

# Vitrimer matrix composites for space applications

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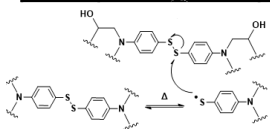
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**Abstract :** Vitrimerers present an alternative to traditional thermosets, offering a dynamic structure that exhibits thermoset properties at application temperatures while it displays enough flow at higher temperatures. In this study, a space-grade epoxy thermoset matrix has been transformed into a high Tg vitrimer matrix with a glass transition temperature (Tg) of 175 ° C. By exploring a non-stoichiometric ratio, the effect of excess amine on the material's Tg is investigated, revealing a decrease in Tg. To separate the influence of stoichiometry and lower Tg on the exchange reactions, a third formulation is examined, maintaining a stoichiometric ratio while achieving a comparable Tg to the non-stoichiometric. Reactivity and rheological properties are evaluated to assess the compatibility of the cross-linking kinetics with classical kinetic models employed in composite manufacturing processes. The filament winding process is used to produce CFRV and reparation of composite parts is investigated.

## Matrix characterisation

**Table 1 : Ratios and Tg of the 3 formulations**

	Formulation 1	Formulation 2	Formulation 3
Epoxy	1	1	1
Amine	1	1,2	1
Tg	199 ° C	175 ° C	170 ° C



The 4-AFD hardener forms a polymer network with disulfide bonds, allowing exchanges when  $T > T_g$ . An amine excess (1/1.2 ratio) adds more disulfide bonds.

### Kamal- Sourour model

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n$$

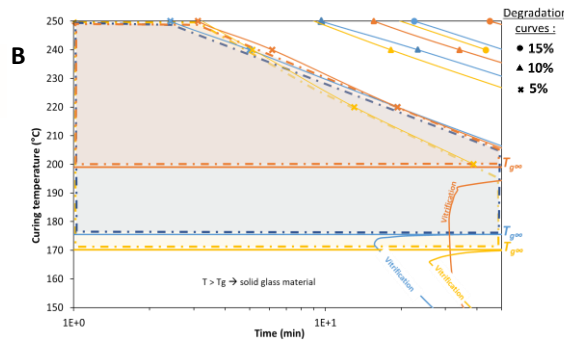
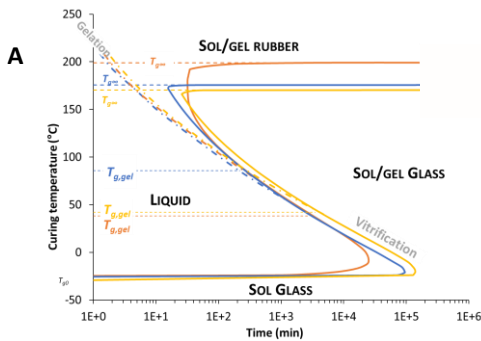
$$k_i(T) = A_i e^{-\frac{E_i}{RT}} \quad i = 1; 2$$

$d\alpha/dt$  the reaction rate,  $k_1$  and  $k_2$  the reaction rate constants  
 $A_i$  is the pre-exponential factor,  $E_i$  the activation energy according to Arrhenius' law,  $R$  the universal gas constant, and  $T$  the curing temperature.

### Di Benedetto model

$$Tg = Tg_0 + (Tg_\infty - Tg_0) \frac{\lambda\alpha}{1 - (1-\lambda)\alpha}$$

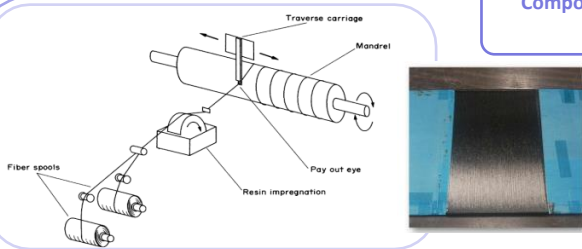
$Tg$  is the transition temperature at a given  $\alpha$ , with  $Tg_\infty$  at  $\alpha=1$  and  $Tg_0$  at  $\alpha=0$ .  
 $\lambda$ , a structure-dependent parameter, is approximated by  $(\Delta Cp_\infty)/\Delta Cp_0$ , where  $\Delta Cp$  is the heat capacity difference between the non-polymerized and fully cured polymer.



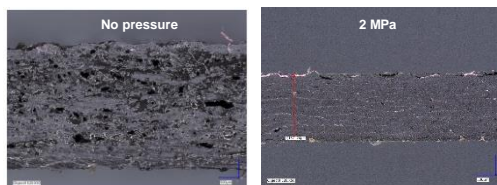
The cure kinetics model fits all formulations, regardless of the ratio. TTT diagrams, extrapolated from experimental results, show non-stoichiometric ratios cure 15% faster than stoichiometric ones at high temperatures (>120 ° C) but slower at lower temperatures, easing resin processing. A vitrimer processing window can be defined by the cured resin's properties, with a lower Tg offering a larger reprocessing window before degradation.

**Figure 2 : TTT diagrams; (A) time temperature transformation diagram for curing stage of the resin; (B) reprocessing diagram with reprocessing area of stoichiometric ( Formulation 1 -orange), non-stoichiometric (Formulation 2- blue) and stoichiometric modified (formulation 3 -yellow) formulations**

## Composite manufacturing and reprocessing



**Figure 3 : filament winding process and an obtained plate CFRV with formulation 2 as vitrimer matrix and M55J carbon fibres**



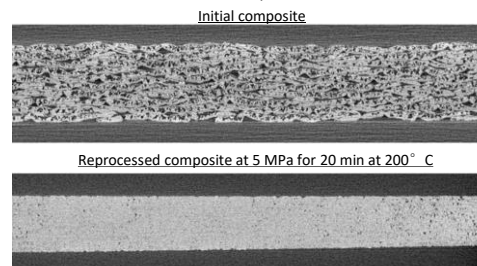
**Figure 4 : microscopic sections of CFRV**

CFRV was initially consolidated without pressure, resulting in voids due to the 20% overlap of fiber strands needed for mechanical strength. Applying a compaction force during consolidation helps minimize these voids.

**Table 3 : neat matrix reprocessing via hot press for the 3 formulations**

	HTG240-V-1/1	HTG240-V-1/1,2	HTG240-mod-V-1/1
10 min 220°C			
10 min 230°C			

The vitrimer matrix allows composite repair (Table 3) and enables a second consolidation phase with controlled pressure and temperature to reduce voids, ensuring high-quality composite parts. As shown in the image, the repaired composite can be reused like a standard composite.



**Figure 5 : X-Ray tomography of initial composite sample and repaired sample**

**Conclusions :** Using a non-stoichiometric ratio, while reducing Tg, results in a more reactive system. Classic cure kinetics model can be applied to control the system's evolution at any temperature and time. The excess amine and the increase in disulfide bonds accelerate the resin's reprocessing, regardless of the reduction in Tg. Composite parts can be manufactured through filament winding using this matrix. Defective parts can be reprocessed and repaired due to the matrix properties, even when carbon fibers are incorporated.

**Perspectives :** Optimization of the process parameters to improve the final quality of composite parts. Comparison of mechanical properties between a well manufactured original part and a reprocessed defective composite part. Durability testing in space environments to ensure that the dynamic bonds within these matrices remain intact, meeting space qualification standards

<sup>(1)</sup> V. Shenk, K. Labastie, M. Destarac, P. Olivier, M. Guerre, *Mater. Adv.* **2022** <sup>(2)</sup> A. Riu de Luzuriaga, N. Markaide, A.M. Salaberria, I. Azcune, A. Rekondo, H.J. Grande, *Polymers*, **2022**, 14 (15), 3180 <sup>(3)</sup> M.R. Kamal, S. Sourour, *Thermomechanica Acta*, **1976**, 14, 41-59