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LONG LATENCY VITRIMER FORMULATION FOR CARBON FIBRES PREPREGS COMPOSITES

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Abstract: *Vitrimers are currently investigated for their potential to produce strong, healable, recyclable and reprocessable matrices. Nonetheless their uses at industrial scale still present new challenges to be addressed. In the present work, we investigate the suitability of vitrimer based carbon fibre reinforced polymers for space application. Especially, we aimed at proving that formulation of catalysed epoxy vitrimer resin can be adapted to form prepregs carbon fibres that have good storage and handling properties. For this purpose, we focused our efforts to develop a vitrimer resin comprised of an epoxide and a crystalline hardener that shows long latency and satisfying viscosity for being stored and laminated in an industrial environment. Spectroscopy and rheology confirmed those requirements before production of a carbon fibres laminates with Thales Alenia Space (TAS). Furthermore, after curing, the vitrimer properties were used to bond laminates without adhesive (exhibiting cohesive fracture after breaking) and separate carbon fibres via depolymerisation.*

Keywords: Composites; Carbon fibres; Vitrimer; Aerospace; Prepregs

1. Introduction

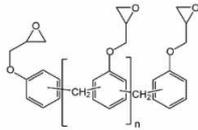
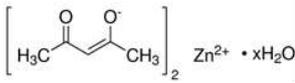
In less than a century, polymers have radically changed our world, becoming a part of almost every aspect in human life. Variety of chemistry and processing techniques combined with affordable primary resources, made polymers indispensable in many applications such as electronics, construction, medical devices, automobile, kitchen utensils etc. [1,2]. Nonetheless, one area that benefits and invests the most for polymers development is the aerospace industry [3,4]. Lightweight, strong, and complex structures are key requirements, improving safety and travelling distance while decreasing costs (*e.g.* fuel consumption). Particularly, carbon fibres composites reinforced polymers (CFRP) have seen increasing development and uses in this industry [5]. Those composites allow to combine fibres strength with processing techniques of polymers to form flat, tubular or more complex shapes. High performance requirements of the aerospace field means that thermosets - especially epoxies - are a preferred choice for matrix in CFRP [4,6]. Despite the variety of advantages brought by those, they also come with their share of drawbacks such as structures hardly repairable, reprocessable or recyclable [7].

Vitrimers, a newer kind of polymer networks, combine the properties of thermosets (insoluble and resistant) with the flow property of thermoplastics, through thermally stimulated covalent bond exchange [8–11]. Many chemistries were developed over the past decade and despite tangible potential for their uses in CFRP applications, their adaptation to classical processes remains barely explored. Techniques, such as resin infusion and resin transfer moulding have been experimented with vitrimers [12], however in high performance CFRP (aerospace, space

automotive, etc.), the prepregs technology is usually favoured as it allows to produce higher fibre/resin ratio, and has yet to be performed with vitrimer. Storage and handling steps are key requirements to meet for prepregs production, and the use of catalyst - in vitrimer made from commercially available monomers - can be seen as a limiting factor as it could trigger cure before layup is performed.

Herein, we report a vitrimer formulation compatible with prepregs preparation in an industrial environment. Comprised of a novolac epoxy type resin, a crystalline dicarboxylic acid hardener with high melting temperature and a Zn(II) transesterification catalyst; those reactants shown in Table 1 give a formulation allowing storage up to one month at ambient temperature. Rheological behaviour satisfies viscosity requirement for carbon fibres impregnation at 100°C while remaining tacky at room temperature for laminates layup. Once cured, this resin displays reparability and adhesive behaviour upon heating and can be successfully depolymerised to recover and separate laminates, opening possibility to form CFRP composites with improved sustainability at industrial scale.

Table 1 Reactants information

Monomers	Epoxy	Hardener	Catalyst
Name	Novolac based epoxy Epalloy 8330	Cyclohexane-1,4-dicarboxylic acid CHDA	Zinc acetyl acetonate ZnAcac
Formula			
Properties	Epoxy eq. wt. 171-183 (g/eq) Viscosity 20 - 30 Pa.s @ 52°C	Mol wt. 172.18 g/mol Melting T°: 164 - 167°C	Mol wt. 263.59g.mol ⁻¹ Melting T°: 135-138°C
Suppliers	Huntsman Ltd.	Abcr	Abcr

2. Results

Resin development latency and curing — Resin to impregnate fibres requires a set of simple, yet, altogether complex properties to obtain:

- I. A low viscosity for impregnation (< 100 Pa.s, preferably < 10 Pa.s) and latency at impregnation temperature (several hours)
- II. Latency at ambient temperature (≥ 7 days)
- III. Tackiness at ambient temperature for layup preparation.

The impregnation capacity of the resin (I) was defined using rheology and DSC measurements. Temperature was set between 100°C and 110°C (above the resin T_g , and well below the melting point of the other monomers), rheology measurements made on the novolac epoxy-CHDA mixture (without catalyst), are presented in Figure 1 a) and b) respectively. Due to the crystalline nature of CHDA, at 100°C, the system has little to no reactivity, hence, the measurement does not give particular information except that the gel point is not reached in 24h. At 110°C, conversion of epoxides and carboxylic acids happens leading to the crosslink of the network and the gel point is reached within ~758 min (12 h 38 min). Before that time, the viscosity of the system is comprised between 18-40 Pa.s satisfying the requirement for a 1-2h

fibres impregnation process. The question then arises if the catalysed version of this resin has similar reactivity time in this temperature range. However, the uncanny behaviour of the system (induced by the crystalline hardener constantly dissolving and recrystallising before the gel point) induces noisy rheological measurements, therefore, the activation energies E_a of the epoxy ring opening addition (for catalysed and non-catalysed system) was measured using the Kissinger di Benetto method [13] based on the assumption that the exothermic peak coincides with the maximum reaction rate as described by equation 1:

$$\ln\left(\frac{\emptyset}{T_p^2}\right) = \ln\left(\frac{k_0 R}{E_a}\right) - \left(\frac{E_a}{RT_p}\right) \quad (1)$$

With \emptyset , the heating rate, T_p the peak of the exothermal reaction and R the ideal gas constant. E_a was thus obtained from the slope of $\ln(\emptyset/T_p^2)$ as a function of $1/T_p$ (Figure 1 c). The catalysed mixture gives an activation energy of $E_a = 63 \text{ kJ.mol}^{-1}$, while the non-catalysed system gives $E_a = 51 \text{ kJ.mol}^{-1}$. This fact shows that the chosen catalyst (ZnAcac) does not decrease the energy barriers involved in the (exothermic) ring opening reactions. In such a system comprised of novolac epoxy resin - with an average number of epoxy group per chain higher than 2, gelation occurs at early stage of conversion, without necessary involvement of transesterification [14]. As a result, the rheological evolution of this system is not critically dependant on the rate of transesterification. ZnAcac will therefore catalyse the transesterification reactions of the final cured vitrimer but not influence much the course of curing. Moreover, the slightly higher value of the apparent activation energy in the catalysed system means potentially better thermolatency than the uncatalysed one, which would only improve the required resin properties for prepregs handling and storage.

One of the primary objective of the resin development is to obtain at least several days of latency at room temperature (II). Indeed, the impregnated fibres should give the possibility to have enough time to layup fibres for a composite structure before the impregnated fibres start to show signs of gelation and become difficult to process. The latency of the novolac epoxy / CHDA system, catalysed with ZnAcac was evaluated via ATR-IR spectroscopy over 25 days at room temperature (Figure 1 d). After this period, there was no noticeable changes in the IR spectrum, indicating no significant conversion on this time scale. This confirms good latency for the formulation which has virtually no reactivity at room temperature due to the stability of CHDA crystals in epoxy at this temperature. The last point (III) is the tackiness of the system at ambient temperature. For this matter, as the system remains in its initial state, stickiness is governed by the inherent properties of the novolac resin producing a system of stable tackiness at ambient temperature, allowing easy layup process. Once these preliminary measurements were obtained, the next step was to develop procedures to prepare prepregs. This brings new considerations regarding the base system. Indeed the crystallinity of the CHDA with high melting temperature gives a satisfactory latency for storing, and handling prepreg plates at room temperature or below. On the other hand, the novolac resin gives satisfying viscosity for impregnation at 100°C and tackiness at ambient temperature. However, the raw mix is a dispersion of small solid particles in a viscous liquid, which brings challenges to obtain homogenous samples: a fast curing at high temperature leads to samples with bubbles and high quantity of unreacted CHDA crystals. Meanwhile, a too low temperature leads to a high level of sedimentation of CHDA and phase separation, with epoxy on a side and CHDA on the other side, potentially inducing unwanted homopolymerisation of the epoxy resin.

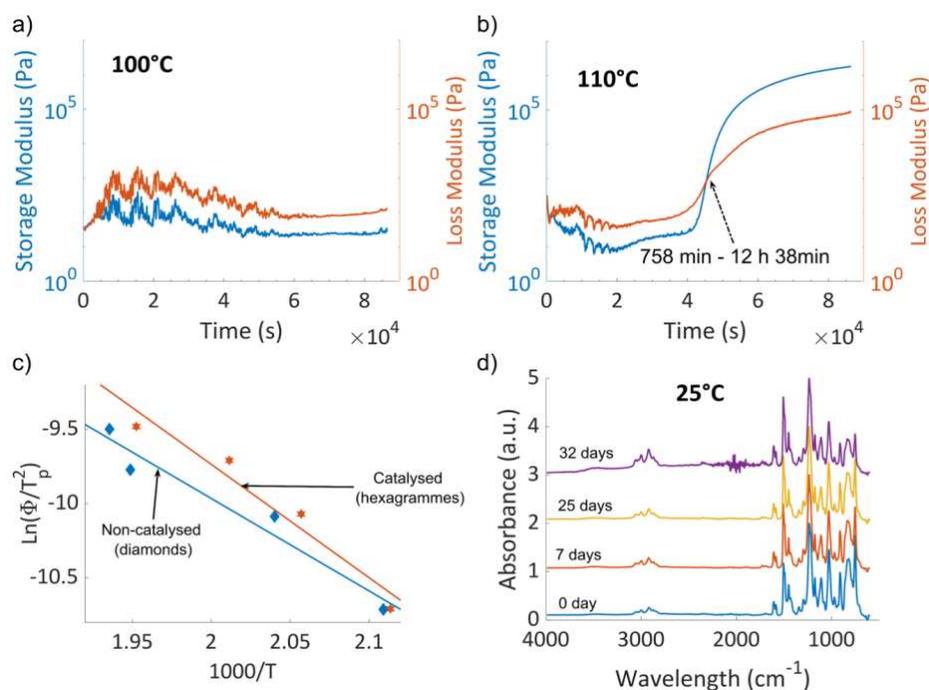


Figure 1 a-b) Rheology measurement: storage and loss modulus of the mix novolac epoxy-CHDA without catalyst at 100°C and 110°C respectively, c) Arrhenius plot of epoxy conversion for catalysed (orange curve) and non-catalysed (blue curve), d) Latency of the catalysed system over 25 days.

In both cases, this would be detrimental to the vitrimer properties and solution to homogenise the system before curing is required. Therefore, CHDA crystals need to be dissolved within the epoxy following procedures developed with similar systems [15,16]. The resin was then pre-cured 1h at 130°C, before starting the curing stage. Although disappearance of CHDA crystals is easily seen by eyes (with the resin becoming transparent), ATR-IR spectroscopy enables to analyse the composition of the reactive mixture throughout the curing process. In this step, our main areas of interest are:

1. The epoxy signal, (asymmetric deformation vibration of the ring) detected at $\sim 917\text{cm}^{-1}$. Its decrease informs us about the epoxy consumption while reacting with the hardener.
2. The C=O stretching vibration of the β -hydroxylester, **3** formed by epoxy-acid addition, detected at $\sim 1730\text{cm}^{-1}$.
3. The C=O stretching vibration of the carboxylic acid, split into two different signals :
 - a. $\nu_{\text{C=O}}$ of the *oxo*-H-bonded form, **2a** is detected at $\sim 1705\text{cm}^{-1}$ (Figure 2a)
 - b. $\nu_{\text{C=O}}$ of the *oxo*-H-bonded form, **2b** is detected at $\sim 1738\text{cm}^{-1}$ (Figure 2b)

The infrared spectrum of the reactive mixture focussing on the -COOH vibration band region at the beginning and at the end of the precure are presented in Figure 2c. The signal of the carboxylic acid hardener is not detected at the beginning of the curing stage. To explain this, it must be reminded that, in the ATR technique utilised here, the region scanned by the infrared radiation is not deeper than the depth of the evanescent wave D_p . Practically, D_p is of the order of a few microns, or less. In case of a two-phase sample, the heterogeneous distribution of the constituents in the vicinity of the interface may cause one of them to disappear. This is what is happening here. Due to the size of CHDA crystals, there is depletion of this component along the interface as long as it remains in the solid form. Conversely, once the medium becomes homogeneous, all the molecules in presence can access the interface and give rise to

detectable IR absorption signals (Figure 2c). As for the epoxy signal (not represented here), it barely changes between the start and the end of post-curing, showing little reaction at this temperature. This is all the more true since the observed decrease is partly due the dilution brought by the melting of CHDA crystals as shown by the transparency of the reactive mixture after the pre-curing stage (Figure 2d).

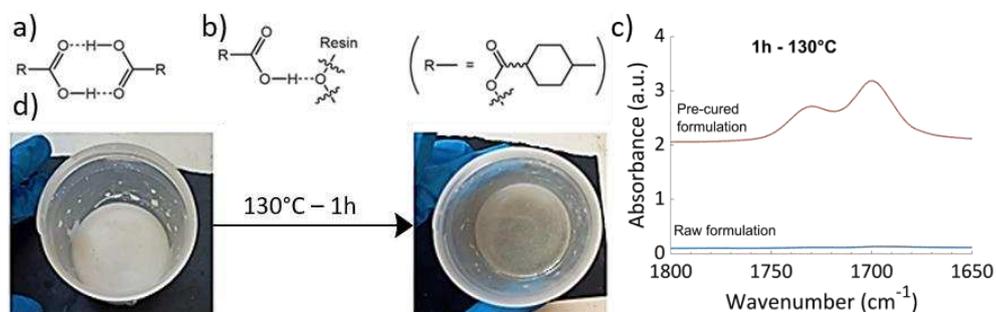


Figure 2 The CHDA crystals dissolution in epoxy: a) oxo-H-bonded acid, b) oxy-H-bonded acid, c) ATR-IR of COOH area before and after the curing stage.

Determining the curing temperature and time was then the next step to insure manufacturing of CFRP composites with satisfying properties. Further analysis of these monitoring was performed by integrating the 3 signals defined earlier over a 24h period at different temperatures: 100°C, 110°C, 130°C and 145°C. At 100°C, after 24h, the characteristic signals of acids and epoxy (Figure 3 a and b respectively) barely evolved indicating that the mixture has little reactivity and thus confirming time to perform impregnation. At 110°C, after 24h, both signals evolved slightly and the characteristic ester's vibration appears (Figure 3c), indicating that the polymerisation started but was not completed (as revealed by the decreasing epoxy signal after 24h (Figure 3b)). At 130°C (Figure 5c), both signatures (carboxylic acids and epoxides) completely disappear within 24 h and a clear ester vibration is seen indicating that the polymerisation reaction was fully achieved on the ATR-IR cell. However, at 130°C, the system takes ~500-600 min (*i.e.* > 10h) to reach a plateau, then the conversion slows down for the rest of the measurement. This indicates that most chemical moieties reacted through polymerisation and once most of reactants are consumed (~80%), the reaction slows down. Another classical reason for slackening is the vicinity between the cure temperature and the so-called T_{∞} (*i.e.* T_g of the fully cured network, reported to be located between 110°C and 130°C for similar network [15]). At 145°C, the plateau is reached within \approx 420 min (7h). Therefore, to optimise the time of impregnation and curing, the process was finally set as follow: (i) mixing of components, (ii) fibres impregnation at 100°C, (iii) layup at ambient temperature, (iv) precuring stage at 130°C for 1h, (v) curing stage at 145°C for 8h and, (vi) postcuring stage at 180°C for 6h insure a maximal conversion of remaining reactive functions.

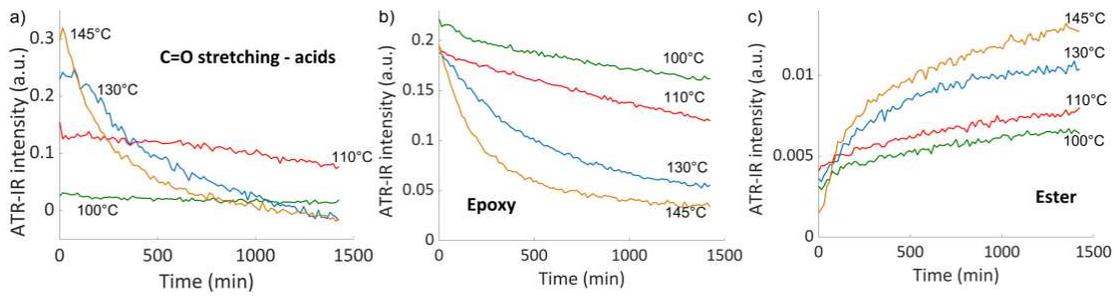


Figure 3 Time dependence of infra-red characteristic signals over a 24h period of time for the pre-cured version of the resin: a) oxy H-bonded acid signal, b) epoxy signal and c) ester signal.

CFRP manufacture and testing — subsequently to the determination of prepregs preparation, the suitability to manufacture large size panels in an industrial environment was verified. TAS and Kalliste composites took upon impregnating a large carbon fibre (1m²) manually as represented in Figure 4. The fibre was then cut in 30cm² size sheets and layed up in a 0/60/-60/0/90/-30/ manner. This panel was then cured under vacuum following procedure determined earlier.

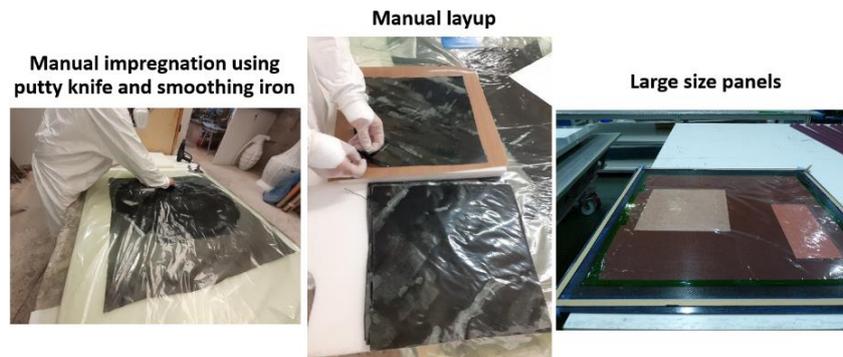


Figure 4 Manufacture of large vitrimer prepreg, layup and curing of 30 cm² panels

Subsequently, the panel was then cut in small samples of 10 x 2 cm to proceed of vitrimer properties exploration. As a proper protocol is yet to be determined in order to measure relaxation of CFRP vitrimer and reshaping is rather limited by the fibres [12], our focus went on showing interest of such CFRP vitrimer for sustainable aerospace applications: capacity of cracks healing, adhesion without the use of glue or bolts, and recovery of fibres at the end of the composites life cycle. Firstly, we chose a damaged sample showing signs of delamination during the cutting step. This sample was pressed at 180°C for 1h under 0.5 bar. It can be seen that after the procedure (Figure 5), the fibres successfully adhered to the matrix, reducing the damages induced either during manufacturing or handling of CFRP panel. Other sample pieces were then prepared for adhesion tests. 6 samples were flattened in a hot press for 1h at 180°C under 0.5 bar pressure, 2.5 cm² surfaces were sanded and cleaned before being pressed against each other by pairs, as to form three lap-shear joints with an overlap area of 2.5 cm². The lap shear specimens were placed for 1h30 at 180°C in a clamp comprising two M5 screws tightened with a torque of 1.7 N.m, thus ensuring a force of approximately 4000 N over the total area of 7.5 cm². After the clamp was removed, the samples adhered to each other. To measure the strength of the adhesion, lap-shear tests were performed, the sample was pulled 4 times to 1 kN pulling force (\approx 4 MPa) without break, showing shear strength equivalent to classical epoxy glue. On the 5th pulling, the sample broke at the interface, exhibiting cohesive

fracture (figure 5), indicating that adhesion of the two CFRP pieces was achieved through effective welding of the matrix, permitted by the vitrimer bond exchanges mechanism. Finally, one of the main issues of thermoset CFRP is their end of life. Not only this led to potential environmental wastes but carbon fibres are expensive, and methods to recover them usually imply destruction of fibres length but also high temperature. Here, we took a small sample (2cm x 1cm), and plunged it into an ethanol/acetone solution (50:50). The sample was then heated for 4h at 180°C in a pressurized reactor to trigger vitrimer depolymerisation. After removal and cooling, the fibre sheets were separated with the help of a spatula and recovered as shown in Figure 5. Despite small damage induced by the separation process, it is clear that the depolymerisation allows to separate laminates in the size of the initial sample without the use of high temperature or harsh chemical usually used to remove classical thermoset epoxy resin.

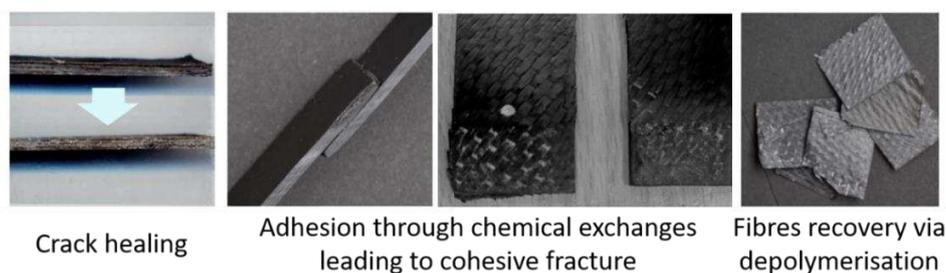


Figure 5 Use of vitrimer properties for crack healing, self-adhesion and CFRP fibres recovery

3. Conclusions and outcomes

The novolac epoxy and crystalline CHDA reactive mixture shows potential for long latency to form prepreg. Combining high melting temperature of the hardener and flow properties of resin at ambient or impregnation temperatures allows to obtain a mixture able to easily impregnate carbon fibres while performing well for storage and handling of CFRP prepregs. The methodology developed at the ESPCI Paris was used at Kallista composites (TAS industrial partner) and led to manufacture of CFRP panels within 3 days of work. Damages that occurred during the manufacturing or cutting of the composites have been repaired. A simple heating under pressure for 1h led to voids and delamination removal, an interesting point which could find practical echo at several stages of composite implementation: (i) improvement of panels after manufacture leading to lower waste on the manufacturing lines. (ii) Repair of damages induces by handling at the pose of composites or even later through their life. Moreover, adhesion tests of CFRP made from vitrimer prepregs show that composite thus produced could be put together in larger scale without the use of adhesive or bolts, reducing weight of structure but also materials costs for production and assembly. It is also envision that this kind of material is relatively suitable for space exploration, CFRP vitrimer prepregs could serve a structure for spacecraft, then disassemble by heat upon arrival to be reassembled as life structure. Finally the CFRP samples have also a greater environmental sustainability, as the fibres can be recovered using soft solvent at relatively low temperature (< 200°C).

Although, results for preparing vitrimer prepregs and their testing with the CHDA formulation are encouraging, many points remained to be determined. Firstly the ratio fibres/matrix obtained through this technique is to be controlled as the main advantages of prepregs samples is to obtain a high fibres proportion relative to the matrix. For this, it is necessary to

verify that the crystallinity of the CHDA does not limit fibres impregnation with automated machines to obtain a constant fibres/resin ratio difficult to obtain by manual impregnation. On the composites properties sides, rheological behaviour, degassing properties and mechanical properties (compression, tensile, bending, etc.) at ambient and above the polymer T_g have to be performed for comparing with a traditional thermoset resin to validate the use of such resin in demanding environments. Those points are currently under investigation with TAS and the European Space Agency, nonetheless, vitrimer networks have ticked a new box at their potential for adoption in industrial uses to replace or complement traditional thermoset resin.

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