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# Enriching an exchangeable network with one of its components: The key to high $T_g$ epoxy vitrimers with accelerated relaxation

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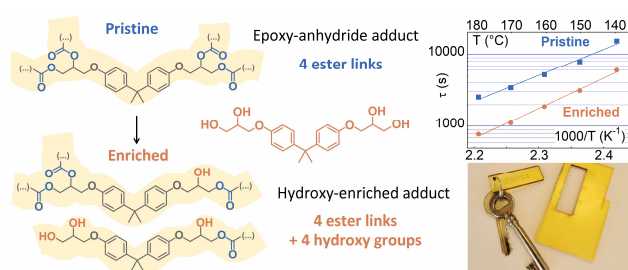
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Key words. epoxy anhydride vitrimer, transesterification, solid state rheology, stress relaxation, high-  $T_g$ , Bisphenol A bis(2,3-dihydroxypropyl) ether.



For Table of Contents use only

## ABSTRACT

The curing of epoxy-anhydride vitrimers involves anionic copolymerization of epoxide and anhydride along with anionic homopolymerization of excess epoxide, giving rise to a poly(ester-*co*-ether) network. By monitoring curing using infrared spectroscopy in different conditions, and mapping the presence of OH groups, we demonstrate that generation of hydroxide groups, necessary for transesterification, exclusively relies on side reactions induced by protic impurities and water. To increase the yield in esters and hydroxides, without depressing the thermal properties, we enrich the network with one of its components: DHEBA (bisphenol A bis(2,3-dihydroxypropyl) ether), potentially available from hydroxylation of the starting epoxy monomer as well as from chemical recycling of the final vitrimer network. In the DHEBA-enriched network, the modulus drop associated with the alpha transition occurs at higher temperature and more steeply than in the pristine network, demonstrating better homogeneity together with improved heat resistance and 3-fold shortened relaxation time throughout the 140–180°C range.

## 1. INTRODUCTION

Vitrimers are polymer networks containing exchangeable bonds,<sup>1,2</sup> a characteristic that allows them to change shape while keeping the number of links constant over time (see refs<sup>3,4,5</sup> for reviews). When the temperature increases, the chemical exchanges between the bonds of the network become fast enough to make the material flow although it remains insoluble. The synthesis of the first vitrimers,<sup>6</sup> involving transesterification as the exchange reaction was exemplified using two reactive systems. In the first one, the reaction between epoxides and carboxylic acids was used to prepare networks containing an equimolar amount of ester and alcohol functions that were taking part in transesterification reactions. These easy-to-access model vitrimers have been extensively studied by several groups,<sup>7,8,9,10,11,12,13,14</sup> but actually,

they are neither real elastomers nor real thermosets since their glass transition temperature,  $T_g$  is close to the ambient temperature. In order to obtain high  $T_g$  vitrimers, which are required in many structural applications, synthesis from anhydrides rather than acids has been proposed as a way of densifying the network. Replacing polycarboxylic acids by cyclic anhydrides, lead to vitrimers with higher  $T_g$  for two reasons: first, the distance between two acyl groups is intrinsically shorter in anhydrides (2 or 3 carbon atoms) and secondly, anhydride form two links instead of one each time an epoxide ring is opened. Another advantage of this strategy is to start from a low viscosity liquid reactive mixture, compliant with the techniques used to process composite materials.<sup>15</sup>

The replacement of a dicarboxylic acid by an anhydride formally implies that the system is deprived of one molecule of water. This difference strongly affects ring opening reactions. The alkoxide liberated by cleavage of the C–O bond can no longer be reprotonated into an OH side group. In other words, generation of alcohol functions, that are necessary to take part in transesterification should not occur in this process.

So far this issue has been treated empirically. Epoxy vitrimers were prepared from anhydrides and from acids and in both cases substantial amounts of hydroxide functions were found. The source of hydroxides has been a matter of debate. In particular the role of ambient humidity, providing the missing water molecule in anhydride vitrimers has been alleged,<sup>6</sup> but never been studied quantitatively. More generally, relying on moisture to reach the desired product poses both conceptual and practical problems.

Co-reacting an epoxy-carboxylic acid composition with a terpene glycoside tricarboxylic fragment was proposed to increase both  $T_g$ , and the number of available OH groups.<sup>16</sup> However, the high melting point of the co-reactant is an obstacle to the efficient mixing of the components. Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid)<sup>17,18</sup> with a lower melting point (153°C) seems a better option for the same purpose. However, this fragment is prone to

dehydration and decarboxylation,<sup>19,20</sup> which makes it poorly suitable for high temperature applications. Epoxy-acid vitrimers using 1,4-Cyclohexanedicarboxylic acid (CHDA) have been synthesized, reaching a  $T_g$  of about 80 °C<sup>21,22</sup> with again the issue of a rather high melting point monomer (MP > 200 °C for the *trans* isomer). The  $T_g$  of an epoxy-sebacic acid vitrimer has been increased by using an off-stoichiometric composition with the [acyl]/[epoxy] ratio lower than unity<sup>22,23</sup> This formulation induces an increase in crosslink density, reflected by a higher plateau modulus,<sup>18</sup> but formation of non-exchangeable ether bonds, detrimental to relaxation properties has been evidenced.<sup>23</sup>

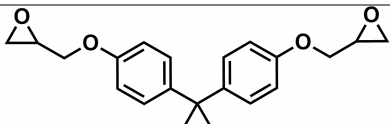
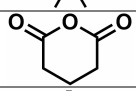
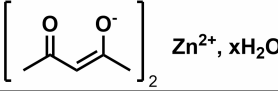
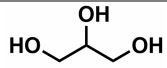
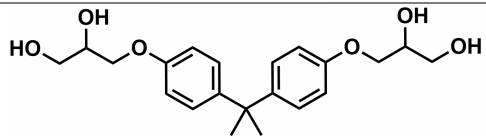
The goal of this paper, is to revisit this still open debate, to examine the role of the main and side reactions in the chemistry of epoxy-anhydride vitrimers and to propose a concept allowing to accelerate transesterification exchanges. This concept consists in introducing a controlled amount of hydroxide groups in a way that maintains high glass transition temperatures. Along this line, we prepare and investigate various epoxy-anhydride vitrimer compositions with the following specifications: 1°) the presence of OH group, essential to dynamic bond exchange, is monitored in different curing conditions, 2°) their distribution throughout the cured material is quantified, 3°) an original chemistry based on enriching the networks with a rigid diglycol compound is developed to achieve a higher content and better distribution of OH, 4°) the thermomechanical properties (like the glass transition temperature) and the thermal stability of the enriched and reference networks are evaluated and compared, 5°) the vitrimer viscoelastic properties are evaluated using stress relaxation data at different temperatures and allowing us to determine the activation energy.

## 2. EXPERIMENTAL

**2.1 Materials.** Monomers and reactants are presented in Table 1. Bisphenol A diglycidyl ether (DGEBA, see ESI Figure S1) are purchased from Sigma-Aldrich, as well as

zinc acetylacetonate, 2-methylimidazole, acetic acid, absolute ethanol and glycerol. The synthesis of bisphenol A bis(2,3-dihydroxypropyl) ether (DHEBA) is described in ESI. Small quantities were also purchased from Sigma-Aldrich to provide reference samples for ATR-IR,  $^1\text{H}$  NMR and SEC analyses (see ESI Figure S2, S3 and S4). Glutaric anhydride are purchased from Alfa Aesar. All reactants were used as received, without purification.

Table 1 – Monomers and reactants used for vitrimer preparation.

Chemical structure	Compound name	Acronym	Molar mass (g/mol)
	<b>Diepoxide monomer</b> Bisphenol A diglycidyl ether*	DGEBA	340.4
	<b>Cyclic anhydride</b> Glutaric anhydride	GA	114.1
	<b>Transesterification catalyst</b> Zinc acetylacetonate	$\text{Zn}(\text{acac})_2$	263.6
	<b>Hydroxyl group donor</b> Glycerol	Glycerol	92.1
	<b>Hydroxyl group donor</b> Bisphenol A bis(2,3-dihydroxypropyl) ether**	DHEBA	376.4

\*The commercial grade of DGEBA (D.E.R.<sup>TM</sup> 332) contains small amounts of bisphenol A/epichlorhydrin higher oligomers; see ESI Figure S1

\*\*Official nomenclature: 2,2-Bis[4-(2,3-dihydroxypropoxy)phenyl]propane.

**2.2 Preparation of reactive mixtures and vitrimer samples.** The compositions of each reactive mixture for sample preparation are reported in Table 2. First, the Zn(II) catalyst is dissolved in DGEBA in a PTFE (poly tetrafluoroethylene) beaker on a heating plate at 150 °C. After cooling down to 120 °C, glutaric anhydride is added. Glycerol-containing samples are prepared by adding glycerol after glutaric anhydride to avoid evaporation since glycerol rapidly reacts with anhydride to produce less volatile compounds. For DHEBA-containing samples, DHEBA is added to the DGEBA/Zn(II) mixture before glutaric anhydride to ease its solubilization and allow evaporation of residual ethanol before reaction.

After 15 min at 120 °C, the temperature is increased to 130 °C for another 15 min. The thickened mixture is then poured in a preheated mold ( $9 \times 6 \times 0.3 \text{ cm}^3$ ) and cured in a heating press for 16 h at 140 °C.

Table 2 - Compositions of reactive mixtures for vitrimer preparation (reactant used with equivalents with respect to epoxy groups).

Formula name	DGEBA	GA	Hydroxyl group donor	Zn(acac) <sub>2</sub>
<b>E/A-Zn(II)</b>	1 epoxy group eq. (15.0 g)	0.5 anhydride eq. (5.0 g)	-	0.1 Zn(II) eq. (2.3 g)
<b>E/A-Zn(II)-Glycerol</b>	1 epoxy group eq. (15.0 g)	0.5 anhydride eq. (5.0 g)	Glycerol - 0.5 OH group eq. (1.4 g)	0.1 Zn(II) eq. (2.3 g)
<b>E/A-Zn(II)-DHEBA</b>	1 epoxy group eq. (15.0 g)	0.5 anhydride eq. (5.0 g)	DHEBA - 0.5 OH group eq. (4.1 g)	0.1 Zn(II) eq. (2.3 g)

**2.3 Depolymerisation of vitrimer samples in ethanol.** Cured samples of about  $0.5 \times 2 \text{ cm}^2$  size are grinded by applying a 3 tons force at 140°C. The coarse powder thereby obtained (2 g) and ethanol (35 g) are put in a Parr Instruments Model 4748A PTFE-lined digestion bomb and heated at 150 °C for 24 h. The resulting mixture is filtered and the solution was evaporated under reduced pressure (40 mbar, 40 °C), to be analyzed by size exclusion chromatography.

**2.4 Chemical and thermal analyses.** Attenuated total reflexion infrared spectroscopy (ATR-IR), nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) experiments are described in ESI. ATR-IR is used to study the local concentration of OH groups at the surface and at different depths inside the samples. To this end, the samples are gradually eroded and analyzed. The measured spectrum characterizes a layer of thickness equal to the penetration depth of the evanescent wave  $D_p$  given by the formula:<sup>24</sup>

$$D_p = \frac{\lambda}{n_1 2\pi \sqrt{\sin^2 \theta - \left(\frac{n_2}{n_1}\right)^2}}$$

where  $n_1 \approx 2.4$  and  $n_2 \approx 1.5$  are refractive indices of the ATR crystal and the sample, respectively,  $\theta \approx 45^\circ$  the incidence angle and  $\lambda = 2.5$  to  $25 \mu\text{m}$ , the wavelength of the infrared radiation.

**2.5 Rectangular torsional rheology.** All experiments are conducted using an ARES G2 rheometer (TA Instruments) in torsion geometry, according to the APN024 application note<sup>25</sup>. The sample size is  $45 \times 10 \times 3 \text{ mm}^3$ . Amplitude sweep experiments in oscillatory mode are performed at  $1 \text{ rad s}^{-1}$  and increasing strain to determine the linear viscoelastic range. Small amplitude oscillatory shear experiments at constant 0.1% strain, i.e. within the linear range, are used to monitor the evolution of the elastic modulus over time, during temperature equilibrations and/or thermal stability assays. The elastic modulus at  $25^\circ \text{C}$  is measured by taking the average of measurements recorded for a time interval of 5 min.

For stress relaxation experiments, temperature is equilibrated for 1 h before each measurement, whereupon a step of 0.5% strain, i.e. within the linear range is applied. The stress relaxation modulus is determined from the decay of the stress over time at constant temperature.

### 3. RESULTS

#### 3.1 Revisiting alcohol formation during curing of epoxy-anhydride vitrimers.

Epoxy-anhydride vitrimer (**E/A-Zn(II)** samples) are synthesized from DGEBA and glutaric anhydride, using 10 mol%  $\text{Zn}(\text{acac})_2$  as the transesterification catalyst. The ratio of anhydride



functions to epoxides is chosen to be 0.5:1 in order to target an average of one ester formed per epoxy ring opened. This is exactly the composition reported in the early works on vitrimers.<sup>1,2,6</sup> In these early studies, the presence of OH functions was observed by transmission IR spectroscopy. These cannot result from a simple reaction between epoxy and anhydride. The role of humidity in ambient atmosphere was hypothesized,<sup>6</sup> but not evaluated nor modeled. The objective here is to quantify this effect by measuring the presence of hydroxide groups under different curing conditions.

First, a drop of the reactive mixture is cured in ambient air on top of a thermalized ATR-IR set-up. The result is shown in Figure 1A. Anhydride consumption can be visualized from the decrease of the C=O stretching band at 1766 – 1810 cm<sup>-1</sup>. Epoxide consumption is followed from the evolution of the C–O deformation band at 914 cm<sup>-1</sup>. The formation of ester bonds is observed using C=O stretching at 1736 cm<sup>-1</sup>. It is difficult to distinguish a specific signature of ether links from the C–O bonds resulting from homopolymerization of the epoxy. Indeed, the region of C–O stretching vibrations ranges from 1280 cm<sup>-1</sup> to 890 cm<sup>-1</sup>. Actually C–O bonds corresponding to aryl ethers are already present in the epoxy monomer. Moreover, C–O bonds coming from the anhydride disappear during curing, while C–O bonds of ester and alcohol groups appear. In a previous work,<sup>23</sup> the 1150-1120 cm<sup>-1</sup> region was deemed the most characteristic signature of aliphatic ester formation and indeed a peak is growing at 1140 cm<sup>-1</sup>. Compared to previous measurements in transmission, the signal of O–H stretching expected to be visible at 3540 cm<sup>-1</sup> appears to be very low. Thus, based on the data presented in Figure 1A, it would be concluded that OH groups hardly form.

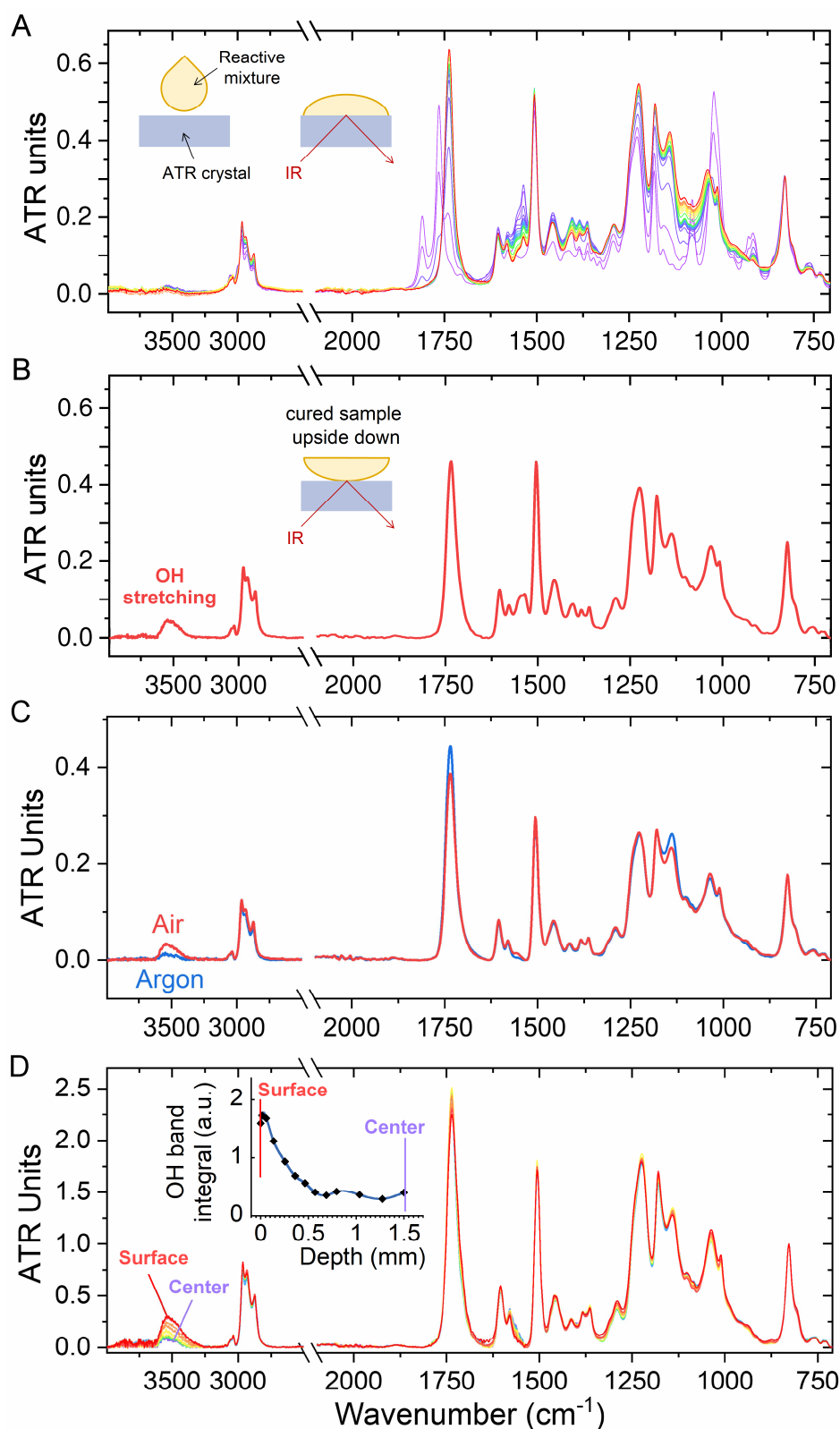


Figure 1 – A): ATR-IR cure monitoring of E/A-Zn(II) mixture at 140 °C for 16 h in ambient air (rainbow colors from purple to red; sampling every 5 min for 1 h, then every hour). B): ATR-IR analysis of the same sample after turning upside down. C) ATR-IR analysis of the E/A-Zn(II) reactive mixture after curing in vials under argon flow (blue) or in ambient air (red). D) – ATR-IR analysis of the E/A-Zn(II) composition after curing in a 3 mm thick closed mold. The outer surface was measured (red trace) and then gradually eroded and the successive layers analyzed until reaching the center of the specimen (purple). The inset shows the integral of the OH band as a function of depth.

It turns out that when we monitor the curing of the epoxy-anhydride system in the ATR geometry depicted in Figure 1A, only the lower part of the sample, in contact with the ATR crystal is measured. Indeed, the depth of penetration of the evanescent wave,  $D_p$  is comparable to the wavelength  $\lambda$  i.e. it is of about a few microns. The upper part of the drop, which is cured in contact with air, is the region where water exchanges with the ambient atmosphere are the most likely to occur. To detect the presence of alcohol groups on the upper surface, the sample is turned upside down after curing on the ATR crystal. The resulting spectrum shown in Figure 1B, gives evidence in the layer cured in contact with the atmosphere for the presence of more hydroxide functions, and comparatively less ester and ether functions

To further evaluate the impact of humidity in ambient air on the formation of alcohol groups in epoxy-anhydride systems, two samples of reactive mixture are cured for 16 h at 140 °C in pressurized vials under argon flow and in ambient air, respectively. The resulting ATR-IR spectra are shown in Figure 1C. Clearly, the intensity of the OH signal is significantly higher in the sample cured in ambient atmosphere, indicating that humidity has a strong impact on OH formation during curing. Under argon flow, a very small amount of OH groups is produced, and concomitantly a higher amount of ether groups is detected from the signal around 1140 cm<sup>-1</sup>.

During the preparation of vitrimer samples, the reactive mixture is generally confined in a closed mold and a natural question is whether hydroxides can be formed under such conditions. In Figure 1D, we report the distribution of OH groups as a function of the depth from the surface of a sample cured in a mold. To achieve these measurements, one side of the sample is gradually eroded and IR spectra recorded, until the center of the sample is reached. As shown in the inset of Figure 1D, the layers close to the surface exhibit a stronger OH signal. Since no special care is taken to avoid humidity during mixing, a mass of moisture is

trapped inside the mold before curing starts. The gradient of composition that is measured is probably due to the accumulation of water at the surfaces of the mold where temperature is controlled by the heating press, whereas the core of the sample, which can be subject to overheating due to the exothermic ring opening reaction, has a lower amount of OH groups. This shows that in a closed mold, water evaporation is sufficiently impeded to enable formation of OH groups. This explains the ability of former epoxy-anhydride vitrimers, typically prepared by compression molding, to show fast stress relaxation, creep and interfacial welding.<sup>1,6,15</sup>

Ultimately, humidity is crucial to yield OH groups in epoxy-anhydride vitrimers but this makes their production difficult to control. Therefore, to increase the amount of OH groups in the system, it is desirable to add a controlled amount of another H-donor molecule, selected in such a way that it will not degrade the properties. To ensure the homogeneity of the OH concentration in the cured sample, the additive should be non-volatile and compatible with the matrix.

### **3.2 Tuning hydroxide concentration by enriching with hydroxylated molecules.**

A higher hydroxide content is hereby achieved by addition of a hydroxylated molecule, either glycerol or DHEBA, in the epoxy-anhydride system. The reactive mixtures are further on referred as **E/A-Zn(II)-Glycerol** and **E/A-Zn(II)-DHEBA** (Table 2). They are analyzed during curing by ATR-IR spectroscopy, as shown in Figure 2.

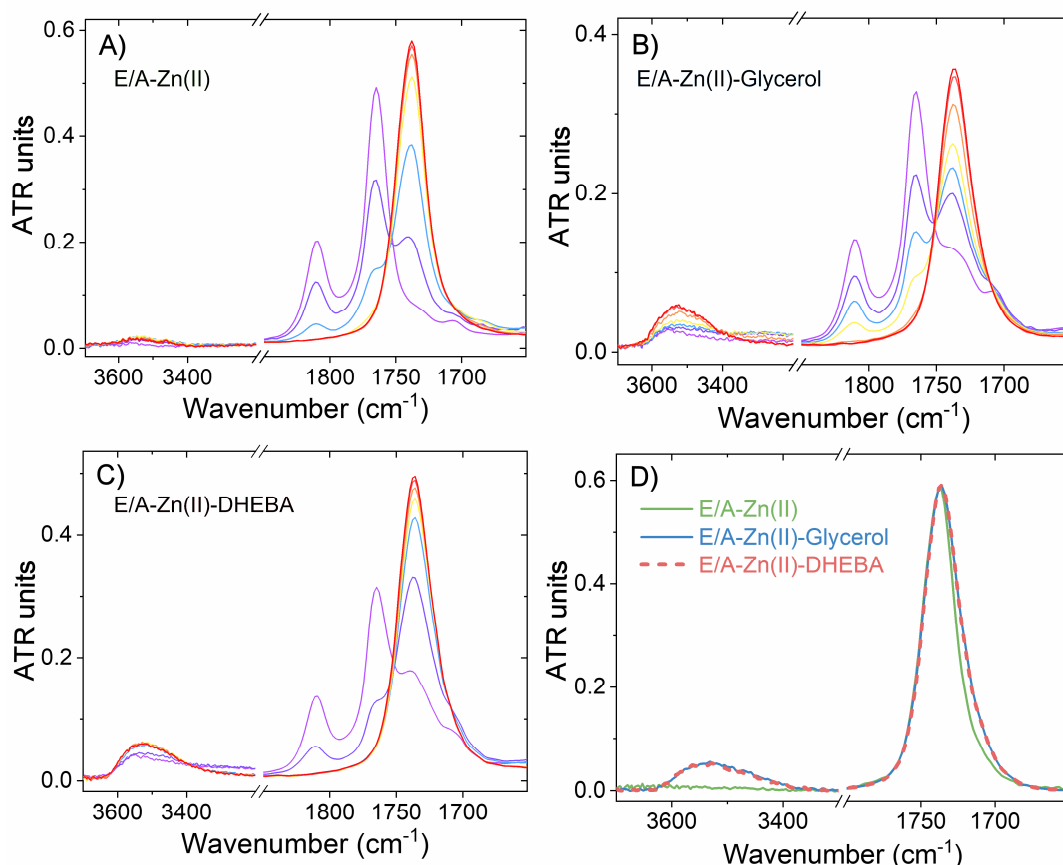


Figure 2 – ATR-IR monitoring (purple to red) during curing and at the end of curing analysis in bold red of the three reactive compositions: A) E/A-Zn(II), B) E/A-Zn(II)-Glycerol and C) E/A-Zn(II)-DHEBA. D) Curve overlay of the O-H and C=O stretching regions of the samples after curing.

Compared to the pristine network (Figure 2A), samples containing glycerol and DHEBA exhibit significant O-H signals at  $3540\text{ cm}^{-1}$ , throughout the curing process (Figures 2B and 2D). During the first minutes of curing, it is possible to detect the transient formation of carboxylic acids functions, with a C=O stretching signal at  $1706\text{ cm}^{-1}$  and a broad O-H stretching band around  $3000\text{ cm}^{-1}$ . Indeed, the ring opening of the anhydride by the alcohol can produce a carboxylic acid and an ester, which can further react with the epoxide by transesterification. Figure 2D shows an overlay of the IR spectra of the three samples at the end of curing. The presence of large amounts of hydroxide functions is clearly evidenced by the strong signal at  $3540\text{ cm}^{-1}$  and the broadening of the C=O stretching band towards lower wavenumbers, which is associated with  $\text{C=O}\cdots\text{H-O}$  hydrogen bonded formation. As a remark, one can wonder whether curing in presence of a hydroxylated co-reactant would

trigger formation of ether links by alcohol-epoxide addition. To answer this question, we have analyzed depolymerization products of **E/A-Zn(II)** and **E/A-Zn(II)-DHEBA** samples using size exclusion chromatography (see ESI Figure S8). Non-hydrolyzable clusters with short retention time are less abundant in the enriched composition, indicating that the presence of DHEBA does not promote the formation of ether bonds during curing.

**3.3 Thermomechanical properties of enriched and pristine vitrimers.** The thermomechanical properties of glycerol, DHEBA and of the three networks under study are presented in Figure S5, S6, S7; the main properties are listed in Table 3. Whereas glycerol completely evaporates below 250°C, DHEBA can be safely heated up to almost 400°C. We report the following indicators of thermal stability of the cured networks: i) the weight loss during curing and the temperature at which a 5 % weight loss is detected, ii) the temperatures of glass transition  $T_g$  and mechanical relaxation  $T_\alpha$ , iii) the shear storage modulus,  $G'$  below  $T_g$ , as well as the tensile and shear moduli,  $E'$  and  $G'$  respectively, above  $T_g$ .

In comparison with the reference sample **E/A-Zn(II)**, addition of glycerol lowers both  $T_g$  and  $T_\alpha$ , as already reported in the literature.<sup>26</sup> In fact, sample **E/A-Zn(II)-Glycerol** shows a degradation of all the thermal properties reported in Table 3; isothermal thermogravimetric experiments also shows faster degradation at 200°C (Figure S6A). Most importantly the glass transition temperature of the sample **E/A-Zn(II)-DHEBA** is similar to that of the reference sample **E/A-Zn(II)** and its thermomechanical properties are equivalent or even improved. In conclusion, addition of the DHEBA molecule does not adversely affect the thermal properties of the networks.

In Figure 3, comparing the  $E'$  and  $\tan(\delta)$  curves of the three samples suggests that the addition of hydroxylated molecules improves homogeneity, since only the reference sample **E/A-Zn(II)** shows a shoulder on  $E'$  and  $\tan(\delta)$  plots, whereas a single and narrow transition is observed for **E/A-Zn(II)-DHEBA** and **E/A-Zn(II)-Glycerol**. The plateaus of tensile modulus  $E'$  above  $T_g$

measured at 180 °C by DMA have the same values for **E/A-Zn(II)** and **E/A-Zn(II)-DHEBA** but it is significantly lower for **E/A-Zn(II)-Glycerol**. The analysis of the tensile modulus  $E'$  in the glassy state (below  $T_\alpha$ ) is not always accurate when measured with DMA in tension configuration because of issues and artefacts occurring when the samples are fastened. The shear moduli  $G'$  reported in Table 3 are measured in torsion configuration using the ARES G2 rheometer allowing reliable comparison. The highest shear modulus at 25 °C is that of the pristine network, the lowest is measured for the glycerol containing network, and **E/A-Zn(II)-DHEBA** lays in between. The highest storage shear modulus measured above  $T_\alpha$ , is that of **E/A-Zn(II)-DHEBA** at 180 °C.

Table 3 – Thermomechanical properties of epoxy vitrimers depending on the addition of an OH group donor.

Formula name	E/A-Zn(II)	E/A-Zn(II)-Glycerol	E/A-Zn(II)-DHEBA	note
Weight loss during cure (%)	-5	-9	-4	<sup>1</sup>
Temp. of 5 % weight loss (°C)	330	310	350	<sup>2</sup>
$T_g$ (°C)	75	45	67	<sup>3</sup>
$T_\alpha$ (°C)	107	77	99	<sup>4</sup>
$G'$ (MPa) at 25 °C	850	690	750	<sup>5</sup>
$G'$ (MPa) at 180 °C	5.5	4.4	8.8	<sup>6</sup>
$E'$ (MPa) at 180 °C	23	13	24	<sup>4</sup>

<sup>1</sup> by ATG, see E.S.I.

<sup>2</sup> by ATG at 10 °C/ min under nitrogen.

<sup>3</sup> by DSC.

<sup>4</sup> by DMA (tensile geometry,  $\gamma = 0.1$  %,  $f = 1$  Hz).

<sup>5</sup> by rheology (torsion geometry,  $\gamma = 0.1$  %,  $\omega = 1$  rad/s).

<sup>6</sup> by rheology (torsion geometry,  $\gamma = 0.5$  %,  $\omega = 1$  rad/s).

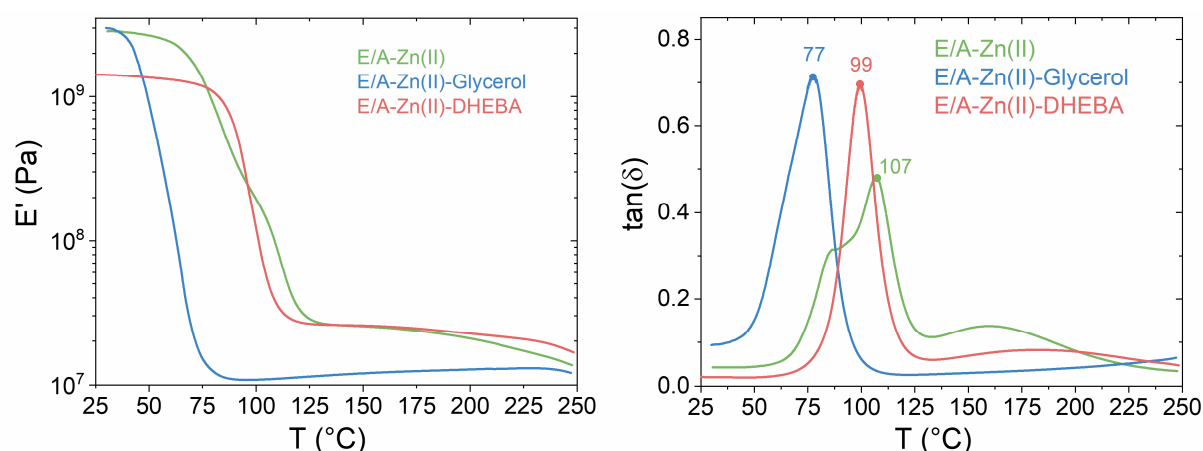


Figure 3– DMA thermograms of the three compositions after curing showing  $E'$  and  $\tan(\delta)$  as a function of temperature obtained by tensile test at  $\gamma = 0.1$  %,  $f = 1$  Hz (second heating ramp).

In the remainder of this paper, we study the impact of increasing the OH concentration on the vitrimer properties. To this end, the pristine material **E/A-Zn(II)** is compared with the DHEBA-enriched one, **E/A-Zn(II)-DHEBA** which shows no loss of thermomechanical properties. The other sample, **E/A-Zn(II)-Glycerol** is no longer considered.

To better understand the impact of degradation at high temperatures, samples were analyzed by rheology and ATR-IR at different temperatures. In Figure 4A, the elastic modulus is followed over time. The elastic modulus increases more rapidly at 200 °C, which would mean more crosslinks are being formed. This hypothesis is compatible with ATR-IR analysis of the sample before and after this step at 200 °C in the rheometer (Figure 4B). While O-H stretching signal diminishes after this step, C-O signal increases in the ether region. This would mean two C-OH groups dehydrate to form an ether bond, implying an increase of links in the network at high temperature. Selective depolymerization by transesterification in ethanol was performed on vitrimer networks (Figure 4C). This treatment only break ester bonds. The remaining polyether is soluble in ethanol and can be analyzed by size exclusion chromatography. The peak at long retention volume reveals the presence of DHEBA monomers in both the pristine vitrimer and the post-cured vitrimer. Species of higher molecular mass are detected at lower retention volumes. The presence of those polyether networks or oligomers is more important in the post-cured vitrimer, confirming post-crosslinking in the vitrimer network at 200°C.



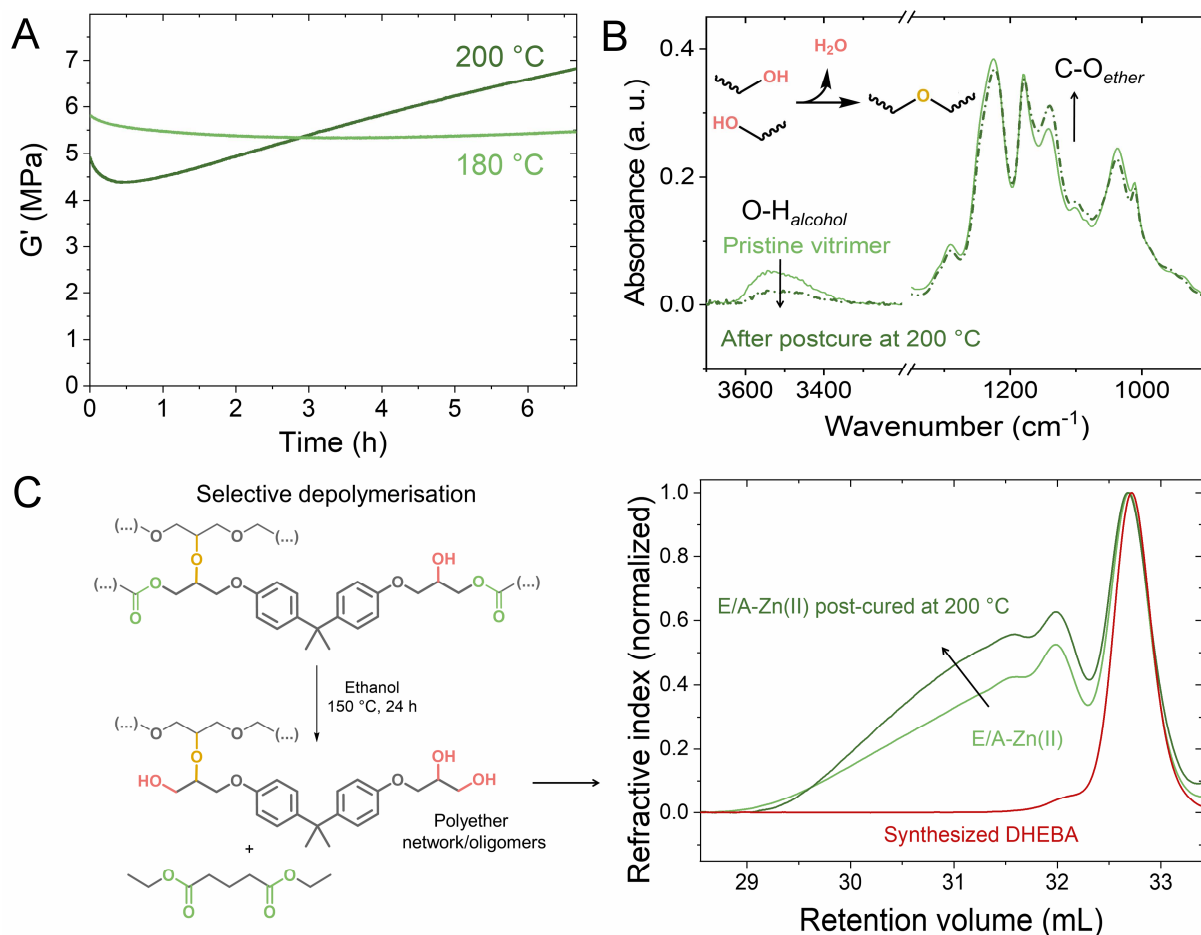


Figure 4 – A) Evolution of elastic modulus of E/A-Zn(II) over time at 180 °C and 200 °C ( $\gamma = 0.5\%$ ,  $\omega = 1$  rad/s). B) ATR-IR analysis of E/A-Zn(II) before and after time sweep at 200 °C. C) Selective depolymerisation of E/A-Zn(II) by transesterification in ethanol with SEC results.

**3.4 Stress relaxation behavior of epoxy vitrimers.** The experimental setup and the stress relaxation moduli measured in torsion mode in the linear regime of deformation at different temperatures for **E/A-Zn(II)** and **E/A-Zn(II)-DHEBA** are presented in Figure 5. The relaxation time  $\tau$  of each curve is determined from  $G(\tau)/G(t_0) = 1/e$ , where  $t_0 = 0.1$  s. Great care has been taken to extend the experiment until complete relaxation, except at 140 °C where complete relaxation would require prohibitive experimental time scales. The relaxation moduli at five different temperatures ranging from 140 to 180 °C are analyzed. The maximum temperature of 180 °C is chosen to be far enough from  $T_g$  and low enough to minimize side reactions as shown in the previous paragraph. At 180 °C, **E/A-Zn(II)-DHEBA** has a relaxation

time of about 15 min, whereas the pristine network, **E/A-Zn(II)** needs about 45 min to relax the stress by the same amount. This 3-fold acceleration is obtained throughout the entire temperature range. The Arrhenius plots showing the variations of the relaxation time versus  $1/T$  for both samples are presented in Figure 5C. Clearly, **E/A-Zn(II)-DHEBA** shows faster relaxation times than **E/A-Zn(II)**, although their activation energy is about the same ( $E_a = 80 \pm 17$  kJ/mol for **E/A-Zn(II)-DHEBA** and  $E_a = 64 \pm 13$  kJ/mol for **E/A-Zn(II)**). This can be explained by considering that the bond exchange reaction is the same but that the increased concentration of reactant in **E/A-Zn(II)-DHEBA** is responsible for faster relaxation. This comparison of Arrhenius plots is similar to the one obtained when varying Zn(II) catalyst concentration in epoxy-acid vitrimers.<sup>2,27</sup>

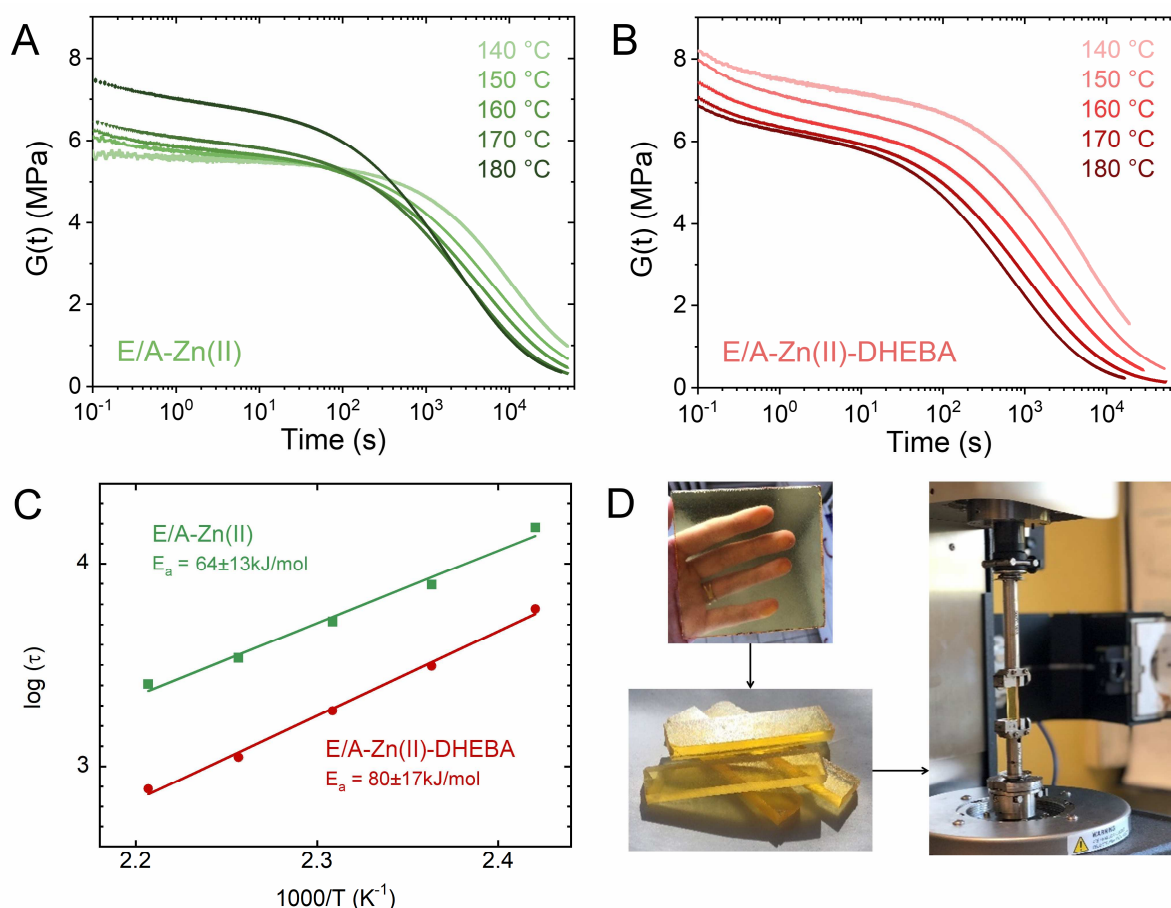


Figure 5 – Stress relaxation experiments (torsion geometry,  $\gamma = 0.5\%$ ). A) Relaxation modulus over time at different temperatures for compound E/A-Zn(II). B) Relaxation modulus over time at different temperatures for compound E/A-Zn(II)-DHEBA. C) Arrhenius plot of both E/A-Zn(II) and E/A-Zn(II)-DHEBA: decimal log of relaxation time as a function of the inverse of temperature. D) Picture of E/A-Zn(II)-DHEBA samples: entire piece, cut for rheology, and in the ARES G2 rheometer in torsion geometry.

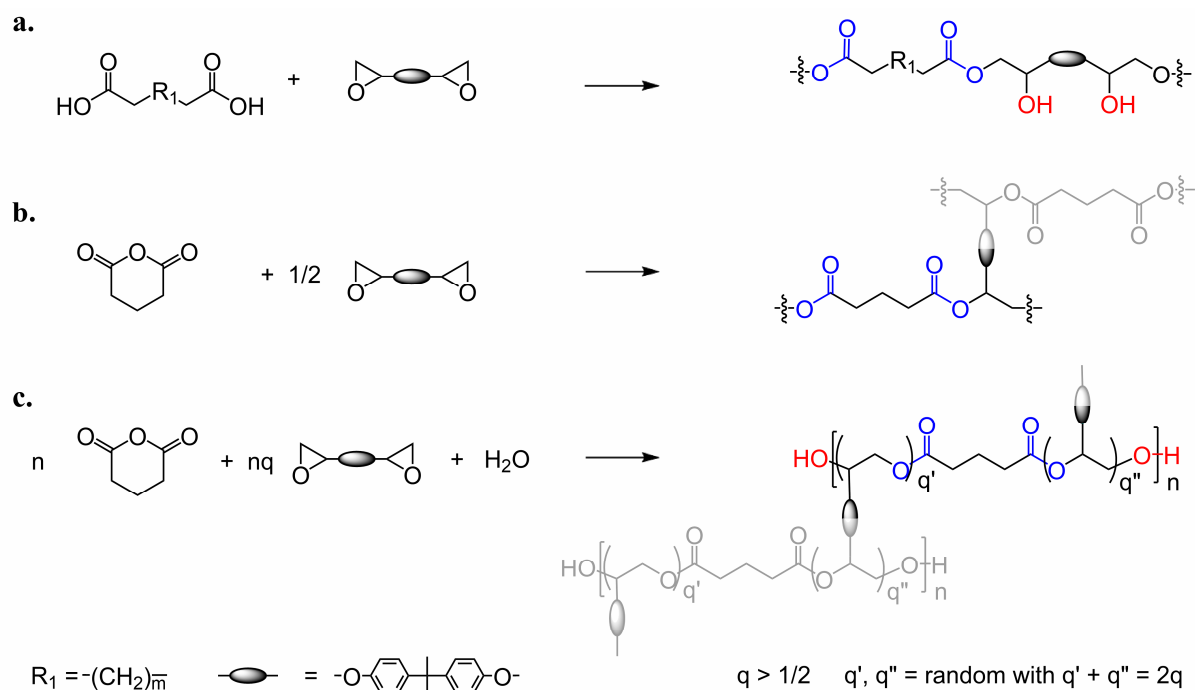
## 4. DISCUSSION

### Enriching the epoxy-anhydride network with one of its components to reach high $T_g$

**vitrimers composition.** — Transesterification has been the first exchange reaction used to impart thermostimulated flow properties without loss of connectivity in a chemically crosslinked polymer network, introducing the concept of vitrimers.<sup>1,2,6</sup> Epoxy-acid systems have been used to synthesize networks containing hydroxide and ester functions, which are able to take part in exchange processes. The key reaction is the addition of carboxylic acids on epoxy functions giving rise to hydroxy-ester links,<sup>28</sup> as shown in Scheme 1. In this reaction,

an equimolar mixture of epoxy and acid provides an equal number of esters and alcohols: the synthesis is controlled. Meanwhile, the glass transition of networks thus synthesized remains close to the ambient, due to the flexibility of monomers involved.<sup>17,29</sup>

**Scheme 1 a. polyaddition at the equimolar ratio of carboxylic acid and epoxide functions, b. alternate copolymerization at equimolar ratio of anhydride and epoxide functions, c. copolymerization of anhydride and epoxide functions in the presence of epoxide functions in excess and water.**



Compared to scheme 1a, the epoxy - anhydride reaction,<sup>28</sup> gives twice more ester bonds making it suitable for the synthesis of tight mesh networks.<sup>1,6,15,30,31,32,33,34,35,36</sup> Thus, at an equimolar ratio of anhydride and epoxide, copolymerization gives rise to a polyester network,<sup>28</sup> virtually deprived from hydroxide side groups, as shown in Scheme 1b. Upon anionic initiation, polymerization proceeds as follows: first an alcoholate opens the anhydride to provide an ester and a carboxylate, then the carboxylate opens an epoxide to provide an

ester and an alcoholate, and the *processus* repeats until termination occurs. Therefore, an equimolar ratio should not theoretically provide the alcohol functions that are required to enable transesterification reactions.<sup>37</sup>

The ratio mainly used for epoxy-anhydride vitrimers was of two epoxides for one anhydride, and the anionic polymerization was not performed in dry conditions, thus allowing two additional reactions:<sup>28</sup> On one hand, the excess of epoxide brings an excess of alcoholates compared to carboxylates; each alcoholate can open another epoxide to form an ether bond and a new alcoholate. This leads to homopolymerization of the epoxide, which contributes to increase the number of branching as shown in scheme 1c, resulting in a higher crosslink density, higher elastic modulus and higher  $T_g$ , but is disadvantageous for vitrimer properties because the ether link is not exchangeable. On the other hand, termination can occur by reprotonation of the alcoholates in excess, thus generating hydroxide end groups. To sum up, this type of curing produces ether, ester, hydroxide functions, and branchings, as depicted in Scheme 1c.

This type of polymerization yet anionic, is not a living one. As no special care is taken to protect against humidity, one might anticipate that the necessary water molecule will always be present. The results of section 3.1 demonstrate that this is not the case and that the hydroxide distribution inside the vitrimer is not uniform. Adding a protic molecule other than water might be an option and, indeed the presence of alcohol functions in an epoxy-anhydride reactive mixture has been shown to accelerate the cure reactions and effectively yield OH groups;<sup>38,39,40,41,42,43</sup> . It has also been shown that adding glycerol in an epoxy-anhydride system accelerates stress relaxation at elevated temperatures.<sup>26,44,45</sup> Here we have found that this modification is detrimental to the thermomechanical properties. In that perspective, our concept is to enrich the formulation without introducing any foreign molecule, solely enriching the network by one of its components i.e. by adding DHEBA (Figure 6).

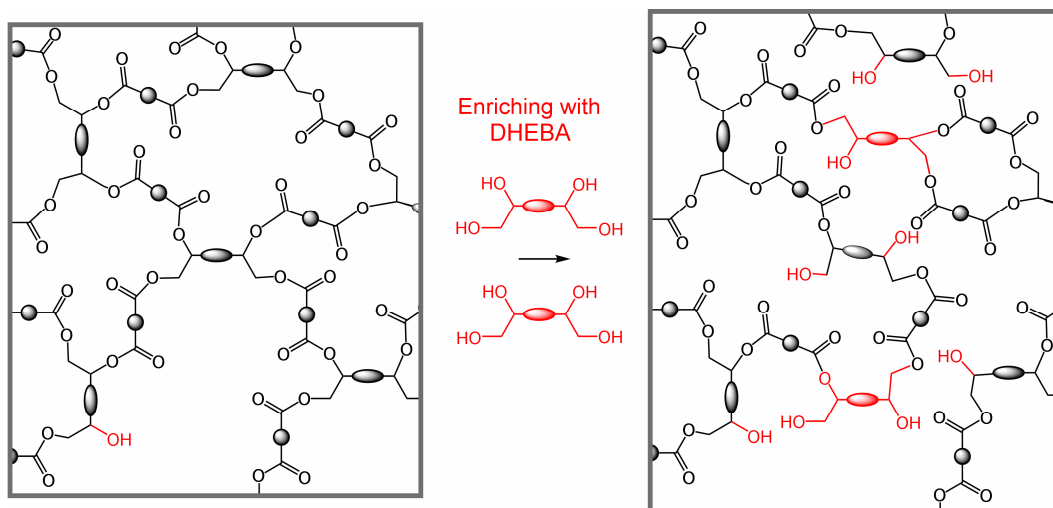


Figure 6 – Strategy to increase the hydroxide constant without adverse effect on stiffness. The network is enriched by one of its own components. Each molecule of DHEBA incorporated adds four OH groups somewhere in the network.

The only chemical difference between DHEBA and the diepoxy monomer is the presence of vicinal diols replacing the epoxides. The integration of the molecule into the network is possible by addition (e.g. with an anhydride), by condensation (with a carboxylic acid) or by transesterification (with an ester). As a result, each DHEBA will add four hydroxyl groups somewhere on the network. As simple as DHEBA seems to be, it is not commercially available at a large scale nor at moderate price. However, it is inherently present in the life cycle of epoxy thermosets, being the major product of the reactive depolymerization of epoxy-acyl networks, and it is not volatile. With that in mind, it seems clear that this alcohol can substantially contribute to eco-conceived epoxy vitrimers, being at the same time an interesting monomer to build networks and one of the products of their chemical recycling.<sup>46</sup>

The synthesis of the monomer DHEBA hereby reported takes inspiration from both the synthesis of epoxy vitrimers and their bond exchange reaction, transesterification. Once incorporated in the network, the decrease of elastic modulus at alpha transition occurs at higher temperature and more steeply, showing better homogeneity, leading to improved heat resistance. Moreover, relaxation time is shortened by a factor 3 throughout the 140–180°C range.

## 5. CONCLUSION

In epoxy-anhydride vitrimers, the formation of OH end groups only relies on hardly controllable side reactions such as hydrolytic termination. This feature gives rise to heterogeneities of OH group concentration in the synthesized networks. Addition of the rigid diglycol molecule: DHEBA appears as an efficient strategy to ensure a higher concentration of OH groups evenly distributed throughout the material, maintaining a high  $T_g$  and low level of outgassing, and simultaneously improving the relaxation properties of the vitrimer. Yet side-reactions conducive to additional ether links remain a limitation at temperatures higher than 200°C. The production of the DHEBA molecule can be based on the depolymerization of vitrimer (or non vitrimer) acyl-cured epoxy networks. As for the eco-conception of a future material, the presence of bisphenol A fragments may be questioned, even though DGEBA-based epoxy formulations are still the most used and food approved.<sup>47</sup> To comply with possible restrictions of use, the process to synthesize a tetrafunctional alcohol and the concept of shifting the transesterification equilibrium presented here can be applied to any polyepoxide, including biobased epoxy resins.<sup>48,49,50,51</sup> For instance, the diglycidylether of divanillyl alcohol (DiGEDVA)<sup>52</sup> might be easily blended with its divanillyl alcohol precursor to reach the same goal as described here.

## Associated content

\*ESI Electronic Supporting Information. The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021>

Materials, Analytical techniques, Synthesis of bisphenol A bis(2,3-dihydroxypropyl) ether (DHEBA), Chemical characterization of DHEBA (<sup>1</sup>H NMR, IR, SEC analysis, thermogravimetric analysis of glycerol, DHEBA and the synthesized networks, Dynamic mechanical analysis and rheology of the synthesized networks (PDF).

## Conflicts of interest

There are no conflicts to declare.

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