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

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Epoxy-acid vitrimer particles with excellent osmotic and hydrolytic stability were synthesized by miniemulsion polymerization thanks to in-situ generation of surfactants from the carboxylic acid reagent and a water-soluble base. The sulfonate-free vitrimers formed in this way show greatly reduced creep viscosities.

Reactions between epoxy and carboxylic acids have been widely used by the industry for over 50 years, typically in polyester-based hot setting powder coatings.^{1,2} Upon catalysis with bases or Lewis acids, poly(hydroxylester)s are obtained,^{3–8} which have found a renewed research interest in the past ten years in the scope of dynamically crosslinked polymer networks.^{9–12} Even after completion of the curing, transesterification reactions between hydroxyl groups and ester bonds enable dynamic reshuffling of the crosslinks in the network, and thus bestow features unknown in conventional thermosets: malleability, weldability, recyclability. These so-called vitrimer materials have been exploited in a large range of applications including weldable long fiber composites,¹³ highly stretchable, recyclable elastomers,¹⁴ mouldable liquid-crystalline elastomers¹⁵ or recyclable 3D-printing.¹⁶ Several catalysts such as Lewis acids or bases have been found to accelerate the transesterification reactions and thus facilitate the reprocessing of cured vitrimers.^{17–19} It must be noted that a few examples such as 2-methylimidazole promote the epoxy-acid addition but not the transesterification whereas, to the best of our knowledge, most transesterification catalysts also promote the epoxy-acid addition.

We have recently reported the first syntheses of epoxy-acid vitrimer latexes by miniemulsion polymerization.²⁰ The formation of colloidal vitrimer particles (e.g. in the 100–200 nm size range) opens vast new possibilities such as straightforward

preparation of “nanopaper”-like vitrimer composites by casting from aqueous solutions.²¹ Upon drying above T_g , particles with such sizes can indeed deform without external pressure to form homogeneous films. In addition, heating the films at high temperature enables both completion of curing reaction and interparticle transesterifications, resulting in homogeneously crosslinked films. The most challenging aspect of the process was to maintain the miniemulsion stability over the long reaction times required for epoxy-acid addition (typically 8h at 120°C). Anionic surfactants such as sodium dodecylsulfate (SDS) with cloud point temperature over 100°C had to be used in large amounts, and simultaneous hydrolysis of the hydroxylesters formed was unavoidable. In addition, we also demonstrated that the presence of SDS in the final vitrimer inhibited the catalytic effect of zinc salts on the transesterification and severely reduced the malleability of the vitrimer.

As a result of our endeavours to eliminate SDS surfactant in the formulation of vitrimer miniemulsions, we report in this paper that generating in-situ carboxylate surfactants from the dimer fatty acid and a strong base provides efficient stabilization of the emulsion, greatly accelerates the epoxy-acid addition and also improves the malleability of the resulting vitrimer films.

Similar strategies relying on in-situ generation of carboxylate surfactants have been used to facilitate emulsification processes,^{22–26} and notably in the field of oil recovery.²⁷ Hydrophobic fatty acids, either long-chain acids purposely added in monomer mixtures, or polycyclic and aromatic acids naturally present in the case of crude oil,²⁸ are ionized by water-soluble strong bases during the emulsification. The oil/water interface generated by high-shearing devices is thus instantly stabilized by local formation of carboxylate salts and does not rely on the diffusion of water-soluble surfactants to the interface. A sizable difference in our case is that the fatty dimer acids are present in very high concentration as main reactive constituents of the miniemulsion.

The epoxy-acid vitrimer system is the same as previously studied²⁰: the organic phase is composed of a mixture of

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hydrogenated dimer acid, epoxy-terminated PDMS and tetrafunctional epoxy crosslinker, compatibilized as a 50 wt% solution in xylene and with stoichiometric amounts of epoxy and carboxylic acids (See Figure S1 and details in Supporting Information). It is well known that Lewis bases also act as catalysts in epoxy-acid addition and in transesterification reactions. In order to compare the respective roles of zinc salts and NaOH in our system, we thus prepared some samples with Zinc acetate pre-dissolved in the dimer acid (5 mol% to COOH) while other samples do not contain any zinc. Pure water is added to this organic phase to reach an overall organic fraction of 20 wt%, then various amounts of 1 M NaOH solution are added to the biphasic system under stirring, immediately forming a white emulsion. The emulsion is ultrasonicated with an ultrasound probe and periodically analyzed by dynamic light scattering (DLS, hydrodynamic diameter: Z_{av}) and pH-meter until an equilibrium is reached, typically within 10 min. Throughout the manuscript, the samples will be referenced as **VIT-OH_x-Zn_y**, where X and Y are the initial molar ratios of sodium hydroxide (in aqueous phase) and zinc salts (in organic phase) to carboxylic acids, respectively.

Stabilization of miniemulsion

Figure 1 displays the variations of pH of the emulsion and the Z_{av} determined by DLS at equilibrium, as a function of the molar ratio r of NaOH added to the carboxylic acids present in the oil phase.

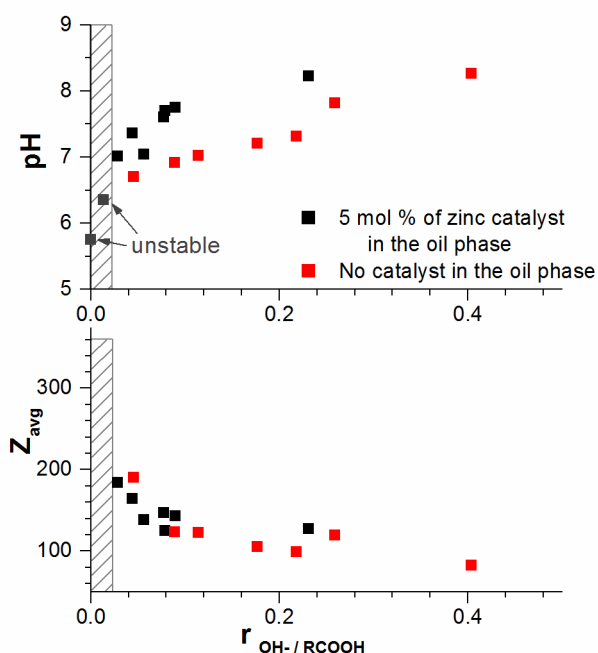


Figure 1: pH and Z_{av} diameter of miniemulsions obtained after ultrasonication of vitrimer precursors for different amounts of NaOH added. In black: zinc catalyst is present in the oil phase. In red: no zinc catalyst added.

Long-term stability of the miniemulsion is achieved for NaOH to carboxylic acids ratios, r , above 0.02 (also corresponding to $\text{pH} > 6.5$). When the ionization ratio is further increased, the droplet sizes continuously decrease from ca. 200 nm to below 100 nm, thus showing clear evidence of increased interfacial stabilization. After six months storage at room temperature, only small variations of droplet sizes are observed (e.g. Z_{av} of sample **VIT-OH_{0.08}-Zn_{0.05}** (unpolymerized) shows an increase from 125 to 148 nm), thus demonstrating high stability of the miniemulsions.

The pH of the miniemulsions seems to plateau up for high ionization ratios, as expected in the titration of a weak acid by a strong base below the equivalence point. It results however from a complex interplay involving weak acid – strong base equilibrium between hydroxide ions in water and dimer fatty acids at the droplet interface, and interrelated increase of effective availability of dimer acids at the interface when the droplet sizes decrease. A slight shift of this titration curve to higher pH is observed when zinc salts are added to the organic phase. We believe this to be due to partial epoxy-acid reaction already occurring in presence of catalyst during the storage of the reactive mixture (a few days at 6°C) or the sonication process: in such conditions the effective r ratio would then be underestimated.

Curing kinetics

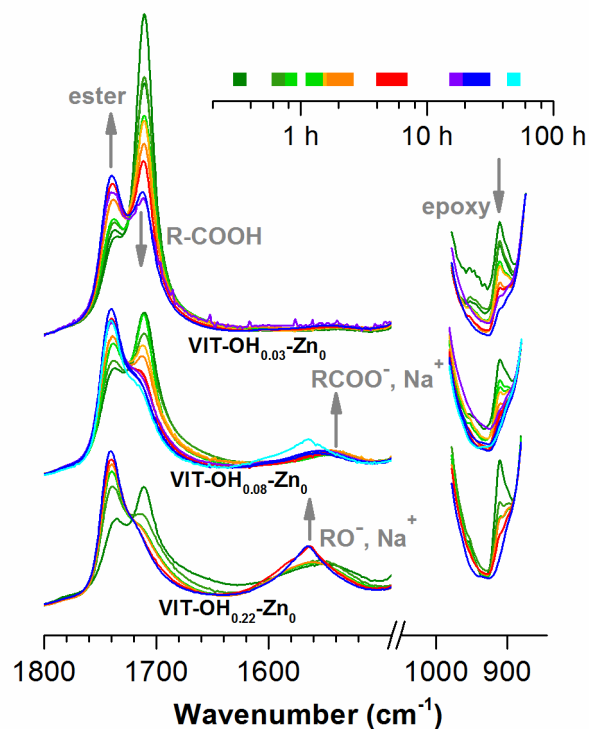


Figure 2: Time-resolved FTIR spectra of samples **VIT-OH_{0.03}-Zn₀** (top), **VIT-OH_{0.08}-Zn₀** (middle) and **VIT-OH_{0.22}-Zn₀** (bottom) during curing at 120°C. The time scale is indicated by different colors (inset).

We previously used ^1H NMR in CDCl_3 to determine the relative occurrence of epoxy-acid addition and subsequent hydrolysis with water in vitrimer miniemulsions stabilized with SDS. Even when crosslinked nanoparticles were formed, well resolved spectra enabled to determine the evolution of different species with good accuracy during curing. When high amounts of carboxylate species are formed in the present case, the polymers cannot be analysed directly with ^1H NMR because of poor solubility in all tested solvents. We resorted therefore to monitoring the evolution of carboxylic acids, carboxylates, esters and epoxides with transmission-FTIR, after drying water and xylene from aliquots of samples cured at 120°C (Figure 2). For the sake of simplicity, we focused on samples without Zinc salts.

Samples with $r = 0.08$ and 0.22 display a concomitant consumption of epoxy ($\nu = 915\text{ cm}^{-1}$) and carboxylic acids ($\nu = 1710\text{ cm}^{-1}$) with increase of esters ($\nu = 1735\text{ cm}^{-1}$), that reach almost full conversion within 20h and 6h, respectively. The large signal at 1550 cm^{-1} , showing constant absorption during most of the reaction, corresponds to carboxylates salts RCOO^- that were initially formed at the water interface. The typical reaction mechanism reported in the present case is a nucleophilic attack from a carboxylate on the epoxy ring, followed by ring-opening into a β -alkoxide ester.⁷ As this alkoxide is highly basic, immediate proton exchange with another neighboring carboxylic acid regenerates a new carboxylate. Eventually, when the amount of carboxylic acids left is reduced, the sodium β -alkoxide ester may remain stable in the organic phase (we attributed it to the signal at 1575 cm^{-1}). It is also interesting to note that for both samples the pH of the aqueous phase and the droplet sizes do not vary appreciatively during the curing, thus demonstrating an excellent osmotic and hydrolytic stability of the miniemulsion during the curing reaction. The completion of esterification was also confirmed by ^1H NMR spectra, after complete neutralization of the salts with excess trifluoroacetic acid and proper solubilization in CDCl_3 : after 49h at 120°C for $\text{VIT-OH}_{0.08}\text{-Zn}_0$ and 24h at 120°C for the other samples, less than 4 mol% of epoxy are remaining while the fraction of esters formed is higher than 90 mol% (See Fig S4 and Table S1 in SI).

Sample with $r = 3\%$ (i.e. barely above the threshold for emulsion stability) displays comparatively slower kinetics, and a consumption of carboxylic acids and production of esters leveling off after 15h. This is consistent with a concomitant hydrolysis of the esters as previously demonstrated when using SDS surfactants. Extended curing of this sample for 49h results in destabilization and complete cracking of the miniemulsion.

Sintering kinetics and malleability

Samples $\text{VIT-OH}_{0.08}\text{-Zn}_0$, $\text{VIT-OH}_{0.22}\text{-Zn}_0$, $\text{VIT-OH}_{0.08}\text{-Zn}_{0.05}$ and $\text{VIT-OH}_{0.23}\text{-Zn}_{0.05}$ were prepared by curing the corresponding latexes for 24h at 120°C (e.g. nearly full completion of esterification reaction for all samples) and thorough drying of water and xylene under vacuum. While the

samples prepared with 8 mol% NaOH behave as transparent viscous oils, samples with 22 mol% NaOH show much higher viscosities at room temperature. As crosslinking is expected to occur in these materials as a result of exchange reactions across the inter-particle interface rather than by gelation from monomers, the glass transition of the vitrimer are not expected to change. DSC analysis (Figure S6 and Table S2 in Supporting Information) show indeed very small variations between the vitrimer latex cured in miniemulsion and fully sintered films (24h at 150°C).

Shear rheology displays however a very clear transition from an initially a viscous behaviour to a crosslinked network within 25 min (Figure S4 in SI). Crosslinking completion can take more than 10h. As expected, the final storage modulus of the materials (Table 1) decreases when higher concentrations of zinc or NaOH are used: in both cases we expect eventually the formation of zinc carboxylates or sodium alkoxide species effectively forming elastically inactive branches. All samples are insoluble in xylene at room temperature, with gel fractions above 93%. We also verified with samples $\text{VIT-OH}_{0.08}\text{-Zn}_0$ and $\text{VIT-OH}_{0.22}\text{-Zn}_0$ that the networks formed are insoluble in hot xylene, for 48h at 135°C , albeit the networks swelled extensively in such harsh conditions and the gel fraction found was much lower, about 63% and 55%, respectively.

| Sample | Shear modulus ^a (Mpa) | E^b (MPa) | T_g^c (DSC) ($^\circ\text{C}$) | $E_{a,\text{flow}}^d$ ($\text{kJ}\cdot\text{mol}^{-1}$) |
|--|----------------------------------|-------------|------------------------------------|---|
| $\text{VIT-SDS}_{0.15}\text{-Zn}_{0.05}$ | 0.31 | - | - | 21 |
| $\text{VIT-OH}_{0.08}\text{-Zn}_0$ | 1.13 | 3.1 | -53 | 49 |
| $\text{VIT-OH}_{0.22}\text{-Zn}_0$ | 0.74 | 2.7 | -52 | 37 |
| $\text{VIT-OH}_{0.08}\text{-Zn}_{0.05}$ | 0.34 | 0.97 | -52 | 45 ($<130^\circ\text{C}$) 110 ($>150^\circ\text{C}$) |
| $\text{VIT-OH}_{0.23}\text{-Zn}_{0.05}$ | 0.17 | 0.73 | -23 | 50 |

Table 1. a) Shear moduli determined after 10h sintering at 150°C , b) Storage modulus (DMA, 1Hz) on latex films cured for 24h@ 150°C c) T_g of fully sintered films determined by DSC and d) Viscous flow activation energy determined by creep tests.

The effective crosslinking of the vitrimer latexes was confirmed by dynamical mechanical analysis carried out on fully sintered films (24h at 150°C): all samples show an elastic plateau up to 200°C (Figure S7 in Supporting Information). The storage moduli at 150°C (Table 1) are in good accordance with the shear moduli obtained by rheology (e.g. with a ratio E/G close to 3). It is interesting to note that sample $\text{VIT-OH}_{0.22}\text{-Zn}_{0.05}$ has a considerably different thermomechanical behaviour than the other samples, with a higher T_g and the presence of a second relaxation above the glass transition, around ambient temperature. We believe this relaxation might be related to the ionic clustering or nanophase separation as commonly observed in ionomers.

The malleability of the vitrimers was measured by creep tests in shear mode. Figure 3 displays the creep viscosities of the different samples at various temperatures. The data obtained in the previous report using SDS as surfactant (15 mol%) and 5 mol% Zinc as catalyst is also reported for comparison.²⁰

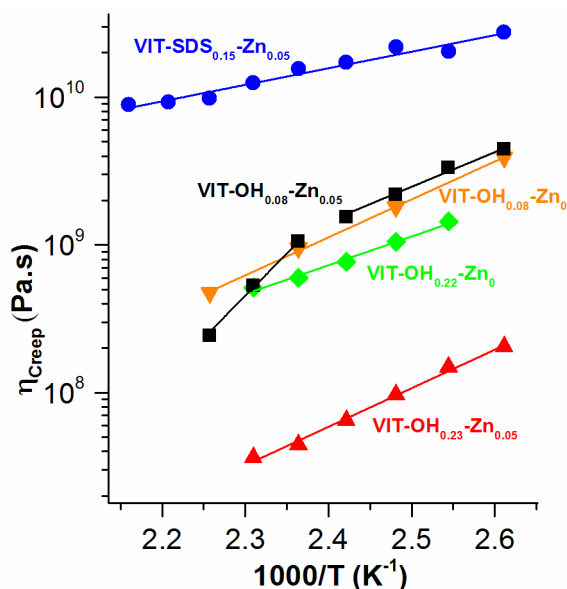


Figure 3: Temperature-dependence of creep viscosities for different vitrimer systems after complete sintering. The viscous flow activation energies reported in Table 1 are obtained from fits with Arrhenius models (lines).

While SDS appears to inhibit exchange reactions and leads to materials with high viscosity and thus poor malleability, the new vitrimers display up to 100 times lower viscosities. In absence of zinc salts, for VIT-OH_{0.08}-Zn₀ and VIT-OH_{0.22}-Zn₀, a similar $E_{a,flow}$ of about 40 kJ.mol⁻¹ is found, with viscosities decreasing when the initial amount of NaOH used is increased. This indicates that the species formed at the end of hydroxide-catalyzed epoxy-acid addition, typically sodium alkoxides are responsible for exchange reactions and malleability. VIT-OH_{0.08}-Zn_{0.05} displays an unusual behaviour, with two separate Arrhenian profiles, with $E_{a,flow}$ of about 45 kJ.mol⁻¹ below 130°C and $E_{a,flow}$ about 110 kJ.mol⁻¹ above 150°C. We believe that at low temperatures, the catalysis by sodium alkoxides (Lewis bases) is dominant as demonstrated by the $E_{a,flow}$ similar to the systems without zinc salts. At higher temperatures, the $E_{a,flow}$ is even higher than $E_{a,flow}$ reported in epoxy-acid vitrimers purely catalysed with zinc (about 75 kJ.mol⁻¹).¹⁹ This suggests that cooperative effects between zinc salts and sodium alkoxide are taking place. A similar dual temperature response has been recently reported in vinylogous urethane vitrimers in which two exchange mechanisms with different activation energies are competing.²⁹ VIT-OH_{0.22}-Zn_{0.05} displays $E_{a,flow}$ about 50 kJ.mol⁻¹, i.e. similar to systems catalyzed only by sodium alkoxides. The creep viscosities are however much lower than the other systems,

and could only partially be explained by the significantly lower crosslinking density.

These results lead us to formulate several hypotheses. First, it is possible that malleability may not be only driven by transesterification exchange reactions, but also by siloxane equilibrations in the PDMS segments, known to occur in presence of strong bases.^{30,31} The formation of volatile cyclic siloxanes would yet be expected, and we did not observe any decrease of Si-CH₃ signal on FTIR after extended curing at 150°C.

Secondly, if malleability is strictly controlled by transesterification exchanges, we conjecture that cooperative effects between Lewis acids and Lewis bases may be highly dependent on the relative concentrations of the two catalysts. A systematic study is required to better understand this phenomenon.

Conclusions

The stabilization of miniemulsions involving long-chain dimer fatty acids through “dimerate” surfactants generated in-situ with strong bases offers thus an ideal platform to synthesize epoxy-acid vitrimer nanoparticles, and could probably be extended to several polyester systems.^{32,33} Straightforward tuning of the ionization degree of carboxylic acids offers some variability over the size of particles while catalyzing the epoxy-acid reaction and offering excellent osmotic and hydrolytic stability even at 120°C. As a result, model vitrimer particles almost fully cured can be obtained.

Furthermore, the malleability of the vitrimers finally formed after sintering of these particles is greatly enhanced in comparison to vitrimers particles obtained with SDS. Further work is required to understand the catalytic cooperative effects of Lewis acids and Lewis bases. This strategy might offer very versatile ways to further accelerate transesterification reactions in epoxy-acid vitrimers, and effectively solve a major bottleneck preventing so far the convenient (re)processing of these materials.

Conflicts of interest

There are no conflicts to declare.

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