Simplification of requalification procedure of outdated carbon/epoxy prepregs and scenarios of reuse

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Abstract. As a result of their combined high mechanical performances and easy processability, carbon/epoxy prepregs are widely used in the manufacture of aerostructures. The resin of these materials is in an intermediate state of polymerisation which makes these materials perishable. Drastic manufacture conditions lead continuously to the generation of expired prepregs that, today, can no more be used in the aeronautic industry nor in other industries. Although requalification procedure can be carried out, its high cost does not always justify such a procedure. This is why large quantities of expired prepregs are send to landfill. The objective of the Cleansky project MANIFICA is to set up a complete recycling chain of carbon fibre composites "from aeronautic waste to innovative composite parts". The aim of this work is to propose a simplified requalification procedure by avoiding unnecessary tests. These studies are illustrated by property measures on compliant and expired prepregs. The main results were that in most cases, aging induces processing difficulties while mechanical performance remains unaffected. It was also shown that a simpler requalification procedure was possible and that expired prepregs can be reused without loss of performance outside the aeronautical field. Rather than considering expired material as waste, MANIFICA offers several new reuse scenarios.

1. Introduction

1.1. Context

Over the last 30 years, the proportion of composites in aircraft (such as Airbus A350 or Boeing's 777X) has risen from 10% to more than 50% [1]. Carbon fibre reinforced polymers (CFRP) are often manufactured with pre-impregnated reinforcements (prepregs) because of their numerous advantages such as easy processing or controlled fibre rate.

The limitation of these semi-finished products is that they are thermodynamically unstable. Indeed, the polymerisation reaction was initiated during the manufacturing of prepregs in order to fix the resin in the fibres and improve the handling. To minimize the advancement of the polymerisation, prepregs must be stored in freezers at -18°C. The processability of the prepregs and the properties of the final composite may be impacted when stored for too long at -18°C or exposed to room temperature. This is why the supplier of the material provides two expiry dates: one during storage at -18°C "shelf life" and one at room temperature "out life". These dates ensure that the progress of the reaction remains sufficiently low for the processing and characteristics of the future composite. The prepreg is considered as expired if one or both of these dates is exceeded.

Even if improvements have been made to limit waste in the aeronautical industry, there are still many issues leading to the generation of expired prepreg [2]. Uncured prepreg waste mainly come from two sources:

i) Expired material due to minimum batch orders higher than the actual need;

ii) Production offcuts generally made of pieces of random size and shape [3].

If the quantity of material is sufficient to manufacture a new series of parts, outdated uncured prepregs can be requalified by the manufacturer. If this requalification is validated, the shelf life of the material is extended. If this requalification is not validated, the material is sent to landfill. However, this requalification is not systematically carried out because this is time consuming and expensive. As a matter of fact, the requalification procedure corresponds to a full qualification procedure. Many unnecessary tests are then carried out which explains that the cost may be higher than the cost of the virgin material [4].

1.2. Methodology of the study

The objectives of this study are to simplify the requalification procedure and to promote the reuse of expired prepregs. For these purposes, evolution of the properties during long storage must be understood. The method adopted was to correlate the evolution of the physical-chemical properties with the drop of the mechanical performances

The current requalification procedure requires almost twenty tests that can be classified in 3 categories: processability, physicochemical and mechanical properties. The aim was to highlight redundant or unnecessary tests. Then, only relevant tests showing the real drop of properties would be retained for a simplified procedure. Tests were performed and analysed on compliant and expired prepregs. Finally, a simplified requalification procedure was proposed to aeronautical manufacturers and possible non-aeronautical users. Reuse scenarios were also suggested.

2. Materials and experiments

Many physical-chemical, mechanical and processability tests have already been performed and published in a previous study [4]. New tests will be detailed here and compared to the previous results to complete the discussion.

Table 1. Tests carried out during the study

Test classification	Tests	Determined parameters	Standard
Mechanical tests	Tensile test at 0°	Young modulus Tensile strength	NF EN 2561
	Tensile tests at ±45°	Modulus at ±45° Shear strength	NF EN 6031
	ILSS test	ILSS	NF EN 2563
	Pure bending	Ultimate compressive strain	I2M system
Physical & chemical tests	Differential scanning calorimetry (DSC)	Polymerization degree	NF EN 6064
	Volatile content measurement	Volatile content	NF EN 2558
	Organic solvent dissolution	Mass percentage of resin	ASTM D3529
	Microscopic observations	Porosity estimation Compaction assessment	N/A
Processability	Tack test “Hot” tack test	Tack grade	NCAMP standard NF L17-461

2.1. Materials and samples

The prepreg M21/34%/UD194/IMA-12K manufactured by Hexcel was studied in this work. The shelf life indicated by the manufacturer is 1 year. Three different expired material were compared:

i) outdated shelf life of 1 year
ii) outdated shelf life of 5 years
iii) outdated shelf life of 9 years

Previous analyses [4] determined the properties of the compliant material (unexpired). These materials were analysed uncured for physical-chemical testing. For mechanical tests and observations, three composite plates were manufactured. Specifications of the different plates are described in the table 2. These composites are manufactured by draping the plies in accordance with the standard NF ISO 1268-4 [5] and then cured by a hot plate press.

Table 2. Characteristics of composites plates

Plate	Length	Width	Thickness	Plies number	Orientation	Tests
1	300 mm	300 mm	≈ 2 mm	10	0°	Tensile 0°, ILSS, DMA
2	450 mm	300 mm	≈ 4 mm	21	0°	Pure bending
3	300 mm	300 mm	≈ 2 mm	10	[0/90]	Tensile ± 45°

2.2. Additional mechanical tests

2.2.1. Tensile test at ± 45°

Samples 250 mm long and 20 mm wide were cut from the plate #3 (table 2). The testing machine used was a 3R Syntech. An extensometer was used in the elastic range and removed before the anelastic range. Following the standard NF EN 6031 [6], the longitudinal modulus ($E_{\pm 45}$) and in-plane shear strength (T) of the composites were determined with equations (1) and (2):

$$E_{\pm 45} = \frac{\Delta\sigma}{\Delta\varepsilon} \tag{1}$$

With Δσ the difference in tensile stress applied between two points in the elastic range (MPa) and Δε the difference in longitudinal strain between the same two points (measured with the extensometer).

$$T = 0{,}5 \times \frac{F_{max}}{wt} \tag{2}$$

With F_{max} the highest tensile load during the test (N), w the average of three width values per specimen (mm) and t the average of three thickness values per specimen (mm)

2.3. Physical chemical tests

2.3.1. Advancement of the polymerization reaction

The enthalpy of the polymerization reaction was determined by integrating the area under the exothermic peak after applying a thermal cycle (ramp at 10°C/min from 20°C to 300°C). It was determined with the software Perseus developed by Netzsch-Gerätebau GmbH. From these results, the degree of cure (α) was determined by comparing the enthalpy of a new sample ($\Delta H_{reference}$) with those of the test sample ($\Delta H_{prepreg}$):

$$\alpha = 1 - \frac{\Delta H_{prepreg}}{\Delta H_{reference}} \tag{3}$$

2.3.2. Compaction analysis

Samples 30 mm long and 10 mm wide were cut from the plate 1. They were then embedded with epoxy resin in 40 mm diameter moulds. The surface to be observed was polished up to 1 µm grain size. Observations were performed with a numerical optical microscope from Keyence that allows the acquisition of micrographs at different magnification levels ranging from ×10 to ×1000. These tests measured the thickness of the plies in the composite and revealed the compaction of the material.

2.4. Processability tests

2.4.1. Tack test

The tack test consists in draping a piece of prepreg on a cleaned metallic substrate and then adding another prepreg of the same size on top. The metal substrate is then placed vertically and a visual control of the adhesion of the prepregs is performed after 30 minutes according to NCAMP standards [7]. The grades are defined from 1 (dry and brittle) to 6 (wet with resin transfer) [4].

2.4.2. "Hot" tack test

A test derived from the original tack test was performed. It was decided to propose a method to recover the tack: applying hot air on the ply with a heat gun. The improvement of the processability can be determined with this new test called "hot" tack test. The grades defined were the same as for the tack tests.

3. Results and discussion

This section provides an overview of the results obtained from all the tests carried out, separated into two parts, those showing evolution of properties and those that do not. Some of the results have already been detailed in the former paper [4].

3.1. Tests showing no evolution of the properties after too long storage

3.1.1. Tensile tests at 0° *[4]*

The Young's modulus and the tensile strength does not vary with aging. On the tested material, the Young's modulus remains stable at about 170 GPa. So, 0° tensile test does not seem to be useful for recertification of expired prepregs.

3.1.2. Pure bending *[4]*

There is no difference in compressive properties between a 9-years aged prepreg and a compliant material. This test is not useful for recertification of expired prepregs.

3.1.3. Tensile measurements at ± 45°

Figure 1. shows that the ±45° tensile modulus varies slightly with aging. A 7% decrease is observed between the material aged for 1 year and the one aged for 9 years (with a rather large scattering).
Figure 2. also shows a little decrease of the shear strength after 9-year of storage. The difference between the two prepreg is only 1% and they were close to the reference value of 97 MPa, indicated on the data sheet. These results are confirmed by the tests carried out by Martin de S de Luis [8]. The properties at ±45° appeared to remain quite constant or little changed with a greater scattering over time. This test is not relevant for the prepreg requalification procedure.

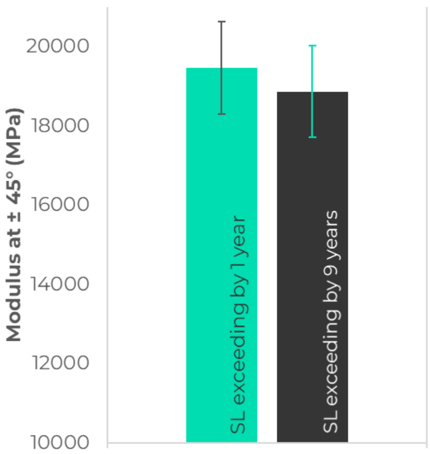

Figure 1. Evolution of the modulus at ±45° with aging

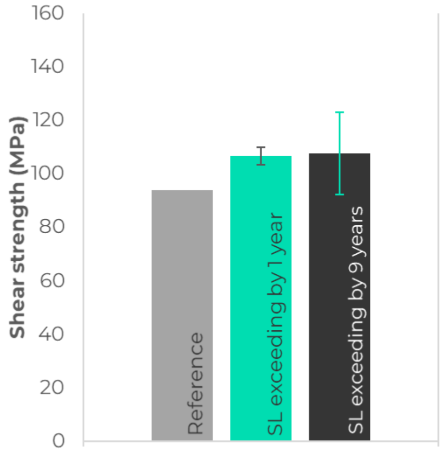

Figure 2. Evolution of the shear strength with aging

3.2. Relevant tests showing an evolution of the properties after too long storage

3.2.1. ILSS *[4]*

A 20% decrease of the interlaminar shear strength was obtained for the tested material after 5 years of storage. It shows that the material becomes sensitive to delamination with time. This test is very representative of the loss of mechanical performance of the prepregs during too long storage.

3.2.2. Volatile content *[4]*

It can be noted an important decrease in the volatile content between the 1-year and 5-years expired prepregs. As the polymerization reaction had advanced, the amount of uncured resin in the prepreg had decreased. This test is very easy to set and give meaningful results.

3.2.3. Evolution of the degree of cure (DSC tests)

Figure 3. shows the evolution of the degree of cure with time during long storage at -18°C.

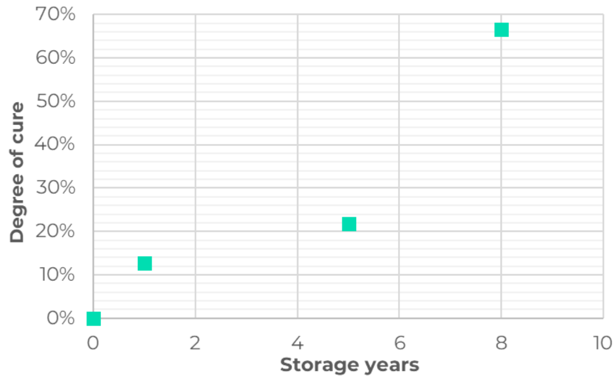

Figure 3. Evolution of the degree of cure

DSC measurements showed that, the degree of cure reached 13%. after 1 year of storage; 20% after 5 years and 65% of polymerisation after 9 years (Figure 3). These values highlight the progress of the reaction during storage in freezer and show a quantitative evolution with aging. This test should be maintained in a simplified requalification procedure

3.2.4. Plies compaction analysis

It is clear that the decrease in mechanical properties of the expired prepreg is small and is not comparable with the evolution of the physical-chemical parameters. In order to explain the small decrease in mechanical properties, optical microscopic observations were made. It highlighted the compaction rate of composites manufactured under the same conditions (pressure and curing temperature). Figure 5 and Figure 4 and 5 display two micrographs of transverse section of the plate number 1 of a compliant vs a 9-years old material. Differences in microstructures can be observed on the micrographs:

- For a 10-ply composite, a thickness of 2.01 mm is measured for the material stored for 9 years, whereas a thickness of 1.86 mm is measured on the compliant material. This shows that compaction was more effective on the compliant material.
- Thermoplastic nodules from the matrix layer were more visible on the older material.
- Larger and more numerous porosities are visible in fibre layers probably due to a more viscous matrix during processing.

These observations show that the processability of the 9 years expired prepreg was very poor. As a consequence, the compaction is lower and the fibre rate is lower too. Moreover, the probability of defects such as porosities is increased.

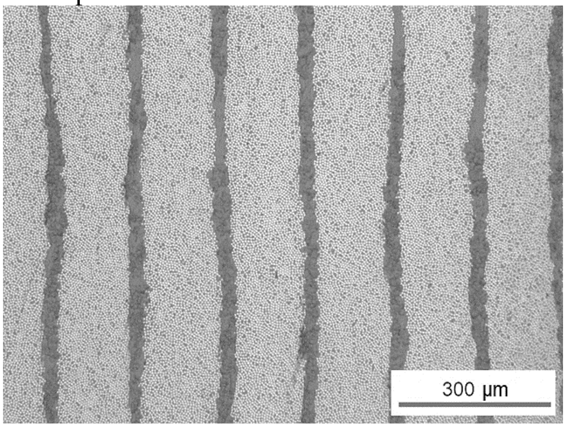

Figure 4. Optical micrograph of a composite manufactured with a compliant prepreg.

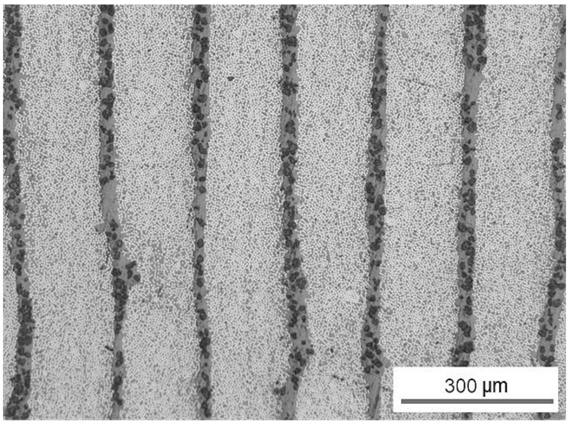

Figure 5. Optical micrograph of a composite manufactured with a prepreg with shelf life exceeded by 9 years.

3.2.5. Evolution of the processability after addition of hot air

To be properly draped, a material must be at least class 4 on the NCAMP scale. It was noted that after 5 years of expiration, the tack of the material was below 4. When the tack is too low, the compaction is poor and the material contains defects, which is the reason for the decrease in mechanical properties. This shows that processing difficulties will occur but it does not mean that the material has lost its performance. As mentioned in chapter 2.4.1, a hot air stream was added to the tack test as part of a new test - the "hot" tack. This technique allows to recover a satisfactory tack. It allows the recovery of mechanical properties.

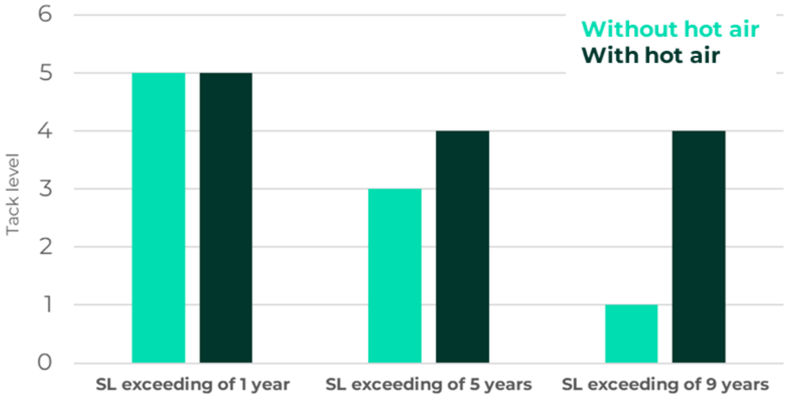

Figure 6. Tack and “hot tack” of expired prepregs

4. Discussion and simplification of the requalification precedure

4.1. Discussion

This study has shown that the loss of mechanical properties is very low and remain difficult to measure, even after 9 years of storage. In contrast, the polymerization advancement can be measured by physical chemical tests such as DSC or volatile content. As a consequence, it is difficult to correlate any evolution of the mechanical properties with the increase of the resin's degree of cure.

Previous studies [8, 9, 10] and the study conducted by MANIFICA showed that the processability was the most affected parameter with aging. Indeed, the compaction of the material becomes difficult when the resin reaches a high viscosity after too long storage. This shows that the loss of processability generates a drop of mechanical performance.

Finally, these tests showed that a sufficient processability of an expired prepreg can be recovered with hot air heating during draping; This assessment shows that a simplification procedure is possible and that reuse scenarios are achievable.

4.2. Simplification of the requalification procedure

For aeronautical use, the current requalification procedure is still mandatory, however it has been shown that this procedure is not representative of the actual decrease in mechanical properties. Today, a material that does not validate the full requalification procedure cannot be reused. In order to consider non-aeronautical uses without useless tests it will be interesting to use a simplified requalification procedure showing the real loss of properties. This simplified procedure will include a hot tack test which shows if the processability properties can be restored.

When the quantity of material to be requalified is sufficient for an aeronautical production, to carry out the complete requalification of the expired prepreg will still be profitable.

- If the requalification is validated, the shelf life of the material can be extended (for the same aeronautical use).
- If the requalification is not validated, a hot tack test could confirm the processability of the material. If this last test is approved, the resell of this material to a non-aeronautical manufacturer can be proposed.

If the quantity of prepreg is too low to justify a full requalification procedure, a simplified requalification can be performed (tack & hot tack test, determination of the polymerisation reaction progress (with DSC) and ILSS test to assess the mechanical properties).

- If it is validated, the resell of this material to a non-aeronautical manufacturer can be proposed.
- If the properties are definitively lost, the usage of this material is no more possible and then, the material can be recycled (after curing) by the MANIFICA process [11].

The advantage of this procedure is to completely avoid landfilling of expired prepregs.

5. Conclusion

Studies to understand the evolutions of the properties of prepregs during too long storage have been conducted. The physicochemical tests showed that the progress of the polymerization reaction was measurable and could be tracked continuously with different parameters (polymerization enthalpy, degree of cure, volatile content for example). On the other hand, the mechanical tests showed that the properties of the material did not vary or very little (slight sensitivity to delamination) with storage time, even after 9 years. Additional processability tests and compaction analysis allowed us to understand that the increase of the resin viscosity due to the polymerization advancement hampered the material good processing which finally drops the mechanical performance.

These forming difficulties are not handled in the aerospace industry, but it was shown that reheating the prepreg would reactivate the tack of the material to facilitate the layup step. These results have been used to propose a new requalification procedure for expired prepregs. t has been proposed to requalify them in a relevant way to enable their resale to non-aeronautical industries. If it is not possible to reuse the material, it can be recycled through the realignment process from MANIFICA after removal of the matrix [11].
In order to implement this new procedure, it must be validated with manufacturers and industries that can reuse the expired material. Logistic, adaptability and traceability of the prepregs waste must also be studied.

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