Innovative test methodology for shelf life extension of carbon fibre prepregs

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Abstract. The aerospace industry makes extensive use of composite materials in the form of fibre fabrics pre-impregnated with thermosetting resin, called prepregs. In order to minimize the resin polymerization before curing, prepregs must be stored at -18°C (0°F). There are therefore expiration dates for prepregs before use. Although manufacturers try to minimize storage time, offcuts and time out of the freezer, it is estimated that 30% to 40% of the prepregs are not used [1]. Today, recertification of expired materials is still complex and expensive, therefore it is generally chosen to send expired prepregs to landfill. The purpose of this work is to correlate physicochemical measurements with the loss of mechanical performance in order to point out and measure the real aging effects during excessive storage time. Processability, physicochemical and mechanical tests were performed in order to understand which tests are truly representative of ageing. This study was illustrated by testing on unidirectional Hexcel carbon/epoxy prepreg. Different expiry dates of this material were studied and the properties were compared. It was shown that the main observed degradation was the processability of the prepreg while mechanical performance was minimally degraded after the expiry date. This study could lead to a simpler measurement of the actual expiry rate of prepregs, which could be useful to speed up recertification procedures or to propose new scenarios to extend the shelf-life of expired prepregs [2].

1. Introduction

1.1. Context

High performance composites can be manufactured by implementation of pre-impregnated reinforcements, called prepregs. These semi-products stored at an intermediate cured state limit variation in fibre/resin ratios and simplify manufacturing. Prepregs have to be stored at low temperature (-18°C) in order to freeze the polymerization reaction. Two dates are considered to ensure that the reaction progress remains sufficiently low and acceptable for the implementation and the characteristics of the future composite:

- **Storage time/Shelf life**: Prepreg manufacturers define a shelf date, corresponding to maximum storage time at -18°C in a waterproof bag. This period is usually close to 1 year.
- **Out time**: Material exposure time to temperatures above -18°C which can accelerate polymerization reaction.

During a too long storage at -18°C, or during exposition > -18°C, the polymerization reaction may progress, with a possible impact on the prepreg processability or on the properties of the final composite. Finally, the material may no longer be usable for production of aeronautical certified parts. When one of these two dates has passed, the material is then considered expired. As the use of these semi-products increases, the amount of scrap generated could lead to important waste. There are several reasons for exceeding expiry dates:

- **Minimum batch orders**: Customer must purchase a minimum quantity of prepreg in order to be supplied. Sometimes, this minimum quantity remains higher than the total quantity required
to produce the entire series of composite parts. Some material will therefore be left unused in
the freezer until expiry.

- **Short expiry date**: Out time of some prepregs can be very short (depending on the resin grade).
  This may be very close to the manufacturing time of complex parts. Indeed, a production
  incident can then lead to a production stop and thus exceeding the out time.
- **Shifts of production**: Exceptional events, such as the Covid19 crisis, can lead to delays or shifts
  in production of several months. This has led to expiries of prepregs stored awaiting production.

Today, two solutions are available for aeronautical manufacturers to deal with expired prepregs:

i) recertify the material to use it for the same application after expiration.

ii) send it to landfill.

Recertification is possible but time consuming and expensive to perform because it is equivalent to a
complete certification procedure. Many tests must be performed and it is often more expensive than the
material itself.

1.2. Proposed method

The objective of this work, carried out in the frame of the MANIFICA European project, is to propose
a simplified procedure to extend the shelf life of prepregs. Then, new reuse scenarios will be developed
to avoid landfilling.

The current physicochemical recertification tests were implemented and compared with the
measurement of mechanical properties drop. Tests were performed on prepregs at different expiry dates.
It could be shown that some tests are redundant or unnecessary. As a consequence, only representative
tests showing a possible loss of property could be retained to simplify recertification procedure. In the
absence of proven loss of property, an extension of the shelf life can be imagined.

1.3. Prepreg manufacturing & aging effect

The fabric reinforcement is impregnated continuously with a thermosetting resin (only epoxy resins will
be considered in the frame of MANIFICA). After impregnation, the polymerization reaction is initiated
in an oven and the material is then in an unstable intermediate polymerization state called stage B [3].

The advance of the polymerization reaction during a too long or improper storage of the prepreg is called
chemical aging. This is by far the most important effect on a B-stage thermoset resin. At the beginning
of the curing reaction,

Step 1) Macromolecules with various structures are formed.

Step 2) The average molecular weight of the molecules increases with time until the size of the chain
is equal to the size of the system, forming a network.

Step 3) The remaining molecules react with the network creating further cross-links.

Step 4) The cross-linking rate grows until the system reaches the end of the chemical reaction [3].

The initial “pre-cure” of the prepreg will promote polymerization. During step 2, cross-linking generates
a decrease of the molecular mobility and an increase of the resin viscosity. This results in low resin flow,
which affects processability (draping of complex shapes and compacting of plies). Depending on the
out-time period, cross-linking can increase beyond limits that will hamper the molecular mobility during
the final curing process and isolate active groups without any connection.

To understand the chemical aging of prepregs, some physical parameters can be studied as the
rheological behavior, the degree of cure, the glass-transition temperature or the resin composition and
quantity. All of these effects lead to a reduction in the reactivity of the resin and degrade the processability and the properties of the final composite.

2. Experimental measurements

This section presents the first results obtained on the physicochemical and mechanical tests selected.

2.1. Material

A unidirectional Hexcel carbon/epoxy prepreg (reference) was used to initiate this study. Its shelf life was 1 year. Three different rolls manufactured in 2012, 2015 and at the beginning of the year 2019 are used. These three materials were therefore considered to be outdated since this work was conducted at the end of 2020.

2.2. Mechanical tests

To carry out mechanical tests, composite plates were manufactured by draping 11 unidirectional plies of prepreg (Standard for the plate lay-up is NF ISO 1268-4 [4]). Two plates of each material were necessary to obtain specimens with specific dimensions (two different thicknesses). Characteristics of the plates and corresponding tests are displayed on Table 1.

Prepreg plies were applied and rolled over successively. Plies were stacked on a PTFE substrate and under vacuum bag. The plate was then covered, with 1) a tear away fabric, 2) a perforated release film and 3) an absorption film. The self-adhesive seal and the vacuum bag were used to create a sealed vacuum during the entire process. Plates were then cured using a heating press (plate 1) or into an autoclave (plate 2) at 180°C during 2 hours with a 7-tonns applied pressure.

| Plate | Length (mm) | Width (mm) | Thickness (mm) | Plies number | Orientation | Tests          |
|-------|-------------|------------|----------------|--------------|-------------|----------------|
| 1     | 300         | 300        | 2              | 11           | 0°          | Tensile 0°, ILSS |
| 2     | 450         | 300        | 4              | 21           | 0°          | Pure bending   |

Table 1: Characteristics of the prepreg plates

(a) Tensile test

This test was performed according to the standard EN 2561 [5]. The Young’s modulus and the tensile strength of the composite were determined with 250 mm long and 20 mm wide samples. The machine was a 3R Syntech. An extensometer was used in the elastic range and removed before the plastic range and fracture.

(b) Measurement of the interlaminar shear strength (ILSS)

The ILSS tests were performed with a 3-point bending system with close supports fitted on the 3R Syntech machine. The length between supports was 10 mm and the diameter of the loading pin were 3 mm according to the standard test EN 2563 [6].

(c) Analysis of the compression behaviour by pure bending test

Pure bending test consists in analysing the compression behaviour of a specimen loaded in pure bending system with a specific specimen (Figure 1). A dumbbell shape specimen with a large thinning radius makes it possible to localise the fracture in the centre while keeping a quasi-homogeneous and uniaxial stress. It was then possible to study the compressive behaviour by simultaneously measuring the bending moment and the tensile and compressive strains at the centre of the specimen [7].
2.3. Processability & Physicochemical tests

(d) “Tack” test

The “tack” corresponds to the ability of a prepreg to adhere to a substrate or on itself. This represents the ability of the prepreg to be stacked. This characteristic is essential to maintain the ability of the plies to be compacted. Without tack, plies cannot adhere to each other or to the mould. To compare prepregs, many parameters have to be considered, such as the weight per unit area and viscosity of the resin or the organization of the reinforcement [8].

The 1993 tack test is currently used and has been standardized for the evaluation of prepreg tack [9]. A method described by NCAMP standards can also be used [10]. In both cases, these tests are qualitative and only a "grade" of tack can be determined. For both standards, the test consists in draping a prepreg to a previously cleaned metal substrate and then adding another prepreg of the same size on top. The metal substrate was then placed vertically and a visual control of the adhesion of the prepregs was performed after 30 minutes (NCAMP standards) or 1 hour (NF L17-461 standard). In this study, the test was derived from these 2 standards and both types of tack classes were presented.

| Class | I | II | III | IV | V |
|-------|---|----|-----|----|---|
| Prepreg adheres to itself | ✔ | ✔ | ✔ | ✖ | ✔ |
| Prepreg can be separated from itself after draping without damage. | ✔ | ✖ | ✔ | ✔ | ✖ |
| Prepreg adheres to the substrate | ✔ | ✔ | ✖ | ✖ | ✖ |

Table 2: example of Standard NCAMP rating after 30 minutes [10]

(e) Thermic measurements by DSC

During the curing of a thermoset system with a DSC, three different events can be identified [11]:

- The glass transition temperature of the uncured system (Tg₀)
- The glass transition temperature of the cured system (Tg)
- The exothermic peak of the polymerisation reaction
The enthalpy of the polymerization reaction was determined by integrating the area under the exothermic reaction peak. In the case of prepreg, this value corresponds to a raw enthalpy value, which must be recalculated according to the mass proportion of the resin, since carbon fibres remain inert below 450°C. The area under the curve was determined with the software Proteus developed by Netzsch-Gerätebau GmbH. The enthalpy of the matrix ($\Delta H_{matrix}$) was calculated with the equation 1:

$$\Delta H_{matrix} = \frac{\Delta H_{prepreg} \times 100}{\% m_{resin}}$$  \hspace{1cm} (Eq1)

A temperature cycle was set up: the peak of the polymerization reaction was detected during a 1st temperature rise and the reaction’s enthalpy and the Tg of the cross-linked system were determined by a 2nd temperature rise. In this study, the glass transition was determined with the software Proteus.

(f) Measurement of the volatile content

The volatile content of an uncured prepreg is an important indicator of the progress of the polymerization reaction (the presence of volatiles is proportional with the amount of gas emitted during polymerisation). Moreover, this amount must remain below a limit in order to avoid porosity in the final composite material. This test is standardized according to the European standard EN 2558 [12]. This test consists in measuring the mass of an uncured prepreg before and after its cure cycle. The mass of the samples must be taken at room temperature, after cooling in a desiccator. However, it is impossible to determine the nature of the volatile material. This test is part of the acceptance test of prepregs in the industry. The volatile content was determined with the equation 2:

$$\% \text{v}olatile = \frac{m_{before} - m_{after}}{m_{before}} \times 100$$  \hspace{1cm} (Eq2)

3. Results and discussions

3.1. Parameters evolving with aging

(a) Tack and processability

| Production year | NCAMP | EN |
|-----------------|-------|----|
| 2012            | 1     | IV |
| 2015            | 4     | II |
| 2019            | 5     | I  |
| New material    | 5     | I  |

Table 4 introduces results of tack test realized on prepregs and the desired result on a new material.

| Production year | NCAMP | EN |
|-----------------|-------|----|
| 2012            | 1     | IV |
| 2015            | 4     | II |
| 2019            | 5     | I  |
| New material    | 5     | I  |

Table 4: Tack results on 2012, 2015 and 2019 rolls

To be properly draped, a material must be class 1 on the EN rating and at least class 4 on the NCAMP rating. These rankings were achieved for the material of 2019. The 2015 material was draped well but...
the plies can be separated from each other after stacking. On the other hand, it was very complicated to drape the 2012 material because it was completely dry and brittle. Tack deteriorates with time and aging of the resin. These tests clearly highlight the influence of polymerization advancement. The limitation of this test is that it is not quantitative. The determination of the tack classification is only based on the qualitative observations of the handler. To correct this uncertainty, different operators could perform this test two times for example.

(b) Thermic events measurements

Figure 2 summarizes the results obtained during the DSC measurements on the different prepregs.

![DSC measurements results: a) Polymerization enthalpy evolution as function of time; b) Glass temperature of the cured sample evolution](image)

It can be shown in Figure 2a) that the enthalpy of reaction did not show a significant difference from 1 year of expiry to 5 years of expiry (loss less than 15%). However, after 9 years, the enthalpy has decreased by 60%. This test therefore shows an effect of aging of the resin during long storage; moreover, the enthalpy measurement results was consistent with the results of the tack test. The longer the prepreg is in the freezer, the lower its enthalpy. It shows that less energy was needed to complete polymerization, which means that the reaction has advanced. Regarding the Tg (Figure 2b), the determination might be difficult but the main observation is that Tg increases as the resin ages. Indeed, $T_{g\,2012}$ is 154.5 °C while $T_{g\,2020}$ is 135.8°C. This increase of Tg can be explained by i) increase of the polymer molecular weight and ii) development of inter-chain links that form a structural 3D polymer (crosslinking). These two phenomena induce a decrease of the molecular mobility and an increase of Tg. This test is coherent with tack test and reaction enthalpy measurement but might be useless because of its lack of precision.

(c) Volatile content

Figure 3 shows the results of the volatile content obtained on the 3 tested materials.

![Volatile content of the rolls from 2019, 2015 and 2012](image)
It can be noted an important decrease in the volatile content between 1 year peremption (2019) and 5 years expiry (2015). After 5 years of peremption, the volatile content did not seem to be reduced. As the polymerization reaction had advanced, the amount of uncured resin in the prepreg had decreased. Therefore, there was fewer organic molecules emitted during the curing process. This test is very easy to set and give meaningful results.

(d) Interlaminar shear strength
Table 5 shows the evolution of the ILSS results with time. It shows a decrease in interlaminar shear strength with time, even if the 2012 result is slightly higher than the 2015 result. ILSS is decreased by about 20% between the 2012 and 2019 samples. It is possible to understand that the aging of the resin leads to poor processability and lack of adhesion between plies. These effects can give to samples a greater sensitivity to delamination. This test is very representative of the loss of mechanical performance of the prepregs during aging.

3.2. Parameters not evolving with aging

|                | Tensile modulus (GPa) | Tensile strength (MPa) | ILSS (MPa) | Ultimate bending strain (%) |
|----------------|------------------------|------------------------|------------|-----------------------------|
| 2019           | 162.9 ± 5.0            | 1697.9 ± 137.7         | 98.4 ± 5.7 | 1.49 ± 0.8                  |
| 2015           | 168.5 ± 11.9           | /                      | 76.10 ± 1.8 | /                           |
| 2012           | 163.1 ± 3.0            | 1713.7 ± 129.1         | 78.26 ± 3.8 | 1.46 ± 0.1                  |

Table 5: Results of mechanical tests

(a) Tensile properties at 0°
Then Table 5 depicts the calculated young modulus for the 2012, 2015 and 2019 rolls. For comparison, the prepreg datasheet indicated a Young's modulus of 178 GPa. The measured values are all lower than this reference but they are very close for the three prepregs. This small deviation may be due to differences in the alignment of the fibres. Considering the average values obtained for the 3 years, it seems that the Young's modulus at 0° in the fibre’s direction does not vary with aging. This result supports the idea that the fibres properties are not affected during aging and that only the matrix properties undergo aging. The same observations are made with the tensile strength values (The tensile strength results of the 2015 samples are not presented due to a technical problem). So, 0° tensile test does not seem to be useful for recertification of expired prepregs.

(b) Compressive behaviour
Finally, Table 5 shows that the ultimate compressive strain at 0° do not vary with aging. As for the tensile strengths value, only the results of the 2012 and 2019 samples are presented. There is no difference of the compressive properties between 2012 and 2019 samples. This test does not seem to be useful for recertification of expired prepregs.

4. Conclusion & Perspectives
This paper presents the first results of a study with the objective of developing a simplified method for expired prepregs recertification. Today, these tests are derived from standards already used for quality control of the virgin prepregs. Some of these tests may not be useful and other tests may be simplified in the future.
During these studies, it was noticed that one of the major problems is the difficult processability of the prepreg induced by the aging of the resin. Thus, compaction of plies, curvatures may become difficult to manufacture, introducing defects that can weaken the final part, especially if it is a complex part.
It has also been shown that some parameters do not vary with time and that simplifying the procedure is possible. As a matter of fact, all tests related to the fibres could be useless as only the resin really ages. The comprehension of the aging mechanisms could show that some parameters can be linked together because they give the same information. To simplify the recertification as much as possible, considerate could be proposed to perform only the tests measuring the real ageing of the resin with time. Several new scenarios could then be considered following simplified recertification. We could imagine to keep the originally defined application, applications in other domains (non-structural aerospace applications or non-aerospace applications) or even the integration of the carbon fibre recycling chain implemented by the MANIFICA project. The final objective of this study is to reduce waste as much as possible. Complete results shall be published in 2022.

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