

Sustainable composite manufacturing from non-expiring carbon fiber/epoxy prepregs based on a vitrimeric matrix

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ABSTRACT

Despite the benefits of manufacturing composite materials from prepregs, its use is nowadays limited to high-production rate industries due to the high costs associated with their limited shelf life. Once this time passes, the material is considered as expired and disposed of as a non-usable waste. To avoid shortening its shelf life, prepregs are stored in refrigerators, increasing energy consumption, and thus magnifying the negative environmental impact. For this reason, the objective of this paper is to develop a new lifelong prepreg material without an expiration date that can be consolidated as a laminate after surpassing the gelation time of the resin, thus allowing composite materials processing technology based on prepregs without the need of freeze storage. To prove this concept, the study is carried out using a vitrimeric resin composed of an epoxy monomer (DGEBA) and 2-Aminophenyl disulfide (AFD) as a hardener. Two prepregs are manufactured and stored for 30 days at different conditions: environmental conditions, considered as the aged or non-conventional prepreg; and at $-18\text{ }^{\circ}\text{C}$ in a freezer, to replicate the conventional prepreg conditions. The results of the cured composites show stable glass transition temperatures and curing degrees between the two laminates. Concerning the mechanical properties, it has been proved that the gelation phenomenon of the non-conventional prepreg does not have any negative effect, showing a 11 % and a 21 % improvement of the flexural strength and failure strain, respectively, together with a 10 % increase of the interlaminar shear strength (ILSS) in comparison with the conventional prepreg, proving the potential of the proposed sustainable prepregs.

1. Introduction

The use of fiber reinforced plastics (FRPs) has been extended over the last years in lightweight structures of several sectors including automotive, aerospace, or civil engineering [1]. Among the different FRPs, carbon-reinforced ones (CFRPs) are used for structural components [2]. Their high strength-to-weight and stiffness-to-weight ratios make them attractive solutions to substitute conventional materials such as steel and aluminum alloys [3].

Industries of high production rates (e.g., aerospace sector with the Airbus A350 XWB [4], or wind energy sector with the wind turbine blades [5]) make extensive use of a more systematic route of mass-producing composites, called prepregs [6]. These materials consist of the impregnation of the carbon fibers with the resin in a partially cured state, referred to as B-stage [7]. Such partial curing of the matrix

prevents it from leaking from the fibers prior to gelation and, therefore, it is possible to perform the lay-up, curing, and consolidation of the final component [8].

Fabrication of composite parts using prepregs has unmatched benefits that include readiness to use, ease of handling and fitting complex geometries, accurate control of fiber/resin ratios, and very low void contents in the final products [9]. Consequently, they are widely used to achieve the best mechanical properties.

However, prepreg systems still have some limitations. First, most prepregs used in industry are based on thermosets, such as epoxy resins, as they present a good balance between the mechanical properties and in-service temperature. Since the matrix is in a B-stage, it shows continuous reactivity at room temperature because the epoxide groups of the resin slowly react with the hardener and, therefore, the gelation may occur at relatively short times [10]. Therefore, prepregs need to be

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stored refrigerated to hinder the crosslinking reaction, thus leading to higher energy consumption than conventional storage [11], as represented in Fig. 1.

The storage time of the prepreg at low temperatures (below 20 °C) in a sealed bag [12], referred to as the shelf-life, is limited to a maximum of 360 days in the best-case scenario [13]. When prepregs are extracted from the refrigerators they need to be kept in the watertight bag prior to use until reaching room temperature to avoid moisture absorption from the condensation process [14]. This process can take hours and limits the entire efficiency of the production. During this period when the material is stored at room conditions, the shelf-life term changes to out-life, which is the maximum accumulated time allowed at room temperature during its manipulation [2].

When one of the abovementioned times has passed the material is considered as expired. Even though the chemical changes are small, the processing properties (i.e., resin viscosity, tack) are degraded to such an extent that it becomes difficult to use the prepreg to form a consolidated laminate, which will result in a composite with poor mechanical properties [15]. Furthermore, prepregs close to the end of the shelf-life cannot be guaranteed to meet performance requirements and are usually rejected, creating a waste product [16]. Recertification of expired materials is still complex and expensive, so these prepregs are often disposed in a landfill, generating a waste material, and leading to a broad range of threats to the environment [17].

For these reasons, there is an urgent need for research on the development of durable and recyclable prepregs. These materials should present a long expiration time together with the ability to be reprocessed to avoid material waste, which is also an ideal method to extend the service life of composites.

However, due to their thermosetting nature, epoxy composites cannot be remolded, reshaped, or dissolved once cured, and therefore, their reprocessing or recycling is extremely difficult [18]. One possible

solution could be the application of thermoplastic polymers since they are not subject to chemical reactions during storage, can be reprocessed [19], and do not require a curing stage, improving the production capabilities [20]. However, current investigations are still far away from reaching the high-performance properties of thermosets and involve difficult manufacturing processes, as the viscosity and temperatures needed for a proper processing route are very high. These facts make them only suitable in secondary structures not supporting high loads [21].

In an approach to solve such limitations, a novel prepreg with a dynamic epoxy network matrix has been developed in this study. The idea underneath is to introduce exchangeable bonds in a polymer network. The bond energy of these dynamic networks is weaker than the covalent bond and become reversible when subjected to an external stimulus, such as temperature, while keeping the network integrity [22]. The dynamic character of this matrix will provide the prepreg good mechanical properties (equivalent to reference epoxy) together with the ability to be reprocessed [23].

The herein developed dynamic epoxy system is based on the exchange reactions of aromatic disulfides, which have been previously reported for the creation of self-healing and recyclable thermosets [24]. In these systems, there are exchange reactions between two adjacent S–S bonds, activated by means of thermal stimulus [25]. These reactions result in a viscosity decrease, as normally observed for thermoplastic materials, that permits the polymer to gain a high molecular mobility state and flow [26]. This capacity enables the manufacturing of lifelong prepregs, since totally cured prepreg sheets could be used for the consolidation of laminated composites. This will allow to create a more sustainable composite industry because these prepregs do not need to be stored in refrigerators at low temperatures, as represented in Fig. 1. In addition, most of them could be reused, repaired, or recycled during their operating life, avoiding all the above-mentioned drawbacks.

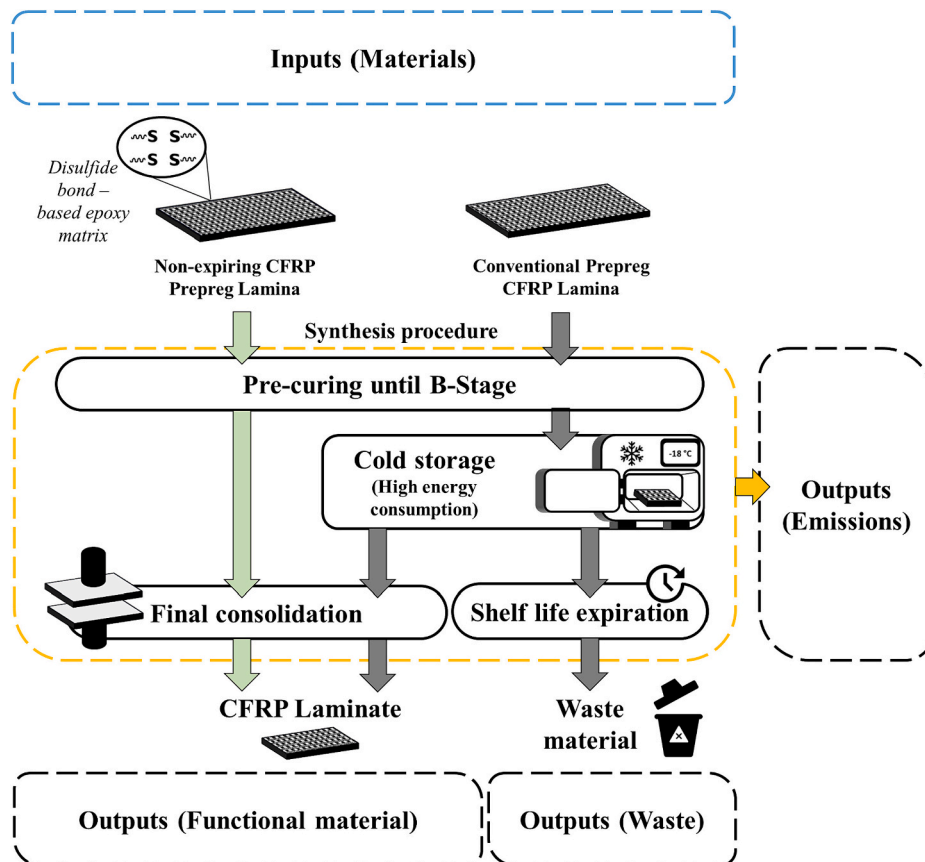


Fig. 1. Schematic illustration comparing the non-expiring and the conventional prepreg life cycles.

In this study, a lifelong prepreg was manufactured from a matrix based on disulfide exchange reactions. These dynamic mechanisms are increasingly being used for research purposes due to their high network rearrangement when exposed to a thermal stimulus. Specifically, the 4-aminophenyl disulfide (4-AFD) is gaining attention in recent literature reviews. In this work, the 2-AFD was selected, which is an isomer of the 4-AFD that is rarely used in research works. The reason behind this selection was its lower price, which is half of that of 4-AFD [27], making it an attractive solution for industry escalation. The combination of this dynamic hardener with the bisphenol A diglycidyl ether (DGEBA), a high-performance epoxy monomer, was used to investigate the room temperature aging effect on these novel prepreps without expiration date. Two sets of carbon fiber prepreg sheets were stored simultaneously at different conditions prior the consolidation of the final composites. One set was refrigerated at low temperature, following the traditional prepreg manufacturing methodology, to be considered as non-aged prepreg. The other set was aged at room temperature in an environmental chamber to simulate shelf life. Dynamic Scanning Calorimetry (DSC) was used to investigate the aging effect at different periods. Mechanical tests were carried out to investigate the aging effect on the mechanical properties of the consolidated composites. The differences between both laminates will be highlighted to demonstrate the feasibility of manufacturing composite materials with these novel lifelong prepreps.

2. Experimental

2.1. Materials

The epoxy resin was composed of bisphenol A diglycidyl ether (DGEBA) and 2-aminophenyl disulfide (AFD) hardener. Chemicals were supplied by Sigma-Aldrich and Tokyo Chemical Industry, respectively, and were used as received.

The reinforcement was a carbon fiber five harness satin (5HS) woven fabric with a surface weight of 280 g/m², supplied by Hexcel.

2.2. Epoxy/AFD synthesis

DGEBA monomer was first degassed during 15 min at 80 °C to remove the possible entrapped air. Then, the 2-AFD was added in a stoichiometric mass ratio of 100:36.5 (DGEBA to AFD proportion) maintaining the temperature at 80 °C. The mixture was magnetically stirred for 5 min until phase miscibility occurred.

2.3. Gelation time tests

Prior to the manufacturing of cured laminates, an investigation of the gelation time of the synthesised resin was carried out to determine the processing time in a low viscosity state of the resin to ease the impregnation of the fiber reinforcement.

In this study, the gelation time was assessed according to the method of Mura et al. [28]. The epoxy/AFD mixture was placed in a 60-ml beaker with a magnetic screw immersed. Then, the mixture was magnetically stirred. Since a solution is considered as a sol phase if it deforms by flow, or a gel phase if there is no flow, the gelation time was recorded when the magnetic screw stopped stirring due to the gelation of the resin. Measurements were conducted at 100, 120, 140, and 160 °C, with a constant stirring at 250 rpm.

2.4. Curing degree tests (B-stage degree of cure)

In addition to the determination of gel time, Differential Scanning Calorimetry (DSC) tests were carried out to determine the curing degree (α) of the resin after being heated at the processing temperature defined in the gelation time tests at different times. Measurements were made with a DSC 25 from TA Instruments (New Castle, DE, USA) device from

0 to 300 °C with a constant heating rate of 10 °C/min.

The enthalpy of reaction, ΔH , was calculated from the integration of the exothermic peak of the heat flow with a linear baseline, following:

$$\Delta H = \int_0^{t_c} \frac{dH}{dt} dt \quad (1)$$

where dH/dt is the heat flux and t_c is the curing time.

Two consecutive scans were performed on each specimen (two for each condition) to ensure the curing enthalpy was fully recorded and consider the possible residual heat of reaction. The evaluation of α with time was then calculated as follows

$$\alpha (\%) = \left(1 - \frac{\Delta H_t}{\Delta H_0} \right) \cdot 100 \quad (2)$$

being ΔH_0 the enthalpy corresponding to the resin immediately after being synthesised ($t_{\text{curing}} = 0$ h) and ΔH_t the enthalpy corresponding to the resin at different times.

2.5. Prepreg preparation

The uncured epoxy/AFD resin was poured on 32 carbon fiber fabrics with dimensions of 200 × 100 mm in a 50/50 weight ratio. The resin content was controlled by individually weighing each fiber lamina before and after pouring the resin using a Sartorius precision balance (Mettler-Toledo) with an accuracy of 0.007 g. The impregnated sheets were then pre-cured in a convection oven until reaching the B-stage defined with the curing degree tests. Each sample was placed in a separate sealed bag to prevent from sticking with each other and to avoid significant moisture absorption from the environment.

The prepreps were divided in two sets and stored at different conditions. Sixteen laminas were stored in the freezer at −18 °C to stop the polymerization reaction, considered as nonaged and referred to as the conventional prepreg, and the other set was stored in a Weiss Temperature and Climate Test Chamber WKL (Weiss Umwelttechnik GmbH) at 25 °C with 50 % humidity to simulate room temperature (RT) conditions, referred to as the RT prepreps.

The prepreps stored at ambient conditions (RT prepreps) were analyzed via DSC at different intervals to monitor the variation of the curing degree with the aging effect. These samples were taken from excess resin regions at the edge of the prepreg fabric, ensuring that the sample was free of fibers and it was pure resin.

2.6. Laminate consolidation

Laminate consolidation was performed once the curing degree of the RT prepreps matched with the curing degree at gelation defined from the previous test.

Each laminate was composed by sixteen plies of prepreg lamina, which were stacked and consolidated using compression molding with hot plates following a curing cycle at 160 °C for 6 h [29] and a compression pressure of 6 bar, as shown in Fig. 2.

2.7. Mechanical tests

Three-point bending and Interlaminar Shear Strength (ILSS) tests were carried out in order to determine the mechanical behavior of the manufactured laminates. These tests were carried out in a Zwick Z100 (Zwick-Roell, Ulm, Germany) universal tensile machine accordingly to standards ASTM D790 and ASTM D2344, respectively. The bending tests were first conducted in 100 × 13 × 3.5 mm samples (four for each condition) at 1.005 mm/min up to 0.8 % strain to determine the flexural modulus and then at 10.05 mm/min up to failure to obtain the flexural strength. ILSS tests were conducted in 24 × 8 × 3.5 mm samples (five for each condition) at a test rate of 1 mm/min and a span/thickness ratio of 4.

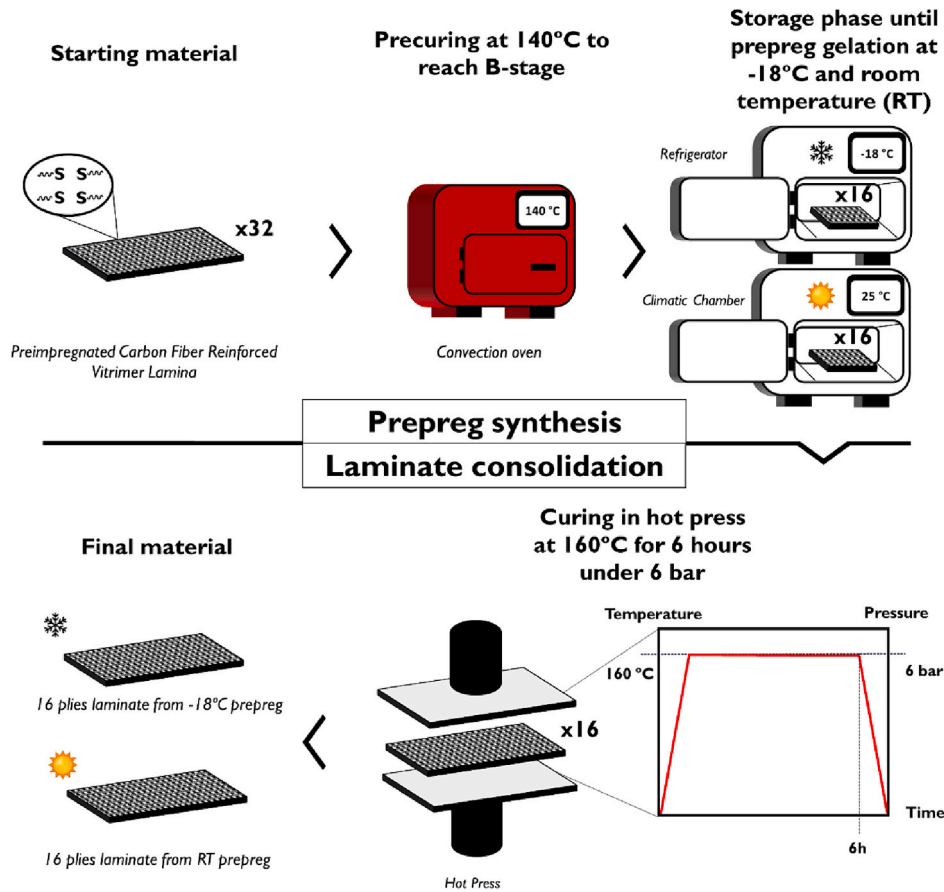


Fig. 2. Schematic illustration of the prepreg synthesis and laminate consolidation procedure.

3. Results and discussion

In this section, first, an analysis of the curing kinetics of CFRPs stored under room temperature and $-18\text{ }^{\circ}\text{C}$ storage is carried out by means of determination of gel time and curing degree at gelation by DSC analysis. Then, the mechanical performance of totally cured CFRPs by using the two types of prepreps is explored, by analyzing the flexural and interlaminar properties, as they will be widely affected by the consolidation degree during curing.

3.1. Analysis of curing degree

3.1.1. Gelation time

The gelation time of the resin is directly related to the processing time available to manufacture and consolidate a composite laminate. Simultaneously, it is necessary to define the time necessary for the prepreg to reach a B-stage, that is, a curing degree which is enough for a proper handling. In this sense, the gelation time was explored for different temperatures. The aim is to select a proper temperature to guarantee a short time to reach this B-stage before the manual layup.

The gelation times obtained at different curing temperatures are shown in Fig. 3 and Table 1. From these results, it can be first stated that the gelation time decreases with the temperature due to the increase of the curing reaction kinetics, as in accordance with previous reports [30]. No further temperatures were studied as the gelation time was too short (above $170\text{ }^{\circ}\text{C}$) or excessively long (below $100\text{ }^{\circ}\text{C}$).

In light of the results of the gelation time, the value of the curing temperature to obtain a B-stage was chosen as $T = 140\text{ }^{\circ}\text{C}$, which corresponds to a gelation time of 2 h. This time enables a processing window wide enough to ease the selection of the degree of cure of the B-stage.

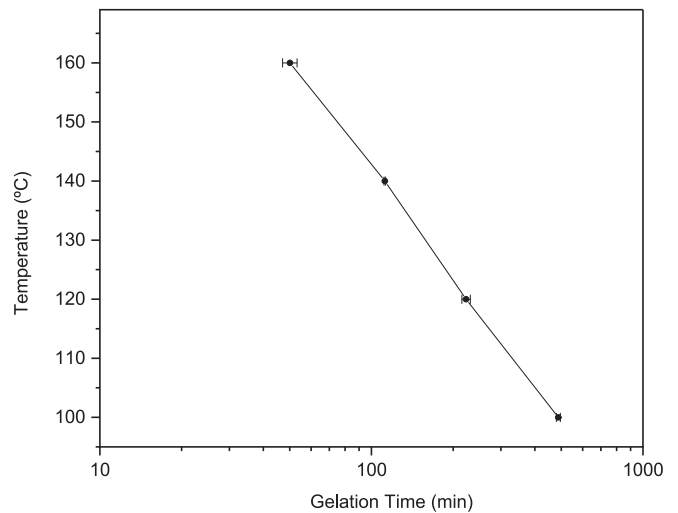


Fig. 3. Variation of the gelation time as a function of the processing temperature.

3.1.2. Curing enthalpy analysis

The B-stage curing degree was defined from the enthalpies of the samples after being isothermally cured at $140\text{ }^{\circ}\text{C}$ at different times. Fig. 4 (a) and (b) show the variation of the exothermic peak of heat flow and the reaction enthalpy, respectively, at 0.5 h intervals from the synthesis (0 h) until the gelation time (2 h). The enthalpy of reaction, ΔH , was evaluated from the DSC measurements as the integration of the exothermic peak of the heat flow with a linear baseline, following Eq.

Table 1
Gelation time values as a function of the processing temperature.

T (°C)	t _{gel} (min)
100	488 ± 8
120	223 ± 8
140	112 ± 1
160	50 ± 3

(1).

Considering that the total heat of reaction corresponds to the sample analyzed immediately after being synthesised (t_{curing} = 0 h), which is ΔH = 427.49 J/g, the curing degrees were calculated from Eq. (2) and are shown in Table 2.

The curing degree of commercial prepregs in B-stage goes from 15 % to 35 % [31]. To prevent the gelation of the prepregs during the pre-curing stage and solidifying, which would also make it difficult to handle during the reference laminate lay-up, an interpolation was performed from these results to define a B-stage curing degree as low as possible, i.e., α = 15 %, being sufficiently far from the gel point at 49.10 %. The obtained value corresponds to a pre-curing time of 0.75 h.

Once determined the B-stage curing degree, Table 3 shows the values of the curing degree of the RT prepreg after 30 days stored at room conditions and the values obtained for the gelled resin. The results prove that the resin of the RT prepreg had reached the gelation state. From a qualitative point of view, the RT prepreg showed the visual characteristics of an expired prepreg, being a rigid sheet with no tackiness or formability.

Therefore, the study continued with the manufacture of the laminates. Prior to the analysis of the mechanical performance in terms of flexural properties and interlaminar shear strength, the thermal behavior of the consolidated laminates was studied via DSC.

The most relevant results were extracted from the glass transition temperatures (T_g), estimated from the midpoint of the heat capacity change, and the curing degree of the laminates, both shown in Table 4.

From these results it can be observed that there is no difference between the T_g values of the CFRPs manufactured with the RT prepregs and the conventional prepregs, proving that the gelling phenomenon

does not induce any effect on the glass transition temperature of the laminate.

However, the curing degree values show a slight difference between the consolidated laminates, being the one stored at RT a 3 % higher than the conventional one. This fact may be explained since the curing progress of the RT prepregs was more advanced than the conventional prepregs prior to the final laminate curing and consolidation, thus reaching a higher curing degree in the first case.

3.2. Mechanical performance

3.2.1. Bending properties

Fig. 5 shows two representative curves of bending tests for CFRPs

Table 2
Curing degree values as a function of the curing time.

t (h)	ΔH _t (J/g)	α (%)
0.5	412.95	3.40
1	304.58	28.75
1.5	286.03	33.09
2	217.60	49.10

Table 3
Curing degree values of the room temperature stored prepreg and the gelled resin at 140 °C.

Sample	ΔH _t (J/g)	α (%)
RT Prepreg (Day 30)	217.56	49.11
Gel time (2 h)	217.60	49.10

Table 4
Glass transition temperature (T_g), residual curing enthalpies and degrees of the laminates from the DSC results.

Condition	T _g (°C)	ΔH _t (J/g)	α (%)
Room temperature	128.06 ± 0.01	35.33	91.74
-18 °C storage	128.35 ± 0.34	48.41	88.68

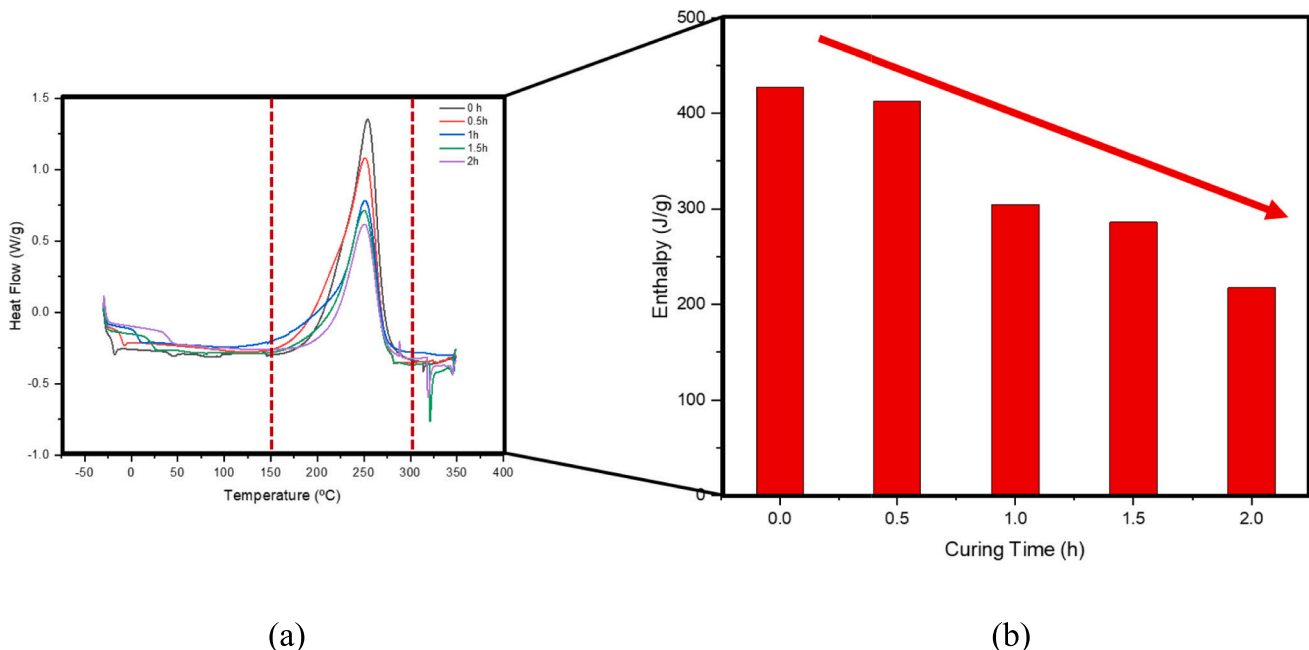


Fig. 4. Variation of the exothermic peak (a) and the enthalpy (b) of the post-curing reaction as a function of the previous curing time at 140 °C.

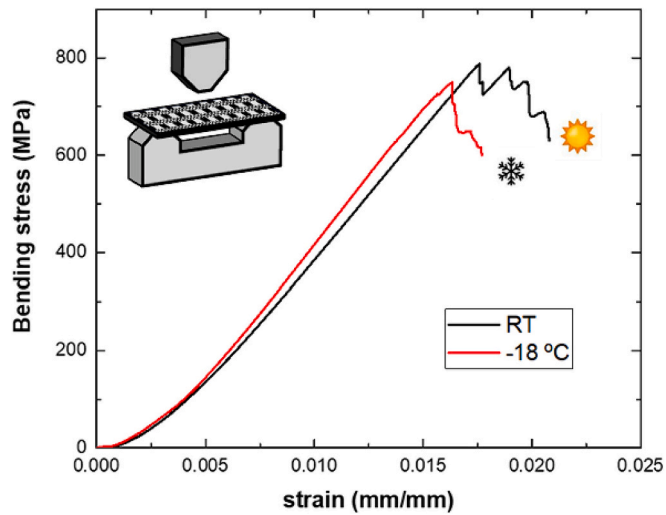


Fig. 5. Representative curves of bending tests for CFRPs made of room temperature and $-18\text{ }^{\circ}\text{C}$ stored prepregs.

made of room temperature and $-18\text{ }^{\circ}\text{C}$ stored prepregs. Here, several facts can be stated. On the one side, it can be observed that a proper consolidation of the plies during curing has been achieved in the case of room-temperature stored prepregs. As mentioned earlier, the curing degree of RT prepregs denoted that gelation occurred during the storage of these prepregs. However, the results of the bending tests showed that this had no negative effect on the flexural strength and failure strain under bending conditions. The reason lies in the fact that, due to the vitrimeric behavior of the AFD/epoxy system, an adequate resin flow took place during curing and, thus, the consolidation of the CFRP plies was achieved.

On the other hand, it can be observed that the CFRP made of RT prepregs showed both a higher flexural strength and failure strain. More specifically, a summary of mechanical properties obtained during bending tests is shown in Table 5. The higher values of both flexural strength and failure strain jointly with the slight reduction of the flexural modulus may be explained accordingly to the morphology of carbon fibers after the consolidation process and how it affects the crack propagation during the test.

More specifically, the results of the density measurements, by Archimedes method, (1.496 versus 1.534 g/cm^3 for room temperature and $-18\text{ }^{\circ}\text{C}$ CFRP, respectively) showed that the resin bleeding during curing was lower in the case of manufacturing with room temperature prepregs, as expected, due to the higher viscosity of the resin in the vitrimeric state in comparison with the resin at initial state [32]. In addition, the higher stiffness of the room temperature stored prepregs during consolidation lead to a higher waviness of the carbon fibers, as shown in Fig. 6. This phenomenon can also be demonstrated from the waviness ratio (WR) and the maximum deflection angle (θ_{max}) of the specimens [33]. The WR was calculated following Eq. (3),

$$\text{WR} = \frac{\delta}{\lambda} \tag{3}$$

where δ is the amplitude and λ is the wavelength. These parameters were

Table 5
Summary of mechanical properties obtained from the bending tests of the CFRPs.

Condition	Flexural strength (MPa)	Flexural modulus (GPa)	Failure strain (%)
Room temperature	838 ± 68	51.9 ± 2.4	2.06 ± 0.36
$-18\text{ }^{\circ}\text{C}$ storage	757 ± 31	56.8 ± 2.1	1.62 ± 0.10

obtained through digital image analysis using *ImageJ* software.

Results show a higher WR of the laminate manufactured with RT prepreg when compared to the values of the reference prepreg (WR of 0.052 and 0.027, respectively). The maximum deflection angle (θ_{max}) was obtained using the same method as the previous parameters. The resulting θ_{max} was 8.42° for the RT laminate and 3.62° for the reference laminate.

These two facts would explain the reduction of the stiffness as it is very affected by the volume fraction of fiber and resin and its waviness. In particular, the resin volume fraction on final CFRP, V_r , can be estimated using ASTM 3171, more specifically Test Method II [34]. The results (V_r of 0.26 versus 0.25 for CFRPs manufactured with room temperature and $-18\text{ }^{\circ}\text{C}$ stored prepregs, respectively) proved the above-commented fact, that is, there is a higher resin content for the CFRPs of RT prepregs and a higher carbon fiber waviness, explaining the slight reduction of the flexure modulus for the non-conventional prepregs.

However, the flexural strength and failure strain are more correlated to how crack propagates during the bending test. Particularly, it can be observed that the slightly higher carbon fiber waviness leads to a more tortuous crack propagation (Fig. 7a) in the case of room temperature CFRPs in comparison with $-18\text{ }^{\circ}\text{C}$ stored ones (Fig. 7b), where the crack propagation is much more prevalent through the specimen thickness. This is also reflected in the curves of Fig. 5, where a less drastic load drop is observed in the case of room temperature CFRPs, indicating that the carbon fibers promote a more prevalent crack-bridging effect. In both cases, the failure was initiated in the compression subjected face, as expected, due to the poor compressive performance of carbon fibers in comparison with their tensile properties.

In addition, the values shown in Table 5 for the flexural strength and modulus are similar or even slightly higher than CFRPs manufactured with a non-reversible resin as the matrix from previous studies [35], where they obtained a flexural modulus of about 45 GPa and a flexural strength of almost 800 MPa, compared to the 51.9 GPa and 838 MPa of the RT prepreg, respectively. This demonstrates the high mechanical performance capabilities of the disulfide bond-based matrix compared to conventional CFRPs.

3.2.2. ILSS analysis

Fig. 8 presents two representative curves of ILSS tests for the CFRP panels made of room temperature and $-18\text{ }^{\circ}\text{C}$ stored prepregs. Here, it can be observed that, first, the maximum load reached during the test is significantly higher in the case of the room temperature CFRP. In fact, accordingly to the results shown in Table 6 the ILSS values of RT prepregs are 10–15 % above those obtained for the CFRP made of the $-18\text{ }^{\circ}\text{C}$ stored prepregs. Therefore, the results prove that the interlaminar properties of room temperature CFRPs are quite well, which is in good agreement with the mechanical performance observed in the bending tests.

Furthermore, the interlaminar properties are very affected by the disposition of the carbon fibers inside the material. More specifically, a higher out-of-plane fiber waviness usually leads to an enhancement of interlaminar properties and impact properties [36]. This is explained by a more difficult crack propagation as the fibers acts as crack-bridging elements. In fact, from the SEM images of Fig. 9, two facts can be observed. On the one side, the crack propagation is more extended in the case of the panel made of $-18\text{ }^{\circ}\text{C}$ stored prepregs (Fig. 9a and Fig. 9b), which is in good agreement with the previously commented poorer out-of-plane properties of these materials induced by the higher fiber waviness [37]. On the other hand, this crack propagation takes places mainly through the carbon fiber-epoxy interface whereas in the case of room temperature stored CFRPs, it takes places mainly within the carbon fiber tows (Fig. 9c and Fig. 9d). In fact, according to load-displacement curves of Fig. 8, a less drastic mechanical drop is observed in the case of the room temperature laminate, indicating that the crack propagation takes place in a more difficult way.

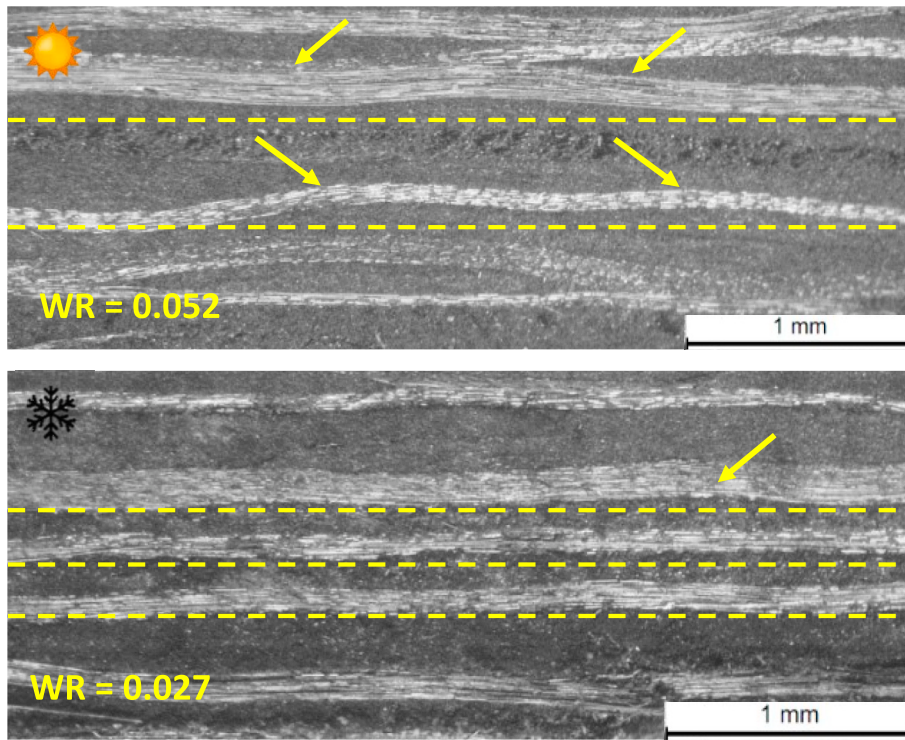


Fig. 6. TOM images of transversal sections for CFRPs manufactured with (a) room temperature and (b) $-18\text{ }^{\circ}\text{C}$ stored prepregs, where the yellow arrows denote the fiber waviness. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

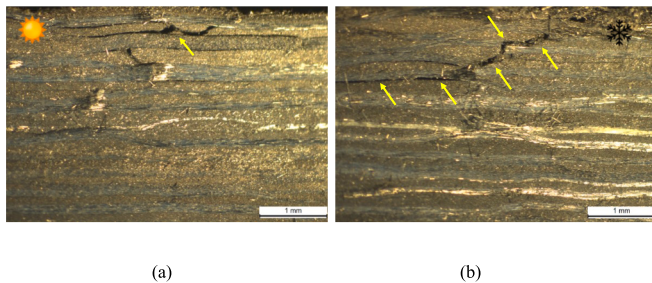


Fig. 7. TOM images of transversal sections for CFRPs manufactured with (a) room temperature and (b) $-18\text{ }^{\circ}\text{C}$ stored prepregs, where the yellow arrows denote the crack propagation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The prevalence of intralaminar crack propagation in the room temperature stored condition would be an indicative of a better fiber-matrix interaction. This could be explained by the effect of the tempering process of $-18\text{ }^{\circ}\text{C}$ stored prepregs, that would promote a water absorption effect, leading to a premature degradation of the fiber-matrix interface [38], facilitating the crack propagation through the interface, as observed, and, therefore, the degradation of interlaminar properties of CFRPs [39].

Therefore, the proposed composite made of room temperature stored prepregs showed higher bending and interlaminar properties when compared to the traditional laminate of $-18\text{ }^{\circ}\text{C}$ stored prepregs, with a positive ply consolidation and fiber-matrix interaction.

4. Conclusions

This work has demonstrated the use of gelled prepregs stored at room temperature conditions to manufacture composite laminates with no negative impact on its properties. Their use would allow the use of preimpregnated fabrics without low temperature storage, thus, reducing

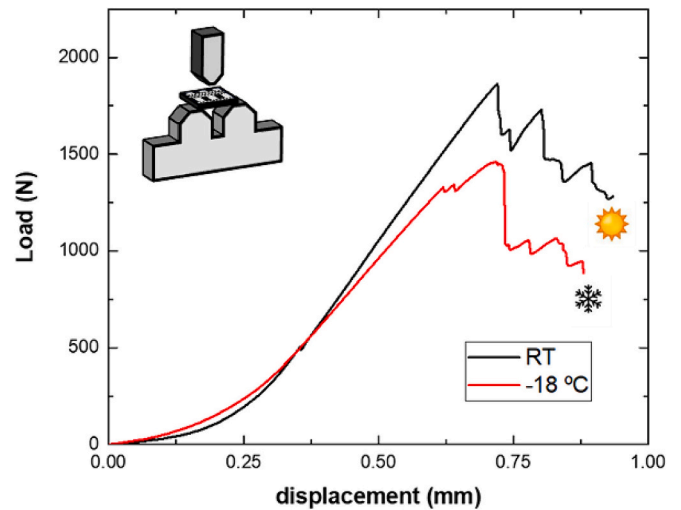


Fig. 8. Representative force-displacement curves of ILSS tests for CFRPs made of room temperature and $-18\text{ }^{\circ}\text{C}$ stored prepregs.

Table 6

ILSS values of room temperature and $-18\text{ }^{\circ}\text{C}$ stored CFRPs.

Condition	ILSS (MPa)
Room temperature	40.8 ± 4.4
$-18\text{ }^{\circ}\text{C}$ storage	36.6 ± 4.4

energy consumption and leading to an unlimited shelf life.

The gelation time tests showed a decrement of the gel time of the resin with increasing the temperature. From these results, the B-stage processing temperature was selected at $140\text{ }^{\circ}\text{C}$, allowing a processing

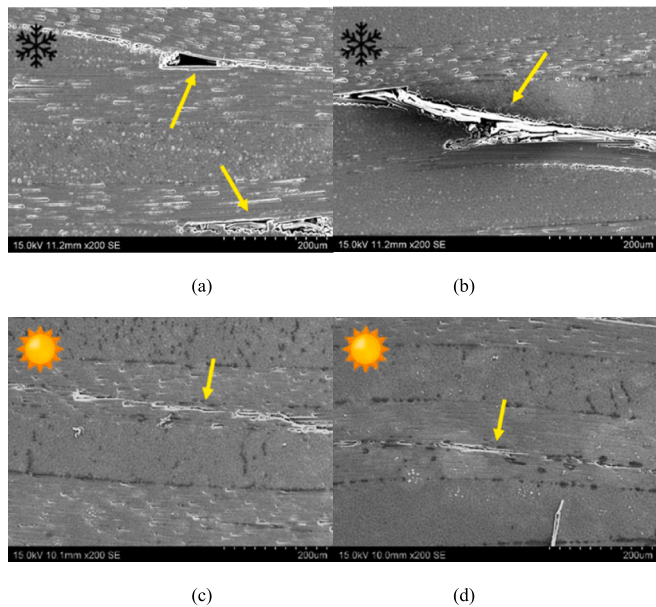


Fig. 9. SEM images of transversal sections after the ILSS test for $-18\text{ }^{\circ}\text{C}$ (a, b) and room temperature stored (c, d) CFRPs.

time of 2 h until the resin reached the gelation state. B-stage was defined from the curing degree analysis and was selected as a 15 % of the curing degree, corresponding to a processing time of 0.75 h.

The glass transition temperatures and curing degree reached for both laminates has been proved to be similar.

The results of the bending tests showed a 9 % reduction of the stiffness for the CFRPs made of RT prepregs. This could be explained from the density measurements, which showed that there is a higher resin content for the room temperature CFRP because of the higher carbon fiber waviness, and the lower resin bleeding during curing.

On the other side, the flexural strength and failure strain results showed an 11 % and a 21 % improvement, respectively, for the RT laminate, since these properties are more correlated to the more tortuous propagation of cracks due the fiber waviness.

The ILSS tests showed that the maximum load reached during the test was significantly higher, with a 10 % increase of the interlaminar shear strength (ILSS) for the RT CFRP, and a lower loading drop after failure. Moreover, the intralaminar crack propagation in the RT CFRP shows a better fiber-matrix interaction than the $-18\text{ }^{\circ}\text{C}$ CFRP because of the tempering process of $-18\text{ }^{\circ}\text{C}$ stored prepregs, which leads to a water absorption effect and thus a degradation of the fiber-matrix interface with the interlaminar properties of the laminates.

Finally, it should be noted that the non-expiring prepreg materials storage phase did not require the use of a refrigerator, unlike conventional prepregs. This reduces energy consumption and related polluting emissions. Furthermore, the vitrimeric prepregs can be stored indefinitely under any temperature related condition, unlike conventional prepregs which expire even when refrigerated after their average shelf life of 360 days, as previously stated. The expiration of these conventional prepregs results in the production of waste materials, which are commonly discarded in landfills without any practical purpose.

Therefore, the use of a vitrimeric matrix on prepreg materials opens a way to a sustainable manufacturing process of prepreg-based composites without energy or material waste.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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