# VITRIMER COMPOSITES FOR AERONAUTICS

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## ABSTRACT

The industry uses more and more thermoset composites thanks to their outstanding properties and high versatility. Nevertheless, this class of materials which cannot be repaired nor recycled raise a major problem regarding the transition from a linear towards a circular economy. One solution to this problem involves a new class of materials coined vitrimers, which exhibit thermosets properties at usage temperature but are reprocessable and recyclable at high temperature thanks to their inherent dynamic exchanges. This discovery opened great opportunities towards a sustainable society with possibilities to repair, reshape or recycle composites. Nonetheless, while being very promising and extensively studied, the development of high performance vitrimers with matrices fitting with aeronautic requirements are rare. Furthermore, the compatibility of vitrimer materials with typical processing techniques requested in composite manufacturing such as resins transfer moulding, infusion or impregnation processes was never reported. In our work, we developed promising high-performance epoxy vitrimers with high glass transition suited for RTM, infusion and impregnation processes towards aeronautics applications. We investigated the capacity of these vitrimers to fulfil all processing specifications such as viscosity, reactivity and gel time. The objective is to mimic as close as possible the specifications of equivalent commercial non-recyclable products. In this regard, different analyses were performed: complete rheological study, thermomechanical properties (DSC, TGA, DMA), reprocessing via compression moulding and reshaping. For the first time a complete rheological study was performed on high performance epoxy vitrimer systems possessing the same thermomechanical properties as the reference thermoset epoxy matrix. Unidirectional vitrimer composite plates were produced by VARTM and mechanically tested showing promising results.

## 1 INTRODUCTION

For several tens of years, aeronautic industry has been using thermosets for high performance applications (e.g. structural parts such as fuselage or wings) thanks to their outstanding mechanical properties, resistance to solvents and versatility in application. They are also used in many other areas such as transportation in general or energy (e.g. wind turbines). Nevertheless, these important materials raise a major problem regarding their recyclability as they are intrinsically insoluble and infusible. Even if these properties are considered as major assets during their lifetime, they become important drawbacks at the end of their life as they are very difficult to recycle. [1]

To improve their mechanical properties, thermosets are generally associated with reinforcements such as carbon fibres, glass fibres, carbon nanotubes, graphene and many others. One of the challenges regarding the recycling process consists in separating the reinforcement from the matrix. Current processes use thermolysis (the matrix is degraded at high temperature) [2,3], solvolysis [4] or other methods [5] enabling reinforcements recovery but mostly with altered mechanical properties. Therefore, these fibres cannot be recycled several times and used for the same applications as they were initially designed for. [6]

An interesting way to recycle thermoset composites would be to work on the chemical structure of the thermosets before they are produced in order to introduce reprocessable and recyclable properties. Vitrimers open up great opportunities towards sustainable materials by producing reprocessable thermosets based on dynamic exchanges endowing the vitrimers with a behaviour similar to that of glass above the glass transition temperature (Tg). [7]

Many efforts have been made in the past two decades to produce reprocessable, healable and recyclable thermosets by introducing reversible bonds into the polymeric networks, including reversible non-covalent interactions (e.g. hydrogen bonds) and reversible covalent exchanges. Thermosets with non-covalent interactions are often weak and could not withstand large stress making them not suitable for structural applications. Alternatively, polymer networks with reversible covalent bonds, known as covalent adaptable networks (CANs), offer an attractive way to make thermosets with good mechanical integrity combined with thermoplastics-like behaviour at high temperature. CANs are generally divided into two groups depending on their exchange mechanism: dissociative CANs and associative CANs. The first group, dissociative CANs, are constituted of reversible chemical reactions based on dissociative exchange mechanisms, meaning the cross-link bonds break upon heating and reform at lower temperature resulting in a decrease of network connectivity and modification of the cross-linking degree during network rearrangement. Hence, such exchange reactions lead to a sudden drop of viscosity with the increasing temperature; as a result, the network cannot maintain its dimensional integrity at high temperature. For instance, the Diels-Alder (DA) reaction is typically representative of dissociative CANs. The second group, associative CANs, keep their cross-link density constant during thermal activation with an unchanged number of chemical bonds during reprocessing. In fact, bond breaking only occurs when a new bond is formed. [8,9]

In 2011, Leibler and co-workers coined this new polymeric material based on associative CANs, “vitrimer”. This first vitrimer was obtained by adding transesterification catalysts into epoxy/acid or epoxy/anhydride polyester networks. This catalyst promoted transesterification reactions with control over the exchange kinetics by varying the quantity of catalyst initially introduced. [10] Vitrimers are now considered as the third class of polymeric material alongside thermoplastics and thermosets. At service temperature, vitrimers behave like traditional thermosets, which have good thermal and mechanical properties. However, when heated above a specific temperature, the exchangeable reaction (such as transesterification) occurs. In the past decade, various chemistries have been implemented for vitrimers purposes including carboxylate transesterification [11], transamination of vinylogous urethanes [12], transalkylation [13], disulfide exchange [14] or imine exchange [15], to name a few.

From the composite standpoint, vitrimer matrices based on chemistries cited above have started to be used to produce composite materials with different reinforcements such as carbon fibres, carbon nanotubes, graphene, glass fibres and few others and are reported in recent review articles. [16,17]

Despite the significant scientific interest of those chemistries, their use in practical industrial applications is not straightforward. Indeed, many issues are inherent to the chemical nature of each system such as scalability, use of a catalyst, thermal stability or low mechanical properties. In our work, we developed a promising high-performance epoxy vitrimer with high glass transition suited for RTM towards aeronautics applications. We investigated the capacity of this vitrimer to fulfil all processing specifications such as viscosity, reactivity and gel time. The objectives are to mimic as close as possible the specifications of equivalent commercial non-recyclable products, such as the widely used epoxy resin RTM6-2; and to compare their physico-chemical and mechanical properties. In addition, unidirectional composite plates were produced by VARTM to obtain several mechanical test specimens, exhibiting promising properties.

## 2 RESEARCH

### 2.1 Materials

HexFlow® RTM6-2 Part A (4,4'-Methylenebis[N,N-bis(2,3-epoxypropyl)aniline]) and Part B (4,4'-Methylenebis(2,6-diethylaniline) 60-100%, 4,4'-Methylenebis(2-isopropyl-6-methylaniline) 30-60%) was purchased from Hexcel. 4-aminophenyl disulfide (4-AFD) was purchased from Molekula group. Unidirectional T700S carbon fibre fabric was purchased from Toray.

### 2.2 Characterizations

Differential scanning calorimetry (DSC) analyses were performed with a DSC 25 TA instruments under nitrogen atmosphere at different isotherms and/or ramps.

Thermogravimetric analyses (TGA) were performed with a TG 209 F3 Tarsus Netzsch under nitrogen atmosphere at a heating rate of 10°C/min from 30°C to 950°C.

Rheological analyses were performed with a rheometer MCR 302 Anton Paar. Oscillatory measurements using parallel plates of 25 mm diameter with a gap of 0.5 mm, an angular velocity of 10 rad/sec and a strain of 4% were typically used.

Dynamic Mechanical Analyses (DMA) were performed with a DMA+ 100 Metravib under air at a heating rate of 3°C from 25°C to 280°C. Measurements were performed in tensile mode with a static strength of 2N, a frequency of 1 Hz, a displacement of 15 µm (in the linear viscoelastic region) on rectangular samples measuring 40 x 6.00 x 1.20 mm.

Tensile tests were performed with a SCHENCK Hydropuls PSB in accordance with the ISO 527-5 standard.

3 point flexural tests were performed with an INSTRON 4466 and an adapted 3 point flexural bench in accordance with the ISO 14125 standard.

### 2.3 Synthesis and manufacturing

The reference epoxy network RTM6-2 was prepared following the recommendations of Hexcel. For the vitrimer network, stoichiometric amounts of RTM6-2 part A and 4-AFD were mixed and stirred at 80°C for 30 minutes. Afterwards, the mixtures were used to produce unreinforced resin and composite (unidirectional) plates by RTM (unreinforced resin) and by VARTM (composite laminates).

## 3 RESULTS AND DISCUSSION

Different analyses were conducted to characterize the physico-chemical properties of both networks (Table 1). The thermal stability of the networks obtained by TGA is a key parameter for processing and reprocessing the vitrimer. An onset degradation of 5% loss of mass is observed at 286.5°C for the vitrimer while the reference is stable up to 345°C, likely due to the presence of the disulfide bonds which are known to be less thermally stable than carbon-carbon bonds. From DSC measurements, comparable glass transition temperatures (Tg) were obtained for both networks but with an enthalpy of crosslinking largely increased for the vitrimer indicating higher reactivity of the vitrimer formulation. In addition, the exothermic peak has been lowered by more than 40°C for the vitrimer showing that cross linking reactions occurred at lower temperatures.

| | $Tg_0$ [°C] | Enthalpy [J/g] | Exothermic peak [°C] | $Tg_\infty$ [°C] | $T_d$ [°C] |
|---|---|---|---|---|---|
| RTM6-2 | -16.7 | 496.1 | 242.0 | 222.5 | 345.0 |
| RTM6 vitrimer | -10.6 | 589.0 | 200.5 | 232.5 | 286.5 |

Table 1: Thermal properties of RTM6-2 and RTM6 vitrimer obtained by DSC and TGA analyses.

Different DSC and rheology experiments have been performed to fully understand the crosslinking kinetics and reactivity of the RTM6 vitrimer compared to the RTM6-2 (Schenk et al, [18]). Those information are paramount to set the parameters of industrial manufacturing processes such as RTM, including the suitable curing cycle as well. The results are combined into so-called TTT (Time, Temperature, Transformation) diagrams widely used for thermoset polymers, and applicable to vitrimers.

Then, unreinforced RTM6 vitrimer plates were produced by RTM and tested. Stress-relaxation experiments were conducted to highlight the reprocessability of the vitrimer. In a very short time, the RTM6 vitrimer could fully relax the stress and we could change its shape above a certain temperature (Figure 1). Furthermore, it was also possible to reprocess the RTM6 vitrimer after grinding using a stainless steel mould and a hot-press.

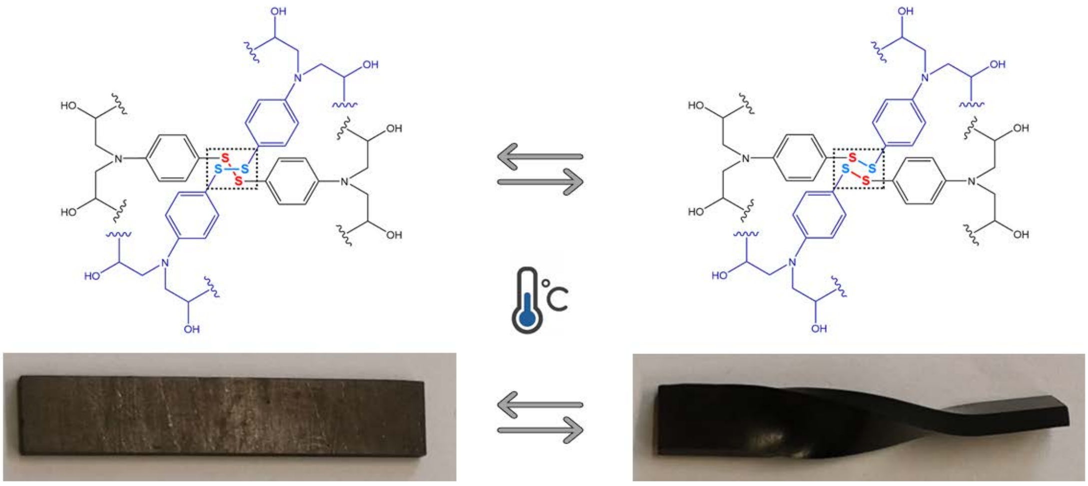

Figure 1: Reshaping of an RTM6 vitrimer sample (bottom) in a few seconds thanks to its dynamic exchanges (top).

Afterwards, the RTM6 vitrimer prepolymer were used to manufacture unidirectional composite parts by VARTM with a $V_f$ of around 44%. The reference RTM6-2 composite parts were also produced in order to compare the mechanical properties of test specimens in accordance with ISO standards. 5 samples were tested in the 0° fibre direction for both the tensile test (ISO 527-5 for UD composites) and the 3 point flexural test (ISO 14125). The results are reported Figure 2. Overall for the tensile and 3 point flexural tests, the strength and modulus of composite samples tested are comparable indicating the RTM6 vitrimer matrix could replace the RTM6-2 in composite parts solicited in tensile or flexural modes.

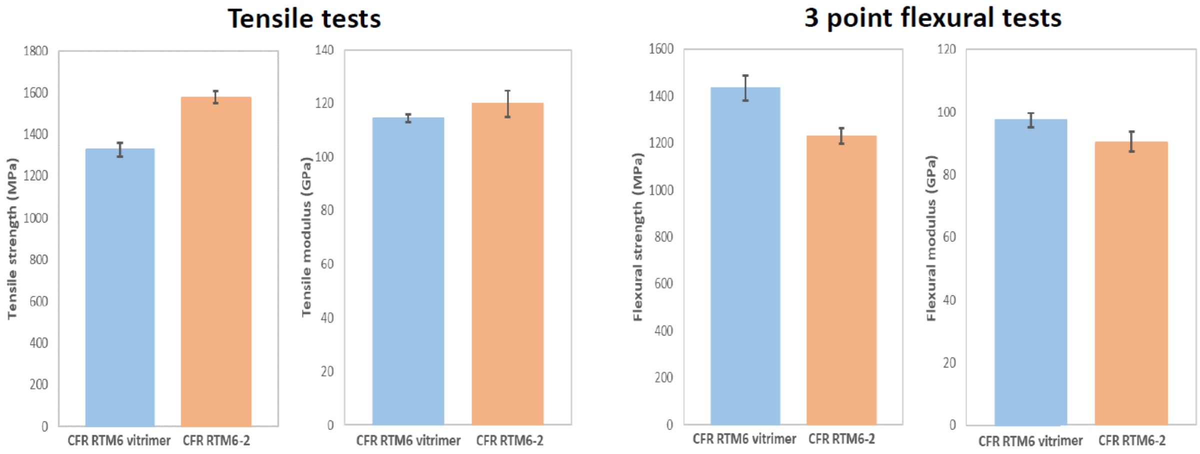

Figure 2: Tensile strength and modulus (left) and flexural strength and modulus (right) for the UD CFR RTM6 vitrimer compared to the reference UD CFR RTM6-2 thermoset.

## 9 CONCLUSIONS

High performance unreinforced vitrimers and vitrimer composites were successfully formulated from commercial products, making them straightforward to produce and easily scalable for industrial composite manufacturing processes. Most of the physico-chemical properties of both systems were comparable and used to produce vitrimer and vitrimer composite plates by RTM/VARTM. Thanks to their inherent dynamic exchanges, vitrimer plates could be reshaped and reprocessed in a very short time by heating. The mechanical properties of vitrimer composite samples obtained were promising opening a new opportunity to replace thermoset composites parts with vitrimer composites parts even for structural applications.

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