



New perspectives in fibres reinforced polymer composites for aerospace structures

Quentin-Arthur Poutrel, Laurence Cornillon, Jolanta Hamerlak, Ludovic Chichignoud, Simon Appel, Ugo Lafont, Shumit Das, Francois Tournilhac, Olivier Damiano

► To cite this version:

Quentin-Arthur Poutrel, Laurence Cornillon, Jolanta Hamerlak, Ludovic Chichignoud, Simon Appel, et al.. New perspectives in fibres reinforced polymer composites for aerospace structures. European Conference on Spacecraft Structures, Materials and Environmental Testing (ECSSMET 2021), DLR-CNES-ESA, Mar 2021, Braunschweig, Germany. hal-04237573

HAL Id: hal-04237573

<https://hal.science/hal-04237573>

Submitted on 11 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

New perspectives in fibres reinforced polymer composites for aerospace structures

Quentin-Arthur POUTREL¹, Laurence CORNILLON², Jolanta HAMERLAK³, Ludovic CHICHIGNOUD⁴,
Simon APPEL⁵, Ugo LAFONT⁶, Shumit DAS⁶, François TOURNILHAC^{1,*}, Olivier DAMIANO^{2,*}

¹ Molecular, Macromolecular Chemistry, and Materials, ESPCI Paris, PSL University, CNRS, 10 rue Vauquelin, 75005 Paris, France
quentin-arthur.poutrel@espci.fr / françois.tournilhac@espci.fr

² Thales Alenia Space, 5 allée des Gabians, 06156 Cannes la Bocca, France
laurence.cornillon@Thales Alenia Space.com / olivier.damiano@Thales Alenia Space.com

³ Slaskie Centrum Naukowo-Technologiczne Przemysłu Lotniczego (SCNTPL), Nad Bialka 25, 43-502 Czechowice-Dziedzice, Poland
j.hamerlak@scntpl.pl

⁴ North Thin Ply Technologies, Chemin du Closel 3, 1020 Renens, Suisse
l.chichignoud@thinplytechnology.com

⁵ ATG-Europe B.V. for the European Space Agency,
simon.appel@esa.int

⁶ ESTEC, European Space Agency, Keplerlaan 1, PO Box 299, 2200 AG, Noordwijk, The Netherlands
shumit.das@esa.int / ugo.lafont@esa.int

KEYWORDS: Composites, vitrimers, Thin Plies

ABSTRACT

The composite field brings constant progress and development with design of new materials and technologies. These aim to reduce cost of manufacture and maintenance, but also, to increase their performances combined with tailorable properties. Thales Alenia Space, always looking for innovative development in composites, is now taking part in two ESA projects focusing on vitrimers materials and thin plies technology. Vitrimers are an emerging class of polymer materials developed in 2011 by Leibler and coworkers. Initially, based on the traditional chemistry of thermosets, they possess their chemical resistances and mechanical strength. Nonetheless, their covalent bonds are exchangeable upon trigger (e.g. heat, UV, etc.). This property is giving them the ability to be weld, reprocessed, or recycled, behaviour usually owned by thermoplastic materials. This covalent bond exchange mechanism makes vitrimers insoluble, yet, weldable onto themselves rendering them highly attractive for the composite field. On the other hand, thin plies technology have been posited as a great alternative to traditional fibres reinforced polymer (FRP) composites. This technique allows to produce lighter and stronger composites while being cost effective. Already used in sports applications, the aerospace field could highly benefits from their development to a larger scale.

Therefore, Thales Alenia Space ESA projects have started to explore simultaneously the potential of both this new class of polymer and technology as follow: (i) a one year TDE project focusing on the development of vitrimer prepreg and laminate for space applications. So far, a vitrimer resin with appropriate properties (T_g , outgassing, latency) for impregnation, lamination and welding has been selected. Further work in the prepreg development is expected to result in vitrimer integration with low investments on the manufacturing lines. (ii) An ongoing Thales Alenia Space/SCNTPL project (TRP) for which materials (resin and fibres) choice, manufacturing and use case trade off resulted in small scale prototypes (2019). Further characterisations and design of full scale prototypes have ensured the continuity of the project during 2020 and first prototypes (full scale) are expected in 2021. This TRP project shows the possibility to apply thin plies technology to real scale aerospace applications.

1. INTRODUCTION

Composite materials have been widely used throughout human history from plywood (3400 B.C.) to the development of modern fibres

reinforced polymer (FRP) in the 1900's. Since their development, FRP composites have positively impacted several industries such as automotive, building, energy production, or aerospace [1]–[3].

The combination of high strength fibres with polymer resin matrices leads to lightweight materials (compared to traditional ones, such as metal), having high mechanical performances while giving a high freedom in designing complex structures or shapes [3].

Thermoset resins have traditionally been a favoured choice as matrices due to their high mechanical properties and chemical resistance [4]. However, their covalently bonded network (giving them these properties) has also its drawbacks. Once the network is cured, processes, repairs, and assembly of different parts become a challenge, often involving high cost interventions [2], [4], [5]. Moreover, the environmental impact of these FRP has risen concerns as recycling is often difficult, involving harsh chemicals and high energy costs [6].

Recently, thermoplastic matrices have attracted attention of both industrials and researchers. Indeed, various properties of these polymer types are appealing such as near-infinite shelf life, recyclability, and weldability. Nevertheless, thermoplastics processing and manufacturing is often not adapted for composites production which are used in the aerospace industry (e.g. infusion, resin transfer moulding, etc.). This fact is currently limiting their applications to wider scales in this area.

In 2011, a third class of resins was developed by Leibler and coworkers, namely, vitrimers [7]. Prototypes of vitrimers were based on epoxy formulations and crosslinked (*i.e.* as a thermoset), while having the inherent property to exchange their covalent bonds under application of heat. The bond exchange relied on transesterification mechanisms which are associative. Hence, vitrimers are reprocessable, healable, recyclable, yet, insoluble and not subject to structural integrity losses [7]. Since the first vitrimers epoxy formulations, various chemistries have been explored to produce different vitrimer networks. Some composites manufacturing involving different chemistries such as transesterification, transiminification or disulphide exchanges have been studied [6]. Despite these studies and outstanding potential of vitrimer as matrices for composites (crosslinked network able to be weld or reprocessed), their use as prepregs for aerospace applications has been barely investigated. Therefore, Thales Alenia Space carried out an initial survey in collaboration with the ESPCI Paris to validate the possibility to produce these prepregs at laboratory scale. In late 2019, following this survey, the European Space Agency (ESA) funded the continuity of the project to further develop manufacture and characterisation of these FRP. This led to the definition of the required resin properties (choice of chemicals: resin, hardener and catalyst) which would require the least investment on scaling up vitrimers uses in aerospace applications.

In the meantime, thin plies composites development was also explored to reach wider scale applications. The plies thicknesses allow to optimise and tailor the FRP properties whilst delaying (or suppressing) crack initiation [8]. Moreover, when compared to traditional prepregs, their surface weight can be reduced by 2 to 10, allowing production of even lighter composites [9]. The better freedom of fibres orientation gives also a wider range of liberties to optimise and design composites. Following this goal, Thales Alenia Space found promising results for various specific applications in aerospace. These results led to two main developments, presented in this work: solar array substrates and integral 3D sandwich structures.

This work is presented as follow: (i) presentation of vitrimer project (general considerations, vitrimers for composites in aerospace applications, preliminary results for resin formulation, and future perspective of this project). (ii) Presentation of the thin plies development including general considerations, their applications in aerospace industry, and a focus on solar array substrates and 3D sandwich structures. (iii) Finally, the potential to combine both of these projects to produce FRP composites for the aerospace field is considered.

2. VITRIMERS

2.1. GENERAL CONSIDERATIONS and BACKGROUND

Internal survey to evaluate the feasibility of prepreg material with a vitrimer resin started in 2018. Initially the project looked at the capacity to integrate vitrimers as matrix for FRP composite and to use their properties akin to thermoplastics (weldability). The rationale behind vitrimer networks rather than thermoplastic ones was the possibility to adapt traditional preparation processes (at workshop level) used for epoxy thermoset. This would, firstly, limit investments; in the meantime, the welding capacity of vitrimer would facilitate the equipment phase on the platforms. Secondly, other properties of vitrimers motivated research efforts such as self-healing and recyclable properties.

Indeed, thermosets based FRP are known to be sensible to internal damages [10], [11]. The stiff polymer matrix, despite its high mechanical strength and chemical resistance, is often brittle. When FRP composites undergo shocks or fatigue, cracks and delamination are likely to occur which could result in catastrophic failures [1]. Detection, monitoring and repairs of these damages are time consuming and difficult. Often repairs (with bolts and joints) can induce new damages during the repairing step which reduces the composites lifespan [11]. Vitrimers, *via* bond exchanges, have demonstrated the capability to heal cracks with either temperature (e.g. 60 min at 180°C [12]) or

light (e.g. 10 s under IR light [13]) triggering. Consequently, their use as FRP composite matrix could also reduce maintenance cost and increase their lifespan. Finally, vitrimers have been shown to be recyclable either by reprocessing of the polymer (crushing samples into pieces followed by a moulding step [7]) or by dissolution in an appropriate solvent - chosen accordingly for the bond exchange mechanism - followed a possible repolymerisation with solvent evaporation [14].

One of the rising concern coming with the increasing use of FRP composites is the end-of-life of these products. Traditional thermoset resins require either application of high temperature or use of harsh chemicals to be removed from the fibre reinforcements. These operations make impossible to re-use the polymer and also severely damage the fibres [6]. In fact, the damages often lead shorter fibre with lowered properties which can only be re-used in applications requiring lower mechanical properties. Several efforts have been made in order to lower the impact of matrix elimination from fibres, and vitrimer matrices were reported as one of the most adequate candidates [6]. The ability to dissolve and repolymerise in "soft" solvent at relatively low temperature (< 200°C) would limit fibre damages but also recycling costs. Moreover, resins repolymerisation for further use would bring a new dimension to the recycling of composites with the possibility to achieve close-loop recyclability on the whole composite's components [15].

Some examples in literature have shown the possibility to prepare vitrimer composites, even using dry prepreg [16]. However, wet prepreg fitting industry requirements, to the authors' knowledge, has not yet be demonstrated. Therefore, NTPT (prepreg manufacturer) and Thales Alenia Space (end user of the materials) set a list of requirements to find a resin producing high performance composites with optimum fibre/resin ratio:

- (i) Low viscosity at impregnation temperature ($\approx 100^\circ\text{C}$).
- (ii) Latency at ambient temperature or cold (-18°C) temperature, for storing and transport before manufacturing.
- (iii) High temperature stability after curing. $T_g \approx 120^\circ\text{C}$.

The results of this preliminary study were satisfying:

- (i) Latency of the hardener/catalyst mix is reasonable.
- (ii) $T_g \approx 100^\circ\text{C}$.
- (iii) Performances obtained with common "Novolac" resin.

At the end of the internal survey, the main concern was the slightly high viscosity of the resin, not yet

suitable for prepreg preparation.

2.2. VITRIMERS IN FRP FOR AEROSPACE APPLICATIONS - TDE

End 2019, the ESPCI Paris was awarded a contract with ESA ("Effect of space environment on Vitrimer based CFRP ") to evaluate, with Thales Alenia Space, the feasibility of such a prepreg for aerospace applications.

Multiple interests motivated and defined this research effort, similarly to that of the initial survey in 2018:

- (i) The 3R (Recyclability, Repairability, Reprocessability) characteristics of vitrimers.
- (ii) Welding of vitrimers onto themselves, like for thermoplastics.
- (iii) Vitrimers, in a prepreg form, should have a transformation process very similar to these of thermoset. For example, the prepreg should be tacky enough to allow manual or automatized layup, and its cure cycle should not force industrials to heavy investments.

Set objectives of the project were:

- (i) Define a resin with appropriate properties for prepregs impregnation and aerospace applications (T_g , outgassing, latency, viscosity at impregnation temperature, tensile and welding properties)
- (ii) Manufacture prepreg with a very common reinforcement (fabric and not UD tape, common industrial grade carbon fiber).
- (iii) Evaluation of process limitations and constraints.
- (iv) Mechanical testing (tensile properties).
- (v) Welding of plates followed by shear and peel tests.

To reach these objectives, the choice of vitrimer network (i.e. bond exchange mechanism, and hardener type) was carefully considered. As aforementioned, first illustration of the vitrimer concept, a number of different systems were investigated based on transesterification [7] and other exchange mechanisms [16]–[19]. In early works, the prototypes of vitrimers have been formulated on the basis of epoxy thermoset mixes [7]. More recently, it has been shown that vitrimer materials can also be implemented with benefit through modification of thermoplastics [20]. Thus, new development of vitrimers has been published through modification of commodity thermoplastics, in which bond can exchange by the metathesis of dioxaborolanes. Recently, improvement of heat-resistance of poly-butylene terephthalate (PBT), an engineering thermoplastics was reported, using Zn(II) catalysed epoxy-vitrimer chemistry [21], [22]. However, for reasons mentioned earlier, the use of

thermoplastics based networks is not favored for this project.

Example of composites with vitrimer as matrix are scarce in literature but few examples can be reported. Chabert et al. [23], showed the possibility to implement composite materials from vitrimers by using current composite techniques. In this work, vitrimer matrices with a T_g value $> 100^\circ\text{C}$ were identified and adapted for processing by resin transfer molding (RTM). Vitrimer composites containing more than 50 vol% of continuous glass fibers showed high bonding strength and repeated welding ability while their mechanical properties were comparable to those of non-vitrimer control samples. Odriozola and coworkers [16] at CIDETEC (Spain) also investigated reprocessing, reparation and recycling of glass-fiber reinforced composites using a matrix made of an epoxy resin with exchangeable disulfide crosslinks. In these works, the starting point composite plates were manufactured from low viscosity reactive mixtures using the RTM technique. Odriozola additionally reports the assembly of multiple layers by compaction of individual prepreg sheets from fully cured dynamic epoxy resin. Although illustrating the original properties of vitrimers, fully cured prepreg sheets have disadvantage of no tack and therefore, this process does not allow precise positioning comparable with handling of prepregs.

Repairable and recyclable woven carbon fiber composites were also reported using malleable polyimine networks [17]. These materials, can show a T_g up to 135°C and are sometimes also called vitrimers. These are however networks made up of small molecules (aldehydes and primary amines) joined to each other by imine bridges. The constitutive molecules, amines and aldehydes are likely to degrade into respectively carbamate and carboxylic acid by contact with atmospheric CO_2 and O_2 . The imination reaction produces water that has to be stripped out during curing and reversely water initiates depolymerisation into volatile compounds. For these reasons, this type of material is not considered potentially suitable for the project.

Therefore, the choice was set onto epoxy vitrimers based on transesterification reactions as they can be easily applied to the epoxy/acid and epoxy/anhydride curing systems which are currently used in the industry of thermoset materials. However, most reported epoxy vitrimers show a low glass transition temperature, $T_g (< 100^\circ\text{C})$, which limits their applications [7], [23]–[26]. To achieve adequate molecular mobility at high temperatures, the cross-linked structures of epoxy vitrimers are mostly constructed with soft epoxy monomer and curing agent, which eventually result in low T_g . Although a rigid building block structure and a high cross-link density can increase the value of T_g [27], they tend to limit the mobility of the

polymer chains and compromise the reparability and reprocessability [28].

Efforts to increase the glass transition temperature of epoxy vitrimers date back to the first publication on vitrimers; a brief review is presented below. To allow comparisons, we denote T_g when the measurement is done by differential scanning calorimetry (DSC) and T_α when done by dynamic mechanical analysis (DMA). Thus, in reference, using the same epoxy resin, Di-Glicidyl Ether of Bisphenol A (DGEBA) cured with either a long chain (C36) fatty diacid or short chain (C5) glutaric anhydride. It was shown the possibility to rise T_g from about 15°C ($T_\alpha = 23^\circ\text{C}$) to above $60\text{--}70^\circ\text{C}$ ($T_\alpha = 98^\circ\text{C}$) [7], [24], [29]. Incorporation of 40 wt % GLYMO-silica in the same system was also found to enhance T_α by a few degrees [25]. Further on, vitrimers based on industrial epoxy monomers (Araldite® LY564 / Aradur® 917CH) were investigated to apply vitrimers through the resin transfer molding (RTM) technique [23]. Vitrimer matrices thus synthesised exhibited a T_g of 103°C , ($T_\alpha = 112^\circ\text{C}$). An epoxy/anhydride infusion system (Epikote® MGS RIM 145) was used in a screening of catalysts for vitrimer application (T_g not reported) [27]. Use of sebacic acid / cyclohexane dicarboxylic acid mixtures as curing agent of DGEBA was reported to bring T_g between 30°C and 80°C [30]. Whereas, use of the same sebacic acid component with various epoxies gave rise to a glass transition temperature of $T_g = 55^\circ\text{C}$ [31], [32]. Recently, a bio-based epoxy resin featuring the triphenylmethane rigid core was proposed to impart a glass temperature as high as $T_\alpha = 187^\circ\text{C}$ in vitrimer chemistry based materials [33].

Hence, the epoxy-anhydride systems already proposed in prototypes of vitrimers is shown to be suitable to formulate thermosets with a high T_g . In addition, conventional epoxy-anhydride formulations always present competition between the anionic homopolymerisation (by opening of the epoxy ring which leads to non-exchangeable ether bonds) and acyl + epoxy addition reactions (which in turn lead to desirable exchangeable ester bonds in vitrimers). However, a high- T_g vitrimer formulation aims at introducing both chemical groups promoting exchange reactions and network elements imparting a high T_g . A problem that arises with acuity is the compatibility of these components. Thus, as shown recently in vitrimerised polyethylene, the final compound has a micro-separated hierarchical structure that may eventually impact stress relaxation ability [34].

2.3. VITRIMER FORMULATION AND MATRIX PRELEMINARY RESULTS

Epoxy Novolac resin was chosen as suitable for its high viscosity at ambient temperature. To find a suitable hardener, a set of

requirements was set for the polymer: (i) $T_{\alpha} \geq 130^{\circ}\text{C}$, (ii) viscosity suitable for impregnation, (iii) gel time ≥ 1 h at $T_{\text{impregnation}}$, (iv) gel time ≥ 1 week at room temperature, and (v) impregnation temperature $\leq 100^{\circ}\text{C}$.

DEN439 from Olin Epoxy, combined with Dyhard 100SF hardener (dicyandiamide, non-vitrimer reference) or “ad-hoc” hardener CHDA (cyclohexane dicarboxylic acid) were investigated with various catalysts. Preliminary DMA results show satisfying $T_{\alpha} \approx 135^{\circ}\text{C}$ (Fig. 1) for the CHDA.

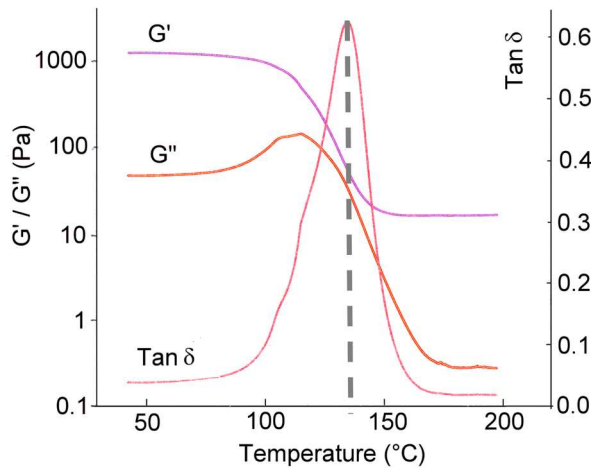


Figure 1 - DMA characterization of DEN439_CHDA resin (no catalyst)

Further SAXS characterisation showed that the cured network were rather homogeneous (despite the initial difficulty to react epoxy with CHDA). However, it can be seen that the sample, at different temperatures, constantly show the presence of fine crystalline peaks in the wide angle region (around $2\pi/q = 5 \text{ \AA}$, Fig. 2). Thereby confirming the presence of crystallized components. Their intensity decrease at the beginning of the curing process but crystalline peaks do not disappear after cure. Thus, even though DMA data indicate formation of a rather homogeneous network, results of time-resolved morphological analyses reveal that the Zn(II) catalyst remains incompletely dissolved at the end of the reaction.

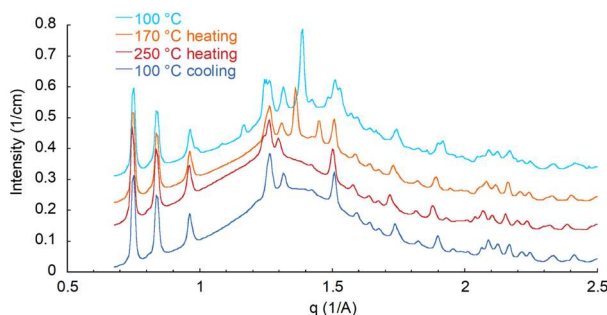


Figure 2 - SAXS data of the network showing only partial solvation of catalyst was achieved for DEN439_CHDA catalysed by Zn(II)

Once the network was defined as sufficiently satisfying, the project passed to the next stage of composites impregnation and lamination. However, as mentioned earlier, a trade-off of materials (fibre) was performed for cost and availability purposes. This trade-off was carefully undertaken to choose the most suitable reinforcement. Contrary to the usual unidirectional tape, fabrics can help the resin to flow through their thickness, and thus, ease the impregnation process, whereas the unidirectional tape somehow acts as a barrier. At the same time, too many fibres crossings may force some resin accumulations, resulting in lower amount of resin on the ply surface, jeopardizing the potential for welding. This delicate balance led to select a 1-1 twill pattern fabric. This activity is still in progress, and the final results are expected by mid-2021. Current work include to manufacture the required quantity of laminates, cure them and characterise their properties on two main points: (i) testing properties of laminates to assess aerospace potential (mechanical [ILSS, tension], outgassing, thermal cycling). (ii) Welding of two plates followed by in plane shearing tests.

2.4. PERSPECTIVES FOR VITRIMERS IN AEROSPACE

The outstanding properties of vitrimers set them to be a remarkable candidate for further use in FRP composites. Many drawbacks associated with thermoset resins, such as processing, reparability and recycling could be tackled by swapping to vitrimers matrices. This would allow, not only to reduce manufacturing costs, but also achieving better carbon footprint through the recovery of fibres and polymer whilst being easily adapted to current industry processes. However, they still suffer, just like thermosets or thermoplastics, from the initial chemistry they come from. Therefore, a PhD work on bio-sourced composite material that will include vitrimers is undergoing with the ESA and the University of Nice.

This study ensures continuity of the presented work, nonetheless vitrimer structures have still a lot of checkmarks to validate before use in aerospace applications. Radiation or ATOX behaviour is still to be demonstrated, and the industrialisation of the prepreg is not yet guaranteed. This does not stop effort to combine vitrimer matrices with other technologies. As presented below, thin plies technology is an efficient method to produce complex and lightweight structures for aerospace applications. And it is envisaged that vitrimers could later, easily fit within this approach.

3. THIN PLIES

3.1. GENERAL CONSIDERATIONS

Thin plies (Fig. 3) have been studied in many areas over the years and have demonstrated

Conventional ply vs Thin ply

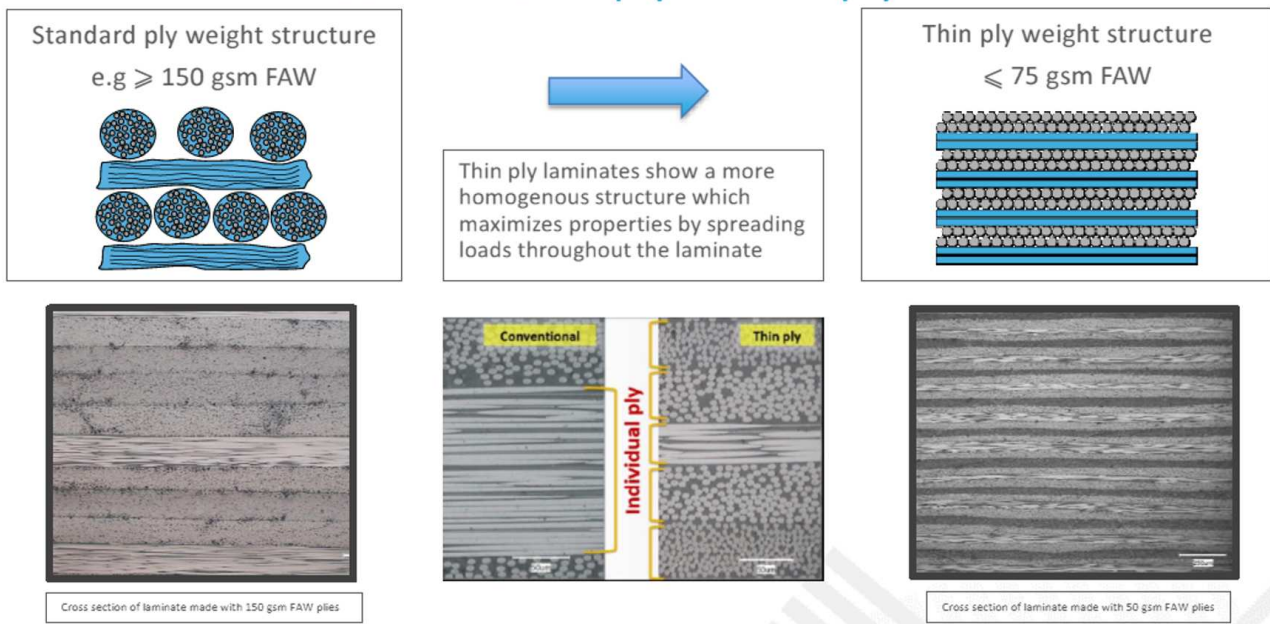


Figure 3 General presentation of Thin Ply (www.thinplytechnology.com)

a wide range of benefits, from mass savings to better material homogeneity or even higher impact resistance. Moreover, the addition of Automated Tape Layering (ATL), combined with the outstanding joining ability of thin plies, is cost efficient for structures assembly, thanks to the reduction of inspection and/or manual compactions required with classical materials.

Therefore, following previous projects focused on performance, a wider approach was

used to determine which kind of space component could get the most benefits from this technology. This study look at performance improvement, cost reduction, design simplification or more global change.

The TDE project (as mentioned earlier) aims to define the most suitable applications of this technique. It is by itself, embedded in a longer term vision as shown in Fig. 4.

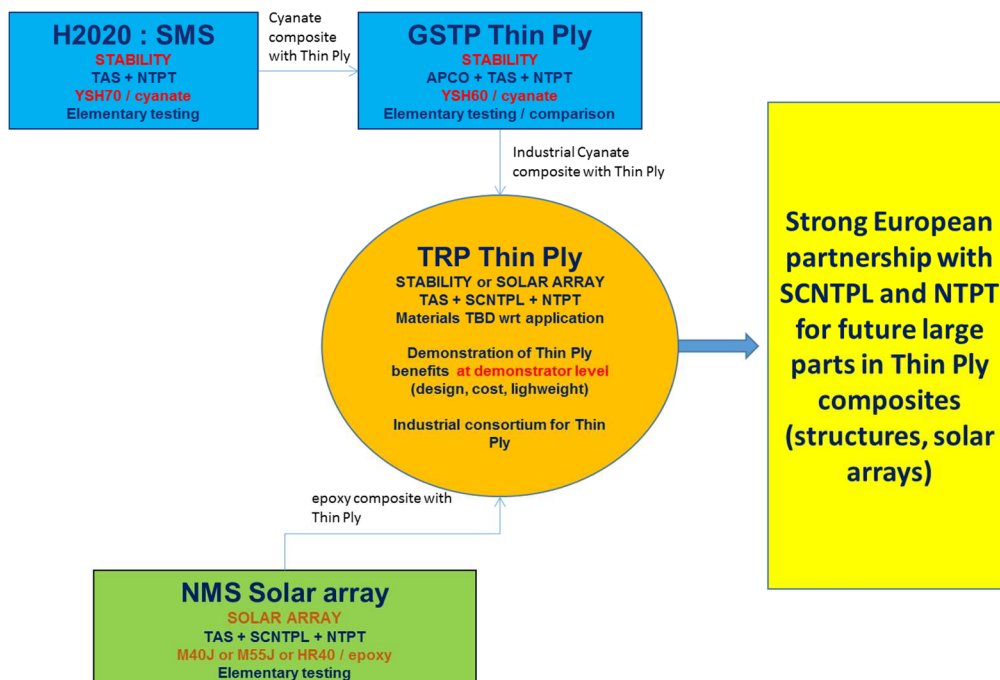


Figure 4 – Thin Ply related projects

3.2. THIN PLIES FOR SPACE STRUCTURES - RATIONALE FOR APPLICATIONS SELECTION

To ensure to cover the full potential benefits of thin plies, the approach has been to evaluate this technology in a wide range of applications, considering several factors:

- (i) Mass savings (thinner sandwich skin while remaining quasi isotropic)
- (ii) Intrinsic performances (better homogeneity, smoother load paths, etc.)
- (iii) Cost (use of industrial grade fibres, reduction of inspections and manual operations)

- (iv) Design freedom (innovative and optimised joining techniques, capacity to be laid on curved surface with less issues than conventional tape, and higher performance than fabrics)

A trade-off has been performed based on the various specificities of the thin plies. Some of these criteria were known at the start of the project (reduction of individual areal weight, better isotropy for thin layups, better ability for complex shapes layup, cost reduction via automatisation, etc.), while some others were hypothetic and needed to be confirmed during the project. Fig. 5 describes the rationale for this trade-off:

IDENTIFICATION OF USE CASES FOR THIN PLY STRUCTURES

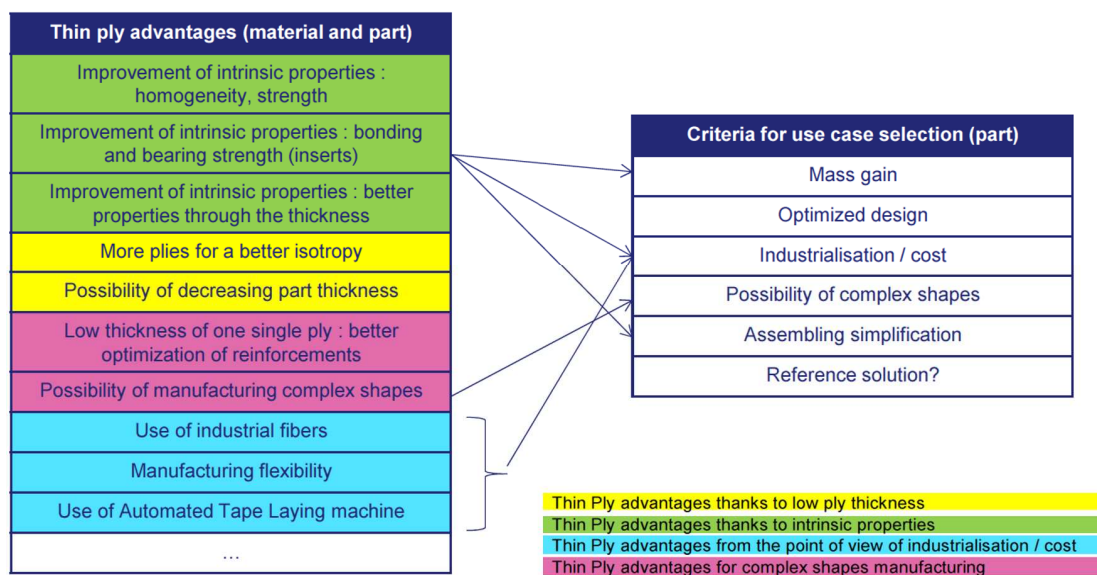


Figure 5 – Rationale for applications selection

The conclusion of the applications selection was that Solar Arrays Substrates (SA) and 3D integral structures were the most suitable candidates. The main goals for each applications are resumed below:

- (i) SA system: challenge was to design a substrate with the same properties as the existing one, but at a much lower cost and, if possible, lower weight.
- (ii) 3D integral structures: challenge was in the capacity to build such a complex structure with unidirectional tapes, without jeopardizing mass savings. Particular attention was brought on curvature areas where poor material and/or process quality are likely to occur.

The development plan has then been set to cover these two very different kinds of challenges.

3.3. SOLAR ARRAYS AND 3D STRUCTURE

3.3.1. SOLAR ARRAY SUBSTRATE

For cost and availability purpose, a compromise was made when selecting the fibre for the SA application. The selected fibre has a Young's modulus 30% lower than the reference, for cost and availability reasons. This choice could influence many properties (mechanicals) of the substrate, but also its local strength (face wrinkling, FW and intracell buckling, IB failure modes are driven by the skin stiffness and are prominent on these large honeycomb cells panels). Such modifications of the structure properties could lead to more reinforcements needed which would go against the weight reduction goal rendering the solution obsolete. However, selected fibre has a 15% higher failure strength, which is beneficial for reinforced and pure compression (PC) modes. To validate this choice, extensive mechanical characterisation has been performed on various layups, defined after a preliminary design (built

upon hypothesis). Edgewise compression testing was performed at various temperatures (Min, ambient and max), for different configurations described in Table 1, in a cross-check approach between THALES ALENIA SPACE and SCNTPL.

Table 1 - Solar array sandwich configurations

Configuration	Skin thickness	Honeycomb	Failure mode
Current skin	0,1 mm	9-20	IB
Current skin	0,1 mm	4-20	FW
Doubler2	0,9 mm	4-20	PC

It appears the IB and FW were slightly higher than expected values, allowing us to add very limited reinforcements, keeping the mass of the substrate at a very acceptable level.

Further tests are currently still in progress, but the first conclusions are very promising for this new generation of solar array substrates, based on an industrial approach.

In this particular case, the use of thin plies allowed us to move from 3k high modulus fibres to 12k intermediate modulus fibre, with obvious benefits at cost and procurement levels.

Apart from the possibility to build thinner quasi isotropic skins, the thin ply technology also allows to distribute the fibres more evenly over the plies, while keeping the initial skin thickness. It was expected that this “progressive” layup could bring some improvement, and tests confirmed that trend, as described in Table 2.

Table 2 - Comparative edgewise compression

Layup style	Edgewise compression strength (MPa)
0°/ -60°/ 60°; ply thickness 0,1 mm	100
0°20°40°60°80°-80°-60°-40°-20°; ply thickness 0,03 mm	100
0°0°0°-60°-60°-60°60°60°60°; ply thickness 0,03 mm	110

3.3.2. 3D INTEGRAL STRUCTURE

Satellites platforms are mostly built from flat sandwich panels, assembled together via bolted joints and inserts. In some cases, 3D structures, manufactured as a whole sandwich on a shaped mould, are used and show some evident benefits when it comes to mass savings or ease of integration. Our vision is to spread this concept as much as possible, even to large platforms equipped with complex and powerful payload. Nonetheless, this kind of structure rises new challenges, and among them, the ability to layup curved shapes with unidirectional tape is of major

importance.

Indeed, the classical way to design and build such structure is to use fabrics, known for their ease of use on complex shapes.

Keeping optimisation as a priority, building these structures with unidirectional tape is an obvious “direction” to follow. Depending on the shape of the structure, two options may be considered:

- Use continuous fibres on several adjacent faces of the structure
- Layup each side separately, and connect them via some “fresh” (uncured) doublers locally on the angles.

The first solution induces some fibre orientation issues, as tape across the curvature area cannot be bent. The second solution creates some local reinforcement, jeopardizing the mass savings expected from such a design. Fibre placement could be another option, but is currently out of the scope of this work.

ThinPlies, with their superior flexibility, can offer a smart alternative:

- The lower individual ply thickness helps applying the tape onto curved surfaces
- The thinner plies make some scarf junctions possible, with very little local mass increase.

In the frame of the “Thin Ply Laminate Composite Structure” TDE project, the integral 3D structure was found to be the second type of applications benefiting the most from thin plies (behind Solar Array Substrate). The concept and design of the 3D structure is shown in Figure 6

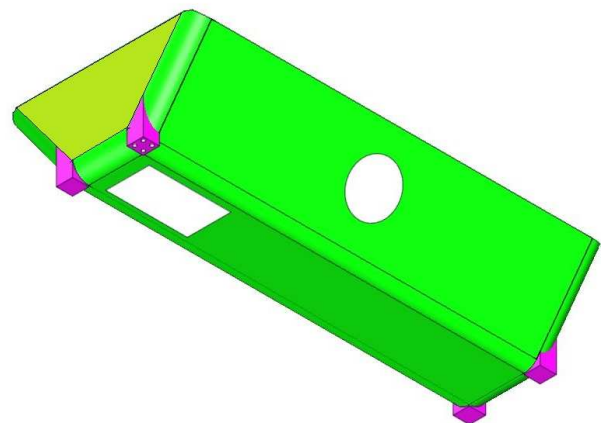


Figure 6 – 3D integral structure concept

To validate the hypothesis of easier manufacturability and better quality across the radii, some representative samples (Figure 7) have been made and testing will be carried out shortly.

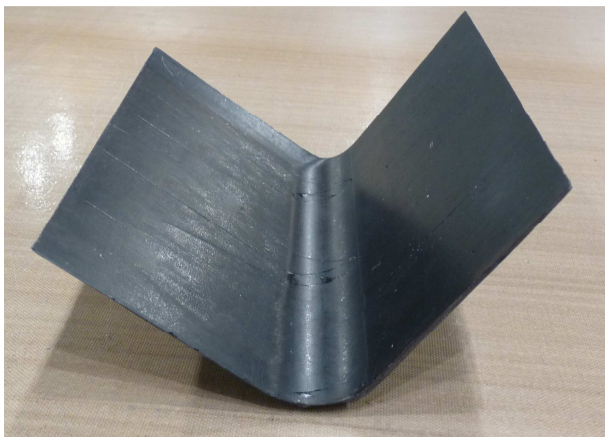


Figure 7 – angles layup with ThinPlies

Both solar arrays substrate and this project are managed in close cooperation between THALES ALLENIA SPACE and SCNTPL. The next steps of these projects consist of testing these samples to then build, inspect and test a full scale integral structure that will prefigure the platforms of the future.

4. CONCLUSION

Vitrimers matrices and thin plies technology are two promising solutions to enhance the FRP composites uses in aerospace applications. On one side, vitrimers show the possibility to be adapted to current manufacture process whilst even having the potential to simplify them (welding of crosslinked networks). Preliminary results demonstrated that epoxy Novolac and CHDA hardener is a potential candidate for the development of resins suitable for infusion process and prepreps preparation. Proper catalyst selection is still undergoing in order to obtain homogeneous networks with stable properties and the high mixture viscosity remains a possible limitation if this specific network for fibres impregnation. All these parameters are to be defined more accurately through 2021 with the start of vitrimer composites design and manufacture using industrial processes.

Concomitantly, thin plies technology have shown promising results to produce lightweight and strong composites compared to their traditional counterparts. Throughout study of aerospace components showed that the applications which could mostly benefit from this technology are solar array substrate and 3D integral structures. Both of these applications have been demonstrated to benefit in lighter weight ratio while reducing costs of manufacture.

The continuity of this work will ensure to develop several approaches to design aerospace composites. The possible combination of vitrimers matrices and thin plies technology would create a high synergy to: (i) simplify and reduce cost of manufacture and process, (ii) produce lighter composites with increased lifespan, (iii) have eco-

friendly FRP composites able to achieve close-loop recyclability. Moreover, investigation of bio-sourced chemicals would only improve the environmental impact of these new composites.

This work shows a small insight in the possible evolution of the FRP composites for aerospace while using new technologies allowing us to envision the future generation of these materials and structures.

5. ACKNOWLEDGEMENT

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We thank Denis T. Keane of the Advanced Photon Source for his help in using beamline DND-CAT 5ID-D. We thank the Aerospace Research Institute and Costantinos Soutis for supports and funding which permitted the preliminary studies on these vitrimers development. The work presented is performed under ESA Contract No. 4000128430 for the Vitrimers project, and ESA Contract No. 4000126111 and No. 4000123840 for the Thin Ply project.

6. REFERENCES

- [1] P. D. Mangalgiri, "Composite materials for aerospace applications," *Bull. Mater. Sci.*, vol. 22, no. 3, pp. 657–664, 1999.
- [2] K. Diamanti and C. Soutis, "Structural health monitoring techniques for aircraft composite structures," *Prog. Aerosp. Sci.*, vol. 46, no. 8, pp. 342–352, 2010.
- [3] S. A. Bello, J. O. Agunsoye, S. B. Hassan, M. G. Z. Kana, and I. A. Raheem, "Epoxy resin based composites, mechanical and tribological properties: A review," *Tribol. Ind.*, vol. 37, no. 4, pp. 500–524, 2015.
- [4] F. L. Jin, X. Li, and S. J. Park, "Synthesis and application of epoxy resins: A review," *J. Ind. Eng. Chem.*, vol. 29, pp. 1–11, 2015.
- [5] W. J. Staszewski, "Ultrasonic/Guided Waves for Structural Health Monitoring," *Key Eng. Mater.*, vol. 293–294, pp. 49–62, 2005.
- [6] G. Oliveux, L. O. Dandy, and G. A. Leeke, "Current status of recycling of fibre reinforced polymers: Review of technologies, reuse and resulting properties," *Prog. Mater. Sci.*, vol. 72, pp. 61–99, 2015.
- [7] D. Montarnal, M. Capelot, F. Tounilhac, and L. Leibler, "Silica-Like Malleable Materials from permanent organic network," *Science*, vol. 334, pp. 965–968, 2011.
- [8] J. Galos, "Thin-ply composite laminates: a review," *Compos. Struct.*, vol. 236, no. September 2019, 2020.

- [9] A. Arteiro, C. Furtado, G. Catalanotti, P. Linde, and P. P. Camanho, "Thin-ply polymer composite materials: A review," *Compos. Part A Appl. Sci. Manuf.*, vol. 132, no. October 2019, 2020.
- [10] T. N. Tallman, S. Gungor, K. W. Wang, and C. E. Bakis, "Damage detection via electrical impedance tomography in glass fiber/epoxy laminates with carbon black filler," *Struct. Heal. Monit.*, vol. 14, no. 1, pp. 100–109, 2015.
- [11] M. H. Ferri Aliabadi and Z. S. Khodaei, "Structural health monitoring for advanced composite structures," *Struct. Heal. Monit. Adv. Compos. Struct.*, pp. 1–274, 2017.
- [12] X. Yang, L. Guo, X. Xu, S. Shang, and H. Liu, "A fully bio-based epoxy vitrimer: Self-healing, triple-shape memory and reprocessing triggered by dynamic covalent bond exchange," *Mater. Des.*, vol. 186, p. 108248, Jan. 2020.
- [13] Y. Yang, Z. Pei, X. Zhang, L. Tao, Y. Wei, and Y. Ji, "Carbon nanotube-vitrimer composite for facile and efficient photo-welding of epoxy," *Chem. Sci.*, vol. 5, no. 9, pp. 3486–3492, 2014.
- [14] C. M. Hamel, X. Kuang, K. Chen, and H. J. Qi, "Reaction-Diffusion Model for Thermosetting Polymer Dissolution through Exchange Reactions Assisted by Small-Molecule Solvents," *Macromolecules*, vol. 52, no. 10, pp. 3636–3645, 2019.
- [15] K. Yu, Q. Shi, M. L. Dunn, T. Wang, and H. J. Qi, "Carbon Fiber Reinforced Thermoset Composite with Near 100% Recyclability," *Adv. Funct. Mater.*, vol. 26, no. 33, pp. 6098–6106, 2016.
- [16] A. Ruiz De Luzuriaga *et al.*, "Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites," *Mater. Horizons*, vol. 3, no. 3, pp. 241–247, 2016.
- [17] P. Taynton, H. Ni, C. Zhu, K. Yu, S. Loob, Y. Jin, H. J. Qi, and W. Zhang, "Repairable woven carbon fiber composites with full recyclability enabled by malleable polyimine networks" *Adv. Mater.* Vol. 28, 2904–2909, 2016.
- [18] W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne, and F. E. Du Prez, "Vinylogous urethane vitrimers," *Adv. Funct. Mater.*, vol. 25, no. 16, pp. 2451–2457, 2015.
- [19] T. Stukenbroeker, W. Wang, J. M. Winne, F. E. Du Prez, R. Nicolaÿ, and L. Leibler, "Polydimethylsiloxane quenchable vitrimers," *Polym. Chem.*, vol. 8, no. 43, pp. 6590–6593, 2017.
- [20] M. Röttger, T. Domenech, R. Van Der Weegen, A. Breuillac, R. Nicolaÿ, and L. Leibler, "High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis," *Science*, vol. 356, no. 6333, pp. 62–65, 2017.
- [21] A. Demongeot, R. Groote, H. Goossens, T. Hoeks, F. Tournilhac, and L. Leibler, "Cross-Linking of Poly(butylene terephthalate) by Reactive Extrusion Using Zn(II) Epoxy-Vitrimer Chemistry," *Macromolecules*, vol. 50, no. 16, pp. 6117–6127, 2017.
- [22] L. Farge, S. Hoppe, V. Daujat, F. Tournilhac, and S. Andr, "Solid Rheological Properties of PBT-Based Vitrimers," *Macromolecules*, 2021.
- [23] E. Chabert, J. Vial, J.-P. Cauchois, M. Mihaluta, and F. Tournilhac, "Multiple welding of long fiber epoxy vitrimer composites," *Soft Matter*, vol. 12, no. 21, pp. 4838–4845, 2016.
- [24] M. Capelot, D. Montarnal, F. Tournilhac, and L. Leibler, "Metal-catalyzed transesterification for healing and assembling of thermosets," *J. Am. Chem. Soc.*, vol. 134, no. 18, pp. 7664–7667, 2012.
- [25] A. Legrand and C. Soulié-Ziakovic, "Silica-Epoxy Vitrimer Nanocomposites," *Macromolecules*, vol. 49, no. 16, pp. 5893–5902, 2016.
- [26] A. Demongeot, S.-J. J. Mougner, S. Okada, C. Soulié-Ziakovic, and F. Tournilhac, "Coordination and Catalysis of Zn²⁺ in Epoxy-Based Vitrimers," *Polym. Chem.*, vol. 7, no. 27, pp. 4486–4493, 2016.
- [27] W. Liu, D. F. Schmidt, and E. Reynaud, "Catalyst Selection, Creep, and Stress Relaxation in High-Performance Epoxy Vitrimers," *Ind. Eng. Chem. Res.*, vol. 56, no. 10, pp. 2667–2672, 2017.
- [28] E. M. Woo and J. C. Seferis, "Cure kinetics of epoxy/anhydride thermosetting matrix systems," *J. Appl. Polym. Sci.*, vol. 40, no. 7–8, pp. 1237–1256, 1990.
- [29] M. Capelot, M. M. Unterlass, F. Tournilhac, and L. Leibler, "Catalytic control of the vitrimer glass transition," *ACS Macro Lett.*, vol. 1, no. 7, pp. 789–792, 2012.
- [30] J. H. Chen, X. P. An, Y. D. Li, M. Wang, and J. B. Zeng, "Reprocessable Epoxy Networks with Tunable Physical Properties: Synthesis, Stress Relaxation and Recyclability," *Chinese J. Polym. Sci. (English Ed.)*, vol. 36, no. 5, pp. 641–648, 2018.
- [31] Z. Pei, Y. Yang, Q. Chen, E. M. Terentjev, Y. Wei, and Y. Ji, "Mouldable liquid-crystalline elastomer actuators with exchangeable covalent bonds," *Nat. Mater.*, vol. 13, no. 1, pp. 36–41, 2014.
- [32] Q.-A. Poutrel, J. Blaker, C. Soutis, F. Tournilhac and M. Gresil "Dicarboxylic acid-

epoxy vitrimers : Influence of off-stoichiometric acid content on cure reactions and thermo-mechanical properties" *Polym. Chem.* Vol. 11, pp. 5327–5338, 2020.

- [33] T. Liu *et al.*, "A Self-Healable High Glass Transition Temperature Bioepoxy Material Based on Vitrimer Chemistry," *Macromolecules*, vol. 51, no. 15, pp. 5577–5585, 2018.
- [34] R. G. Ricarte, F. Tournilhac, M. Cloître, and L. Leibler, "Linear Viscoelasticity and Flow of Self-Assembled Vitrimers: The Case of a Polyethylene/Dioxaborolane System," *Macromolecules*, vol. 53, no. 5, pp. 1852–1866, 2020.