

Viscoelastic characterization of reformable epoxy vitrimers composites

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Abstract. Epoxy Vitrimers are gathering attention as a development in the field of more easily re-processable and self-healing thermosets. Incorporating a catalyst should activate the transesterification reaction within the polymeric macromolecule inducing topological modification of the network. Reacting epoxy precursors with suitable anhydrides and acids will promote exchange reactions between esters and beta-hydroxyls, adding the vitrimeric behaviour. In the present work, a commercial epoxy system suitable for CFRP manufacturing has been modified to induce vitrimeric behaviour by exploiting the catalytic activity towards the transesterification reaction of Zn²⁺. Creep experiments confirm that the resin starts to flow above a critical “Vitrimeric” temperature (T_v). Moreover, the thermoformability of vitrimer-CFRP has been investigated by reprocessing CFRP coupons.

Introduction

Unlike thermoplastic polymers, thermosetting resins and their composite materials are very difficult to recycle. A stable cross-linked structure prevents long-range molecular mobility necessary to activate material flow at temperatures high enough to reform and recycle. As a result, thermosetting composites are hardly recycled, and most components are sent to landfills at the end of their service life.

Increasing environmental awareness and industrial competitiveness encourage introduction and development of repairable and recyclable structural materials to reduce polymer waste and extend their service life. Recently, the development of thermoreversible cross-linked networks has been introduced as a viable alternative to produce composite components that can be recycled and reformed as thermoplastic materials [1,2]

Introducing a thermoreversible covalent bond in the cross-linked backbone allows the topological reshuffling of polymeric networks and makes it possible to rework and reform the cross-linked material. The dissociative Diels- Alder reaction between furans and maleimides is a well-established approach for designing and synthesising covalent adaptable networks (CAN) [3]. As a further development in more easily re-processable and self-healing thermosets, vitrimers are gathering attention for outdoing the current drawbacks of CANs [4].

One possible mechanism that enables the vitrimeric behaviour in epoxy resins is based on transesterification exchange reactions between esters and beta-hydroxyls formed by reacting epoxy precursors with suitable acids/anhydrides [1,5]. Incorporating a catalyst activates the transesterification reaction and induces topological variations, stress relaxation and flow in the cross-linked networks, even though the total number of cross-links does not change [6,7].

However, there have been difficulties in realising such behaviour in rigid thermosets until 2011, when Leibler et al. [4] introduced a new group of materials named vitrimers. They applied the

well-established transesterification reaction to the hydroxyl and ester groups in an anhydride-cured epoxy matrix to create a reworkable thermosetting network.

During transesterification, the network's connectivity is altered via exchange reactions, inducing stress relaxation and plastic flow at elevated temperatures without depolymerisation.

In the presence of a transesterification catalyst, it was shown that elastomeric epoxy/acid and rigid epoxy/anhydride networks possess gradually decreasing viscosity with increasing temperature, as is characteristic of other vitreous materials such as inorganic glass. Shi et al. [8] investigated such systems' capability to be welded and reprocessed. Demongeot et al. [9] investigated the mechanism of action of the catalytic zinc species active in these materials.

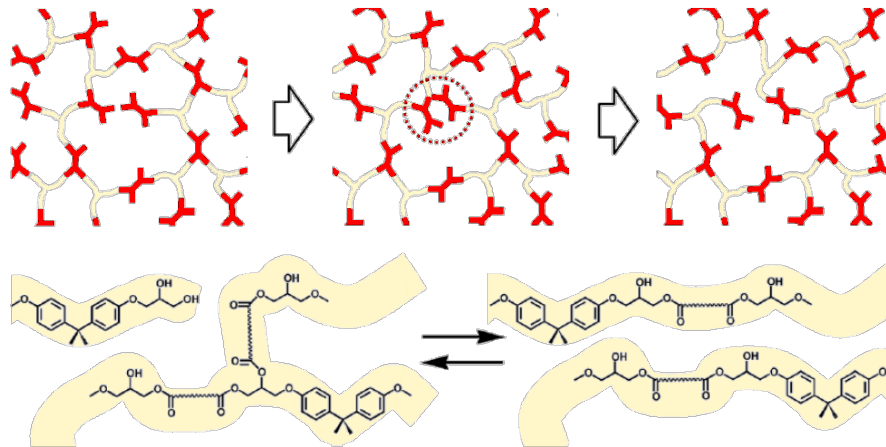


Fig. 1. Exchange reaction scheme and related topological changes. Adapted from [7,9].

In the present work, a commercial epoxy system (*araldite*® LY 3508 and *aradur*® 917-1 by Huntsman Corporation) suitable for CFRP manufacturing was selected for its modification as a vitrimer. Furthermore, zinc acetate was selected as a transesterification catalyst. Two formulations at a different stoichiometric ratio between epoxy precursor and curing agent have been prepared and modified by adding Zinc acetate into anhydride. Creep experiments showed a flow above a critical temperature (about 170°C) that confirms the achievement of a vitrimeric behaviour. In addition, a vitrimer-CFRP was realised using one of the formulations analysed and was thermoformed.

Materials and Methods

The used resin is a mixture of Bisphenol A diglycidyl ether (DGEBA) epoxy resin with an Epoxy Equivalent Weight (EEW) of 196.5 g/eq, tetrahydro-methyl phthalic anhydride (THMPA) curing agent and 2,4,6-tris(dimethyl aminomethyl)phenol as the catalyst, kindly provided by Huntsman corporation with product names *araldite*® LY 3508, *aradur*® 917-1 and Accelerator 960-1 respectively. The vitrimers formulations are based on ester interchange reaction, and Anhydrous zinc acetate (ZnAc₂) (99.99%) was used as the catalyst, purchased by Merck Sigma-Aldrich. All reagents were used without further purification.

The Epoxy resin *araldite*® LY 3508 and cross-linking anhydride *aradur*® 917-1 were mixed at room temperature with a mechanical mixer in a glass beaker until a homogeneous mixture was achieved. Subsequently, the Accelerator 960-1 was added and further mechanically mixed. The total weight of the prepared mixture was in the range of 100 g.

Two different formulations were realised, varying the epoxy to acyl ratio between 0.6 (M2) to 1.0 (M2A).

In addition, zinc acetate is added to the epoxy resin formulations to promote the ester interchange reaction and induce cross-linked resin's vitrimeric behaviour. First, an adduct is synthesised between tetrahydro-methyl phthalic anhydride (THMPA) and zinc acetate. Then, the

required amount of *aradur* 917-1 (20.00 g, 0.120 mol) and zinc acetate (3.22 g, 0.018 mol) are reacted in a round bottom flask at 120°C for 2 hours under nitrogen flow.

The THMPA/zinc acetate adduct is cooled to room temperature and used without further purification. Then, the epoxy vitrimeric mixture is prepared according to the above procedure while substituting *aradur*® 917-1 with the THMPA/zinc acetate adduct.

After mixing, samples were degassed under a vacuum and cured for 1h @ 120°C and 2h at 140°C. Table 1 summarises the cross-linked sample condition realised.

Table 1. Cross-linked sample composition.

Sample Codex	LY 3508 [phr]	Aradur 917-1 [phr]	960-1 acc. [phr]	r epoxy/acyl ratio	ZnAc ₂ * [%]
M2 **	100	70	3	0.6	-
M2A	100	40	3	1.0	-
M2-V	100	70	3	0.6	5
M2A-V	100	40	3	1.0	5

* ZnAc₂ percentage is calculated to the total acyl groups.

** Commercial Huntsman formulation

Experimental Methods

DSC was performed with a *Discovery DSC* of *TA Instruments* under a nitrogen atmosphere with a heating and cooling rate of 10°C min⁻¹, from room temperature to 250°C. About 10 mg samples were encapsulated in aluminium pans before measurements.

DMA experiments were conducted with a *Dynamic Mechanical Analyzer Q800* from *TA Instruments* in the single cantilever mode. Samples were measured from 30 to 160°C at 3 °C/min, a strain amplitude of 15 µm, and a frequency of 1 Hz. The samples were cut into a rectangular shape of 25 mm × 5.5 mm and a thickness of ca. 2.5 mm.

Creep tests were performed using a *Dynamic Mechanical Analyzer Q800* from *TA Instruments*. The Tension Film clamp with preload of 0.1 N was applied. The specimen dimensions were c.a. 10x5.5x2 mm³. Five minutes of isothermal hold was used before each creep segment, starting from 70°C to 220°C with 50°C incremental steps to evaluate sample strain variation from the glassy to the rubbery state. The stress of 0.1 MPa was applied for 45 minutes.

The ability of the vitrimer composite to be thermoformed has been assessed by applying plastic deformation in a three-point bending configuration with a span of 50 mm. The forming temperature (200°C) was chosen according to the vitrimeric temperature (in the actual epoxy system T_v is expected at 220°C,[10]). The sample was kept at the temperature of 200°C for 600s. Therefore, a load was applied (displacement control mode) with a speed of 500 µm/min up to a maximum deflection of 10 mm. The force needed to deform the sample was 0.1 N.

Results and Discussion

The preparation of cross-linked systems with semi-flexible molecular structures facilitates topological interchange reactions; however, it reduces the glass transition temperature and elastic modulus. Therefore, a balance must be sought between the reactivity of interchange linkages and thermomechanical properties. It is well known that bifunctional epoxy precursors can be cross-linked with monocarboxylic anhydrides using either an excess or a defect of the curing agent. Usually, the reaction is promoted by the presence of substituted amines as the catalyst. If a stoichiometric ratio between epoxy and acyl groups is used, the cross-linked density is lower, but the presence of hydroxyl and ester groups highly facilitates the ester interchange reaction [11].

The transesterification reaction can be activated by the presence of Zn²⁺ ions at an elevated temperature beyond vitrimeric temperature (T_v), leading to a topological rearrangement.

This study will discuss the influence of the THMPA/ZnAc2 molecular ratio on the epoxy formulations' mechanical properties. In addition, temperature-dependent creep experiments have verified the occurrence of molecular long-range rearrangements.

Epoxy mixture M2 described in Table 1 has been formulated as reference material. The epoxy is used with a stoichiometric defect, with a mole ratio of epoxy/acyl equal to 0.6. The acyl groups in stoichiometric excess can further react with -OH groups formed due to oxirane ring addition to carboxylic acid.

The curing behaviour and glass transition temperature of the M2 system are illustrated in Fig. 2a. The absence of an exothermic peak in the second heating ramp of DSC is a clear indication of a complete conversion. The observed T_g is about 120°C. The epoxy mixture M2A was subsequently prepared with a stoichiometric ratio between epoxy and acyls equal to unity.

The cure of M2A system is illustrated in Fig. 2b (DSC Thermogram). As expected, the T_g drops to 99°C due to a lower cross-linking density.

To obtain a vitrimerized version of M2 and M2A, zinc acetate is introduced as a suitable catalyst for ester interchange reactions. The amount of zinc acetate has been fixed at 5% of the acyl groups, the obtained systems have been named M2-V and M2A-V, respectively.

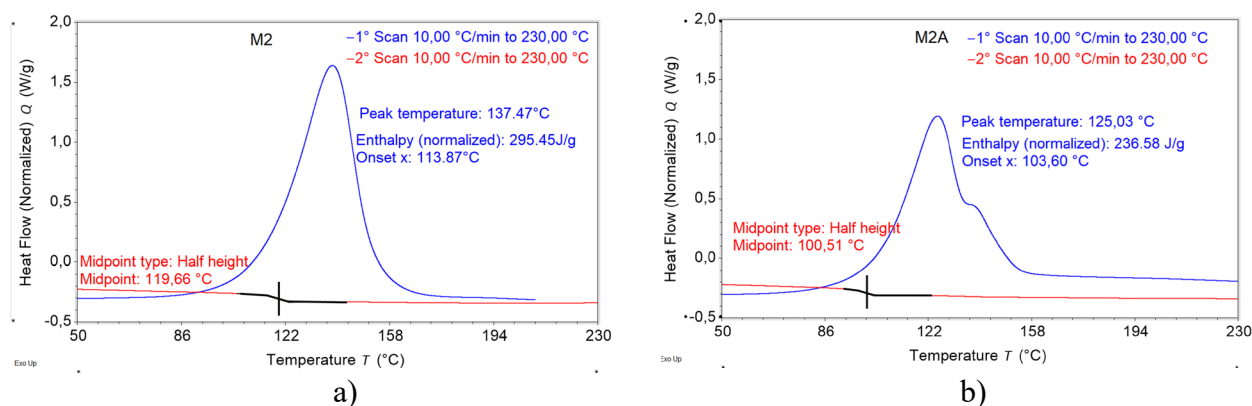


Fig. 2. DSC curves of the samples at different epoxy/acyl ratio. Reference resin a); stoichiometric ratio (epoxy/acyl 1.0, M2A) b).

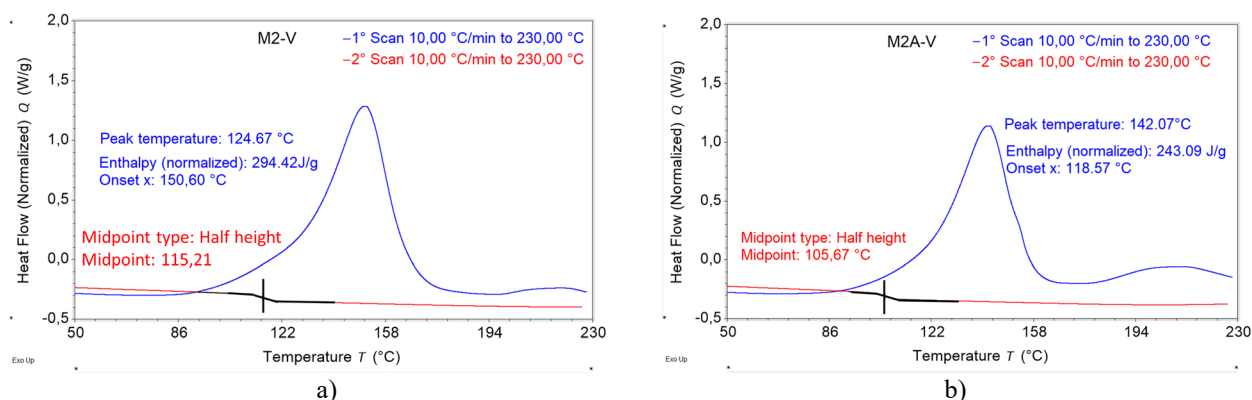


Fig. 3. DSC curves of the samples at different epoxy/acyl ratios. Modified formulation, "Vitrimer" M2-V a) and M2A-V b).

The zinc acetate influences the primary cross-linking reaction and activates a secondary reaction in the temperature range between 180 and 230°C, while the T_g of the cross-linked sample appears to be dominated by the ratio between epoxy and acyl groups (Fig. 3).

DMA experiments, shown in Fig. 4, have been performed in the linear viscoelastic deformation range to confirm cross-linked samples' glass transition temperatures and elastic modulus. The

glass transition temperature has been evaluated as the value at the inflection point of the storage modulus diagram.

The effects of catalyst addition and the different stoichiometric ratio between epoxy and acyls are shown in Fig. 5 and highlight three main phenomena:

- The glass transition temperatures obtained by DMA confirm the corresponding values measured by DSC;
- The addition of the Zn²⁺ catalyst produces an increase in the glassy elastic modulus;
- The $\tan\delta$ (ratio between loss and storage moduli) of vitrimeric systems (M2-V and M2A-V) @160°C is higher than corresponding conventional formulations (M2 and M2A, respectively). Indeed, this experimental observation could be related to a residual viscous flow, confirmed by following creep experiments.

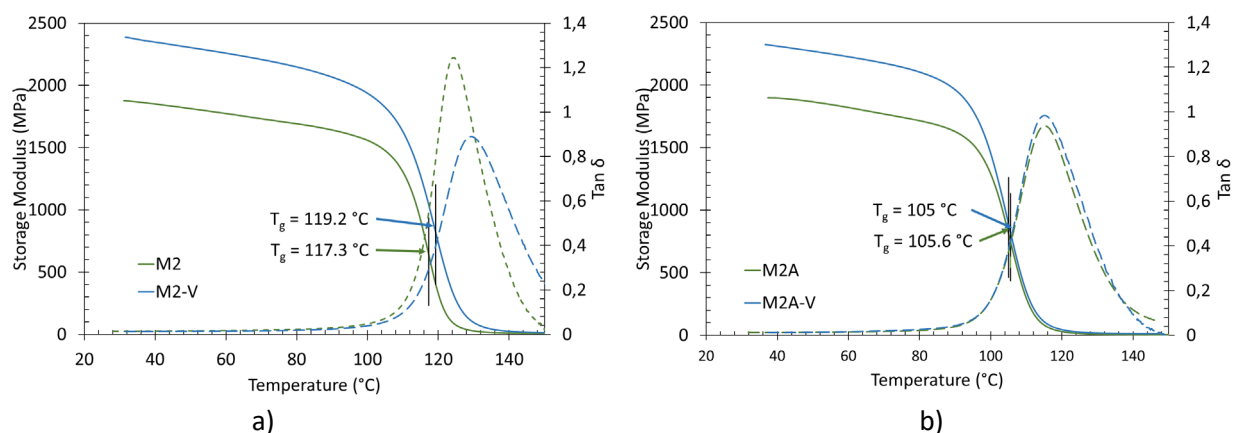


Fig. 4. DMA curves at different epoxy/acyl ratios M2 and its vitrimer a); M2A and its vitrimer b).

Table 2 summarises the thermomechanical properties of the analysed systems characterised by DSC, DMA and CREEP experiments.

Table 2. Thermo-mechanical properties.

Description	T _g (DSC) [°C]	T _g (DMA) [°C]	Reaction Enthalpy [J/g]	Elastic Modulus [GPa]
M2	119.7	119.2	295.5	1.88
M2A	100.5	105.6	236.6	1.89
M2-V	115.2	117.3	294.4	2.38
M2A-V	105.7	105.0	243.1	2.34

In addition to the DMA experiment, the explicit and robust confirmation of vitrimeric behaviour due to thermoreversible cross-linking rearrangements has been obtained by creep experiments.

Samples in the form of thin slabs have been subjected to creep experiments under tension deformation. The creep experiments have been performed in the temperature range between 70 and 220°C.

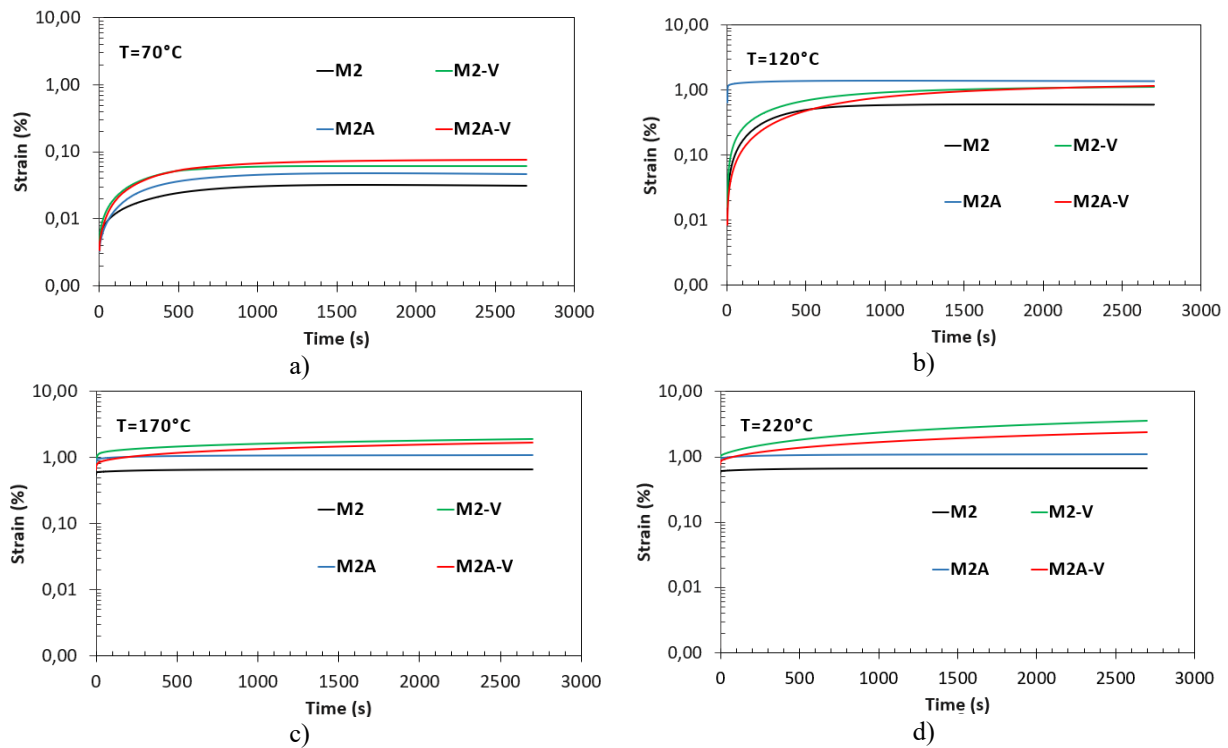


Fig. 5. Creep curves at different temperatures.

Specimen M2 and M2A showed stable behaviour; in fact, creep is negligible at each temperature. Even at temperatures higher than T_g , no molecular flow has been observed.

Things change when zinc acetate is added to the formulation. The presence of metallic ions strongly catalyses the ester interchange reaction, resulting in evident creep of samples subjected to tensile load at different temperatures, as reported in Fig. 5. The effects are higher in the case of the M2A-V sample with an equivalent amount of epoxy and acyls ($r=1.0$).

To verify the thermoformability of the vitrimeric matrix developed, a carbon fibre-reinforced composite has been realised using the matrix M2A-V.

The vitrimer-CFRP laminates were produced by hand lay-up and vacuum consolidation at 120°C (Fig. 6).

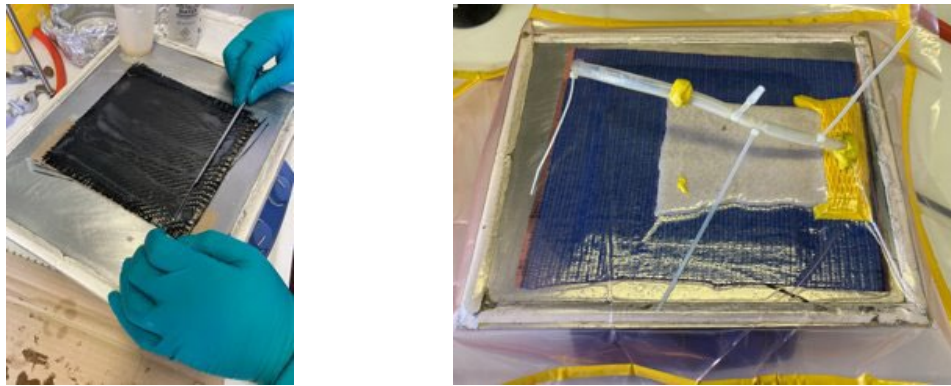


Fig. 6. Manufacturing procedure for vitrimer-CFRP.

Then, test specimens were cut to the dimensions 60x12 mm, and thermoformed following the procedure reported in Fig. 7.

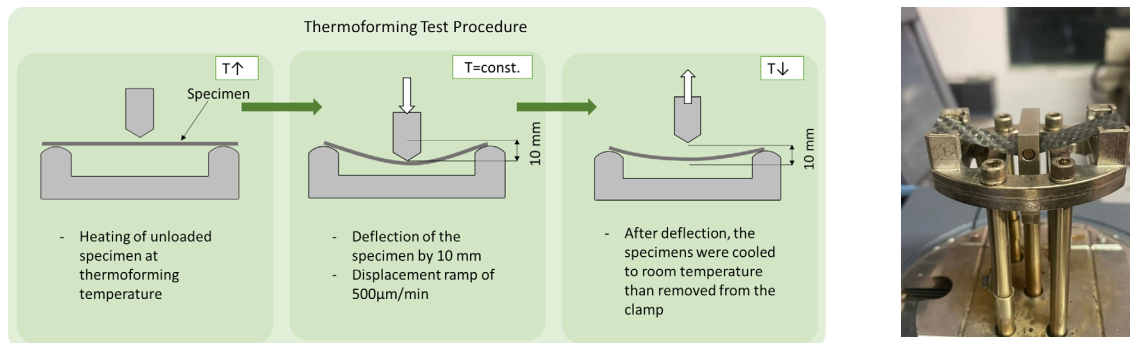


Fig. 7. Experimental set-up and 3-point bending thermoforming test procedure.

After the cooling stage, the sample was frozen in the deformed configuration, even if a spring-back (13%) had been detected. By observing the reshaped sample, no flaws or other defects have been observed, therefore, the polymeric phase is able to flow and is prone to be reprocessed to improve the sustainability of parts made by vitrimers.

Summary

The epoxy groups can efficiently react with carboxylic acids or anhydrides. Therefore, bi/multifunctional epoxy precursors can be efficiently cross-linked with carboxylic anhydrides, resulting in very stable materials with a glass transition temperature of 100-140°C and an elastic modulus in the range of 1.5-2.0 GPa.

In this work, two different formulations with the adjustable stoichiometric ratio between epoxy precursor and curing agent have been prepared. In order to promote the polymer modification into vitrimer, the catalyst Zn^{2+} has been introduced into the formulation by synthesising an adduct between $ZnAc_2$ and the THMPA curing agent, with a catalyst concentration of 5 % than to acyl groups. The presence of metallic ions strongly catalyses the ester interchange reaction, resulting in evident creep of samples subjected to tensile load at different temperatures. Moreover, an empirical approach to investigate the thermoformability of vitrimer-CFRP has been presented with satisfactory results.

Even if epoxy vitrimers have shown important features for increasing the sustainability of composite materials, major challenges will have to be faced to transfer this from an academic concept into real-world materials. First of all, it is mandatory to increase the glass transition to meet the requirements of structural applications, in addition, industrialisation needs affordable catalysts to sustain mass production, by the way, their development is very promising.

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