** is obtained from adding an excess of Zn catalyst to a vitrimer latex stabilized with 20 mM SDS. Both samples were subsequently cured with the same method (15h at 150°C). The different compositions of these vitrimer networks are summarized in Table 1. Creep measurements on **VN2** and **VN3** (Figure 5b) also reveal a vitrimer behavior for both polymers, this time with much lower viscosities. **VN2** and **VN3** contain a similar catalyst loading, about 16 mol% Zn to initial COOH groups, yet the larger amounts of SDS present in **VN2** leads to viscosities ca. 50% higher than **VN3**.

Table 1. Compositions of vitrimer networks used in creep experiments.

#	[SDS] (mmol.kg ⁻¹)	[Zn] (mmol.kg ⁻¹)	[Zn]/[SDS]	[Zn]/COOH ^a (mol%)
VN1	216	69	0.32	4.8
VN2	209	225	1.06	15.5
VN3	143	237	1.66	16.3

a) molar fraction of Zn catalyst based on the amount of COOH initially present in the vitrimer.

It must be noted that such PDMS-based vitrimers may not be compatible with all transesterification catalysts. It is indeed well known that in the presence of bases, PDMS undergoes depolymerization and backbiting through siloxane equilibrations,²⁵ eventually resulting in the formation of volatile cyclic species. In the present system, we monitored the weight of sample **VP12** during a 3h curing cycle at 150°C (Figure S6 in Supplementary Information). The loss of weight is lower than 7 wt% and is consistent with evaporation of traces of xylene and water produced during hydroxyl/acid esterification reactions. Siloxane equilibrations in the current system are therefore relatively insignificant.

In conclusion, we have shown that miniemulsion polymerization is a promising strategy in order to obtain vitrimer particles. The choice of surfactant is critical to maintaining the stability of the emulsion, especially when vitrimer curing must be carried out at high temperatures. In addition, we have also shown that SDS interferes with the transesterification when catalyzed by zinc salts and should therefore be used in minimal amounts. We believe that, while our strategy should be generalizable to other vitrimer materials, optimization of the miniemulsion stabilization should be made for each system on a case-by-case basis. With the exception of a few exchange reactions such as trans-alkylation in 1,2,3-triazoliums^{26,27} or sulfoniums,²⁸ or chalcogenide metathesis,^{29,30} most vitrimer chemistries developed so far might be sensitive to water. Yet the miniemulsion approach presented here allows hydrolysis to be minimized; we have shown that with careful monitoring of the curing reactions, particles with a high gel fraction can be obtained.

In our system, xylene was used as a co-solvent to promote the miscibility of the initially incompatible reactants. It is a non-desirable VOC, but we emphasize that it should be beneficial to dismiss it during the syntheses of other vitrimer nanoparticles whose precursors do not present any compatibilization issues: i) xylene decreases the precursor reactivity and ii) it is less hydro-

phobic than our vitrimer precursors and does not help in stabilizing the miniemulsion.

We envision that the sintering of vitrimer particles at high temperatures might open new opportunities in the processing of thermosetting materials such as paints or coatings but also as matrixes for composite materials; their low viscosity and delayed sintering kinetics might be well-suited to injection processes such as reaction injection molding (RIM) or resin transfer molding (RTM).

Supporting Information

Details of syntheses and characterizations, Surfactants description, cryo-TEM images, NMR spectra, rheology and creep characterizations.

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank Pierre-Yves Dugas for his help with cryo-TEM analyses. We are also indebted to Eric Drockenmuller for stimulating discussions.

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