EFFECTS OF MULTIPLE POST CURE CYCLES ON PROPERTIES OF COMPOSITE CARBON FIBRE AND EPOXY MATERIALS

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Abstract

Post-curing cycles have an effective impact on the thermal and mechanical properties of thermoset composite materials. Typically, post-cure cycles use heat to expose cured resin parts to high temperatures in an attempt to maximize their final properties. In most cases, these processes allow composite parts to achieve the highest possible strength and become stable. In industrial practice, however, it has been found that there are potential consequences of performing localized repairs on composite parts in an autoclave where the localized repair undergoes a normal curing process while the parent part undergoes an additional curing process. Thus, for the parent part, prolonged exposure to high temperatures can trigger a process of decomposition of the resin matrix, as could be the aging phenomena of composites in service. In such a scenario, two practical questions are worth asking: (1) to what extent can a resin matrix be post cured without risking degrading its thermal properties? (2) what are the residual mechanical and physical properties resulting from prolonged exposure of composite parts to elevated temperatures?

In this work, an analysis was carried out to estimate the potential adverse effects on thermoset composite parts made of carbon fibre and epoxy resin materials commonly used in aerospace, in terms of thermal, physical and mechanical properties after a long exposure to high temperatures caused by multiple post cure cycles. Two types of prepreg laminates were used to make monolithic test panels using twill and plain weave architectures for the M21 and 8552 test panels respectively.

Thermal tests were conducted to evaluate the evolution of the degree of cure, the glass transition temperature and the inter-laminar shear strength of post-cured panels, which were subjected to a different number of post cure cycles. The study found that multiple post cure cycles alter thermal properties, which in turn have adverse effects on physical and mechanical properties. The results demonstrated that the two types of composite materials respond differently to changes in properties. Twill weave panels quickly reach full cure after three stages while plain weave panels have undergone gradual curing. This difference in the curing process of the resin matrix clearly influenced the changes in the measurements of shear, surface hardness and compressive strengths.

Keywords: Post curing, carbon fibre reinforced composite, epoxy matrix resin, hardness tests, thermal properties and mechanical properties.

1. Introduction

Thermosets and thermoplastics are increasingly used in manufacturing, as they outperform conventional materials in high strength and stiffness to weight ratios. This results in an overall reduction in the weight of the parts manufactured by selecting composite materials with high

breaking strengths. These advantages have successfully enabled the replacement of metals by composite materials in many applications in the aerospace and automotive industries.

However, there are several challenges to overcome when considering the mass production of composite parts based on carbon fibre reinforced polymer (CFRP) and an epoxy resin matrix. For example, the overall process of certification, qualification and production of composites is always test-based, unlike the production of metals, which is standard-based [1]. This is why the move from metals to composites is still evolving in terms of setting standard properties.

Mass production of composites involves multiple variabilities, which are difficult to control and can significantly affect the properties of the final product. These variabilities can be introduced by differences in batches of raw materials, differences in freezing conditions, differences in the laying-up of laminates, the use of de-bulking, the type of tooling, differences in the bagging process, the vacuum, the type of curing as well as the choice of curing temperatures. All these variables pose potential design risks and their influence on mass production could be high. Thus, the probability of getting a defective part is also high. The variability of the manufacturing processes is here minimised to the maximum by using the same batch for each resin system, the same operators and full adherence to the test methods.

It is clear that the production of composite components free of imperfections or damage is often not achieved optimally. In addition, several defects caused by accidental events such as dents due to dropping or handling parts; or in-service events such as bird strikes are also common. Although it is known that thermoplastics have slightly better properties than thermosets, industrial practice shows that thermoset resins are more frequently used than thermoplastic resins due to their ease of processing. Consequently, thermosetting components are often the subject of multiple localized repairs whereas it is difficult to implement repair processes on thermoplastic components. Repairs always require curing processes where the parent parts undergo additional cure cycles, while the localized repair is in its first cure treatment. This difference in hardening treatment can result in differences in properties between the parent part and that of the localized repaired part. This study is therefore part of the identification of risks associated with a continuous increase in the degree of cure (DOC) that can significantly affect other thermal properties, which in turn can alter the physical and mechanical properties. To this end, a design of experiment approach was implemented to systematically vary the number of post cure cycles and determine its effects on properties.

Two types of prepreg laminates based on CFRP and epoxy resin matrix were used to make monolithic test panels. To ensure good quality of the manufactured test panels, the composition of the technical sheet (CTS) of composite materials required successful measurements of DOC, glass transition temperature (Tg) and inter-laminar shear strength (ILSS).

The novelty of this article is that it is an investigation, which represents a first systematic study of the effects of the number of post curing cycles on the properties of composite materials based on carbon fibre and epoxy resin. Composite materials degrade over time, either by aging due to exposure to high temperatures or sometimes to fire phenomena. This study has the advantage of presenting results that could be useful in the characterisation of the composite parts at different periods of their lifetime. In the case of repair operations, the study can also contribute to limiting the number of admissible repairs.

2. Literature Review

It is important to differentiate panels cured in an autoclave from panels cured due to exposure to ambient temperature and relative humidity. In general, composite parts are cured at room temperature (RT) or using an oven or an autoclave. It is known that composite parts are fully cured after post cure treatments at higher temperatures [14], whereas ambient temperatures produce incompletely cured parts. Thus, the RT curing process that uses wet laminates is usually a partial process that requires post cure treatment to improve their properties to an optimal level. Consequently, there is a continuous improvement in properties until the composite part reaches full cure. Thus, properties such as DOC gradually increases until it reaches a limit beyond which, little change takes place. However, it is possible to obtain complete curing of composite materials by using an autoclave and stepped stage curing under optimal conditions as proposed in the work of Cao and Cameron (2007). They found that a stepped stage curing procedure generates composite samples with up to 47 percent and 14 percent improved properties over curing at RT and elevated isothermal temperature, respectively.

All these processes involve the effects of temperature during the curing process, through either temperature rise or exposure to the environment over the lifetime of the composite parts. In both situations, adverse effects on the matrix resin, which crystallizes with increasing temperature, have been reported [3].

The literature on post curing mainly presents results related to the treatment of composite parts subjected to a single cycle of post curing in order to improve their properties. Although this claim is conventionally accepted, the results of this investigation showed some limitations in improving properties with evidence of adverse effects due to multiple cycles of post curing.

Several researchers have studied and published the use of thermal curing to improve the properties of composites. In these different studies, high temperature curing as well as post curing were beneficial to improve the properties with optimal values achieved [2–14]. This is the case with Na et al. (2018), who investigated the effects of temperature on the mechanical properties of adhesively bonded basalt fibre reinforced polymer and aluminium joints. Their results showed that the mechanical properties change significantly, when the temperature approaches or exceeds the Tg. Along the same line, Qin et al. (2018) investigated the effects of continuous high temperature exposure on the adhesive strength of adhesively bonded CFRP-aluminium alloy joints to elucidate the degradation mechanism. They observed significant changes in chemical and mechanical properties due to exposure to the thermal environment. Another study by Lopes et al. (2018) determined the mechanical behaviour of pultruded polyester/e-glass before and after exposure to high temperature. They observed a degradation of mechanical properties after a long exposure to temperature, while there was improvement for less time of exposure. They attributed the behaviour to a post curing effect on the composite's polymeric matrix during the heat treatment. Atkas and Karakuzu (2009) determined the mechanical properties of glass epoxy composite at high temperature. Their experimental results showed that mechanical properties of glass/epoxy composites deteriorated by increasing temperature. Finally, Cao et al. (2009) also found that the tensile properties of fibre-reinforced polymer (FRP) reduced at high temperatures.

Other researchers focus their efforts on post curing to improve composite properties. This is the case for Aruniit et al. (2012), who reported improvements in mechanical and physical

properties after determining suitable post cure parameters. They concluded that each material has an individual optimal post curing process that depends on the specific raw materials. Similarly, Chavan (2018) successfully explored the effects of post curing on hybrid composites. He found that composites with filler materials exhibited satisfactory mechanical properties when compared to unfilled counterparts. In their study, Veronica et al. (2014) evaluated the effects of additional post curing procedures on the flexural strengths and the elastic modulus of composite materials. Their results showed that the elastic modulus was significantly higher after additional curing treatment on all materials. Kumar et al. (2015) investigated the effect of post curing on the thermal and mechanical behaviour of GFRP composites. The results showed that post curing at 140°C for 6 hours gave better thermal and mechanical properties than post curing at lower different temperatures and times. Another study by Hiremath et al. (2014) investigated the effects of post curing on viscoelastic and flexural properties of epoxy/alumina polymer nanocomposite. The results indicated that post curing at a temperature below the glass transition temperature of epoxy, enhanced the viscoelastic and flexural properties, while it has a detrimental effect on the properties above the glass transition temperature. Finally, Khan et al. (2013) evaluate the effect of post curing on the edgewise compressive and flexural strengths of a sandwich structure, constructed with a composite sandwich structure with carbo fibre/epoxy as face sheets. The results showed that post curing significantly affects bending and compressive strengths of the sandwich structure.

Articles published in references [2–14] demonstrate that exposing composite parts to high temperatures or applying a single post cure cycle affects their thermal, physical and mechanical properties. However, the literature barely addresses the effects of multiple post cure cycles, such as those encountered in thermosetting composite repairs or composite aging phenomena due to exposure to high temperature. This is why it appears necessary to systematically study, document and publish the effects of prolonged exposure of composites to high temperatures on the properties.

3. Material Systems and Test Panels

The fibre reinforced composite materials used in this experimental study are made from two types of carbon/epoxy prepreg laminates, trading as M21/40%/46280/6K and AGP 193-PW/8552S RC40 supplied by Hexcel Composites (These composite materials will hereafter be referred to as M21 and 8552 respectively). The two sets of laminate materials used to manufacture monolithic test panels are symmetrical with the stacking sequence lay-ups designation of $[0/90/\pm45/0/90/\pm45/0/90/\pm45]_s$ and $[0/90/\pm45/0/90/0/90/\pm45/0/90/0/90/\pm45]_s$ for the M21 and 8552 laminates respectively. The values 0 and 90 indicate the directions of the woven ply with the warp fibres oriented at 0 degrees and the weft fibres oriented at 90 degrees.

The process used to manufacture and produce test panels in an autoclave encompasses obtaining raw materials, defrosting, tooling, cutting of materials, laying-up, de-bulking, bagging, curing, de-bagging, de-moulding and cutting into specimens. Seven test panels were produced from each laminate architecture and these panels could be differentiated by the number of post cure cycles undergone using the second stage cure cycle. The curing process begins with laying up all seven panels of a typical architecture on the same tool, starting with laying five plies of M21 laminates/six plies of 8552 laminates and applying de-bulking between plies to avoid the presence of voids, and then applying the first stage cure cycle to the laminates. After completing the first stage cure cycle, proceed by bonding the M21 six-ply laminates/

8552 nine-ply laminates to the cured panels, using an adhesive film (FM300K.05PSF36) and then apply the second stage cure cycle to the laminates.

After removing the first panel from the tool, reapply the second stage cure cycle to the remaining panels. The process was repeated until the last panel has undergone seven post cure cycles.

Figure 1 shows the first stage cure cycle showing autoclave pressure, vacuum and temperature as functions of time. Figure 2 shows the characteristics of the second stage cure cycle applied to the M21 panels and Figure 3 that of the 8552 panels. The dwell period temperature of the second stage cure cycle is set at 135º C for the M21 panels and 110 °C for the 8552 panels.

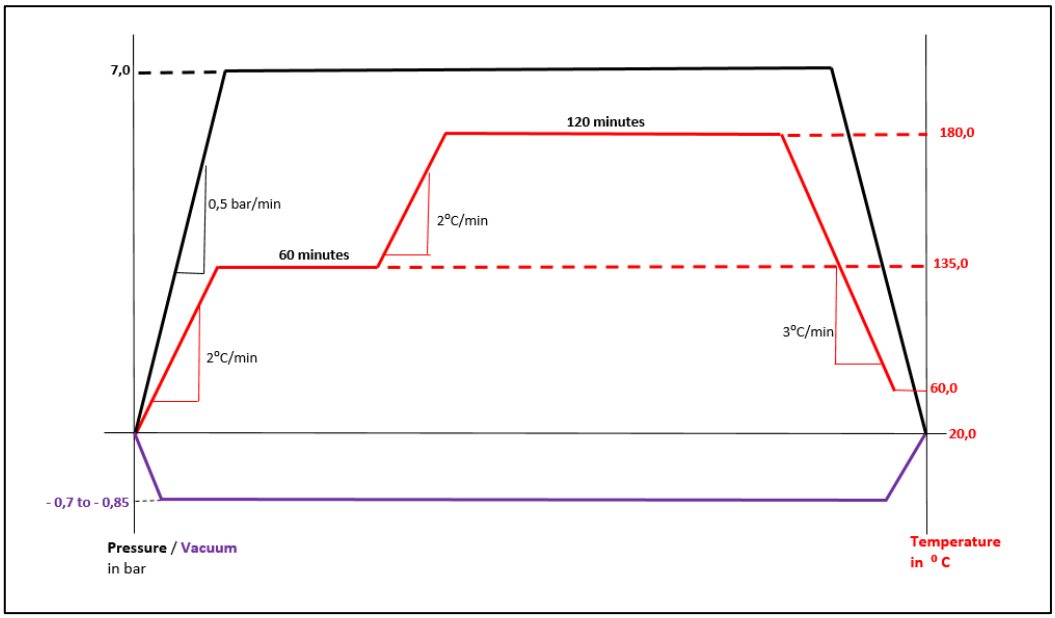


Figure 1: First stage cure cycle performed on the M21 and 8552 panels (references, [21] and [22])

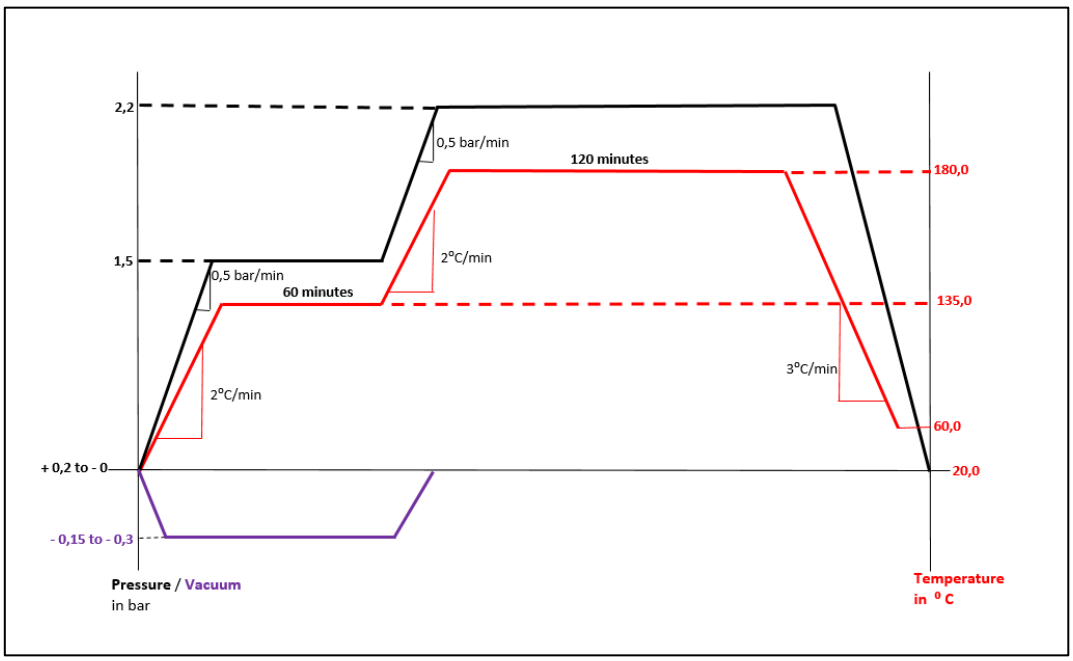


Figure 2: Second stage cure cycle performed on the M21 panels (reference, [21])

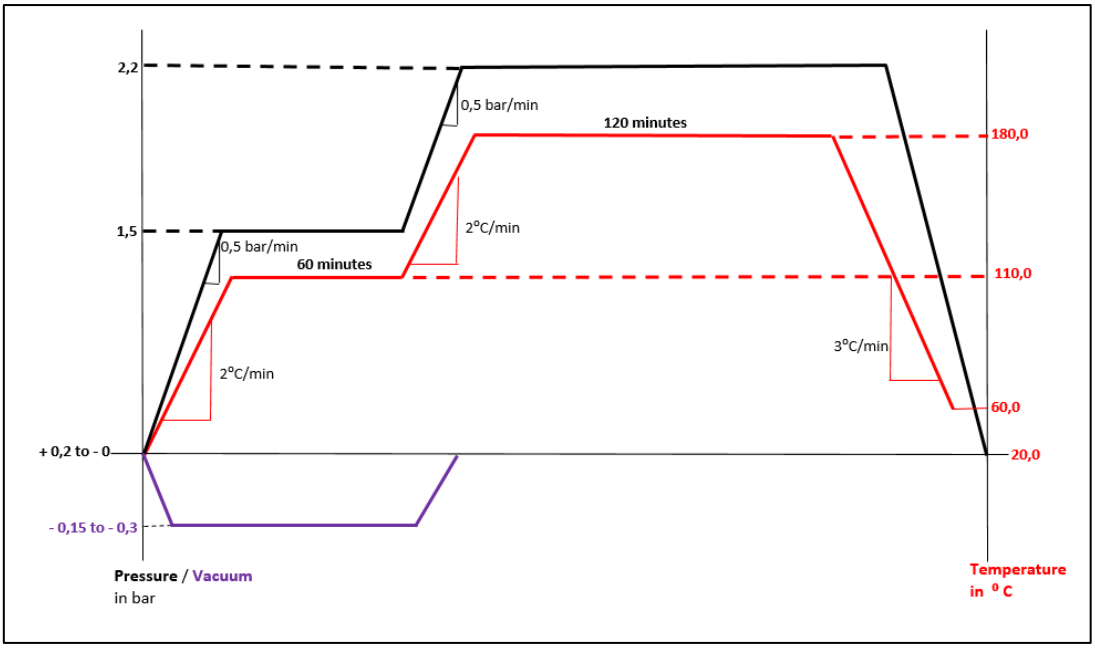
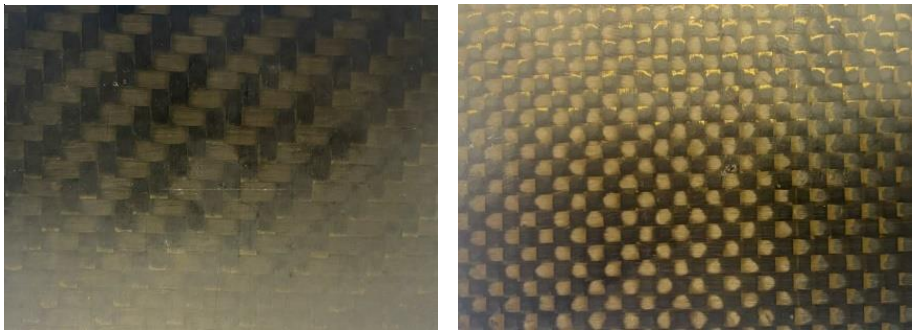


Figure 3: Second stage cure cycle performed on the 8552 panels (references, [21] and [22])

All test panels were subjected to visual inspection and non-destructive testing (NDT) using a phased array technique to ensure that no defects or delamination of the panels were present.

Figure 4 shows typical cured panels illustrating twill and plain weave architectures used to manufacture the M21 and 8552 test panels.



a) b)

Figure 4: Typical woven test panels manufactured from a) M21 resin and b) 8552 resin

Table 1 details the two types of prepreg carbon fabrics used to make the test panels, lay-ups, panel identification and CTS requirements for qualification and acceptance of panels cured to each material's specification (see references [21] and [22]).

Table 1: Details and properties requirements of manufactured panels (references, [21] and [22])

TYPE OF CARBON FABRIC/ TYPE OF RESIN	**M21/40%/46280/6K**	**AGP 193-PW/8552S RC40**
LAY-UPS	**$[0/90/\pm45/0/90/\pm45/0/90/\pm45]_s$**	**$[0/90/\pm45/0/90/0/90/\pm45/0/90/0/90/\pm45]_s$**
PANEL IDENTIFICATION	**M21 – 1 to 7**	**8552 – 1 to 7**
PROPERTIES	**VALUES**	
Inter-laminar Shear Strength (MPa)	56	62
DOC (%) (references, [21and 22])	> 90	> 90
Tg Onset /(⁰C) (references, [21 and 22])	> 190	> 190

4. Experimental Work and Test Methods

The objective of the experimental tests was to follow the evolution of the thermal, physical and mechanical properties with an increase in the number of post cure cycles. All panels tested had to pass quality control based on the thermal requirements described in the CTS (see references [21] and [22]). However, changes in thermal properties can potentially alter other properties such as surface hardness and mechanical strengths. Hardness and compression tests were therefore carried out to evaluate the evolution of these physical and mechanical properties. All tests were performed with at least six specimens taken from each of the seven post-cured panels with the exception of the hardness test where ten specimens were tested.

4.1. Composition of the Technical Sheet

The CTS is a set of three tests whose results determine the quality of the manufactured panels. These tests include the determination of DOC, Tg and apparent ILSS.

4.1.1. Degree of cure tests using DSC

The extent of cure is estimated by differential scanning calorimetry (DSC) measurements of uncured (reference) and cured composite materials. The value of the extent of cure α is determined as per the formula (1), according to the test method described in reference [18]. All test samples were cured in a nitrogen atmosphere.

$$\alpha\,[\%] = \frac{\Delta H_A - \Delta H_B}{\Delta H_A} \times 100 \qquad (1)$$

where ΔH_A is the reaction enthalpy of uncured composite material as reference, and ΔH_B is the reaction enthalpy of cured composite material.

4.1.2. Glass transition temperature tests using DMA

The Tg is determined by using dynamic mechanical analysis (DMA). It is defined as the temperature at which the sample exhibits a dramatic change in mechanical and damping behaviour with increasing temperature when subjected to an oscillation displacement. The Tg values are determined according to the test method described in reference [19] by measuring the sample stiffness (the storage modulus) and the damping (the loss modulus/tan δ). By evaluating the resulting plots against temperature, three readings of Tg values are derived: Tg-onset (storage modulus), Tg-loss (damping) and the Tg-peak. Only Tg-onset is considered for the purposes of this investigation because of its correlation with the stiffness of the material.

4.1.3. Inter-laminar shear tests using short beam

The ILS test was performed on an Instron 5967 universal testing machine using a three point bending fixture as shown in Figure 5. The apparent ILSS was determined according to the test method described in reference [17]. All specimens tested were cut out with the span / thickness ratio maintained at six and with the length / thickness ratio of ten. Each sample was tested at RT at a loading rate of 1 mm/min. The apparent ILSS expressed in MPa was determined according to equation (2).

$$\tau = \frac{3}{4} \times \frac{P_R}{b \times h} \qquad (2)$$

where τ is the apparent inter-laminar shear strength in MPa, P_R is the maximum load at the moment of the first failure in N, b is the width of the specimen in mm and h is the thickness of the specimen in mm.

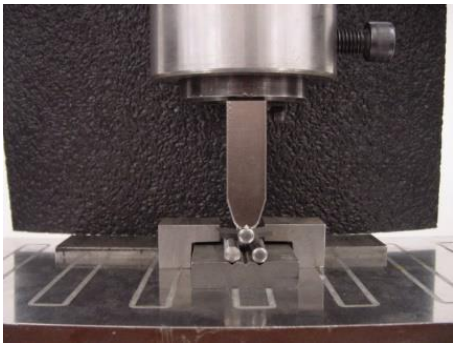


*Figure 5: I*nter-laminar shear test setup

4.2. Indentation hardness

The indentation hardness of the composite parts was measured with a GYZJ 934-1 Barber – Colman Impressor according to the test method described in reference [20]. Applications of composite materials demand high scratch and wear resistance, so indentation hardness is of great importance in the composite manufacturing process. The Barcol reading recommended by the International Cast Polymer Alliance (ICPA) is between 45 and 65. A lower number may indicate that the part is under-cured and a higher value that the cured part is too brittle [10]. To determine the Barcol hardness, place the sample under the indenter of the tester, then by applying steady pressure until the dial indication reaches a maximum. The penetration depth is then converted to an absolute Barcol number.

4.3. Mechanical properties

Compression tests were carried out on an Instron universal testing machine equipped with hydraulic grips as shown in Figure 6 in accordance with the test method described in reference [15]. This standard determines compressive strength and the modulus of elasticity of composite beams using a combined loading compression (CLC). The compressive load is introduced in compression at the ends of specimens and in shear. The sample was loaded to failure at 1.3 mm/min and the load versus strain (displacement, time) recorded. The compressive strength was calculated using equation (3).

$$F^{cu} = \frac{P_f}{w \times h} \tag{3}$$

where F^{cu} is the specimen compressive strength in [MPa], P_f is the maximum load failure in [N], w is the specimen gauge width in [mm] and h is the specimen gauge thickness in [mm].

The compressive modulus of elasticity was calculated over an axial strain range of 10% to 50% of the ultimate failure load using equation (4).

$$E^c = \frac{P_2 - P_1}{(\epsilon_{x2} - \varepsilon_{x1}) \times w \times h} \tag{4}$$

where E^c is the compressive modulus in [MPa], P_1 is the load at 10% failure load, P_2 is the load at 50 % failure load, ε_{x1} is the actual strain measured at 10% failure load and ε_{x2} is the actual strain measured at 50 % failure load.

Figure 6: Compressive test setup

To check the validity of the compressive test, the percentage bending is calculated using equation (5). This percentage is required to be less than 10 percent.

$$B_y = Percent\ Bending = \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \quad (5)$$

where ε_1 is the indicated strain from gauge 1 and ε_2 is the indicated strain from gauge 2.

5. Results and Discussions

5.1. Thermal Analysis

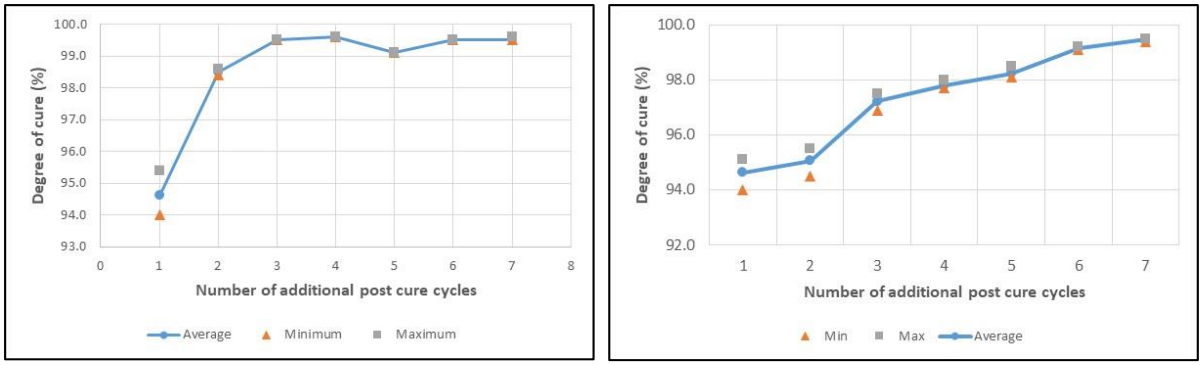
The thermal properties depend on various factors, including the composition of the resin matrix, the architecture of the woven prepreg laminates, the crosslink density between the carbon fibres and the resin, not to mention the type of curing process, which depends on parameters such as time and temperature. In any case, most of these factors are beyond the scope of this work, even if the results obtained relate changes in thermal properties to the behaviour of the crosslinking density of the cured resin as well as bonding efficiency to carbon fibres between laminates. This is why it is important to analyse the evolution of the thermal properties due to the additional post cure cycles to fully understand the phenomena that occur at the interfaces of the fibres and the resin matrix as well as their behaviours under longitudinal, transverse and shear loads. Additionally, it is industrial practice to use thermal testing to perform quality control on manufactured parts by comparing thermal results with those of allowable values of DOC, Tg and ILSS. For the different post-cured panels, six samples were tested and the confidence of the data was analysed by analysis of covariance. The results show that the calculated covariance for each post cure cycle is less than 0.5 percent for DOC, 1.0 percent for Tg and 3.5 percent for ILSS. These data disparities are at the six-sigma level. Thus, no significant change is expected in these statistical data including the minimum, maximum and average of each post cure cycle batch.

5.1.1. Degree of cure

The graphs presented in Figure 7 show the evolution of the DOC as functions of the number of post cure cycles for the M21 and 8552 cured test panels. The results demonstrate that the DOC is markedly affected by the number of additional post cure cycles, the type of materials and its woven architecture and by the crosslinking density of the resin. Indeed, after the first post cure cycle, the DOC measured on panels from the two types of materials greatly exceeds the allowable value of 90 percent by at least 4.5 percent. Despite this good result in the first post curing cycle, it is observed that the curing reaction is not complete. In effect, the DOC curves continue with their upward trend as if a measurable part of the uncured epoxy resin distributed throughout the section of the panel continues the process of crystallisation. This is why the difference in reaction enthalpies between uncured and cured materials also increases before reaching the full curing reaction. At this stage, we notice that the difference in DOC between two successive curing cycles becomes almost insignificant and the curve stabilise. However, the fluidity of the epoxy resin and the hardening conversion rate depend of the type of woven architectures.

The M21 test panels achieved full cure after three post cure cycles with DOC reaching 99.5 percent. At this point, the DOC of the test panels no longer improve, as further post cure cycles insignificantly increase the crosslink density. Therefore, the resin begins to degrade with excessive heating of the cured resin, which could negatively affect crosslinking between the carbon and the resin. In addition, over-cured composite parts become more brittle and tend to crack and break. If the crosslink density is evaluated based on the DOC curve, it can be seen that increasing the number of post cure cycles of the M21 test panels using step cure process leads to an increase in the crosslink density until the curve reaches the full cure when the reaction is complete. However, the DOC difference becomes insignificant after the third post cure cycle with the stabilisation of the curve.

On the other hand, the curve from 8552 panels shows that the DOC gradually increases with increasing the number of post curing. This upward trend can be explained by facts observed during the manufacturing process. After the de-bagging process, resin bleeding was visible on the impregnated cellophane release film, indicating that there was still a portion of uncured epoxy resin. This loss in epoxy resin density gradually diminished until the seventh post cure cycle when there was virtually no resin bleeding. At this point, the DOC has reached 99.5 percent. This shows how the two architectures reacted differently to long exposure to high temperature. The curing conversion rate of twill weave is higher than that of plain weave, which shows higher mobility of epoxy resin. Looking at both architectures, the interstices of plain weave are porous compared to those of twill weave. This appears to improve the fluidity of the resin through the gaps to the point of retarding the cure conversion rate of some uncured resin. The delay leads to gradual curing with low resin conversion rate and light crosslink density.



a) b)

Figure 7: Extent of cure results – a) M21 specimens and b) 8552 specimens

5.1.2. Glass transition temperature

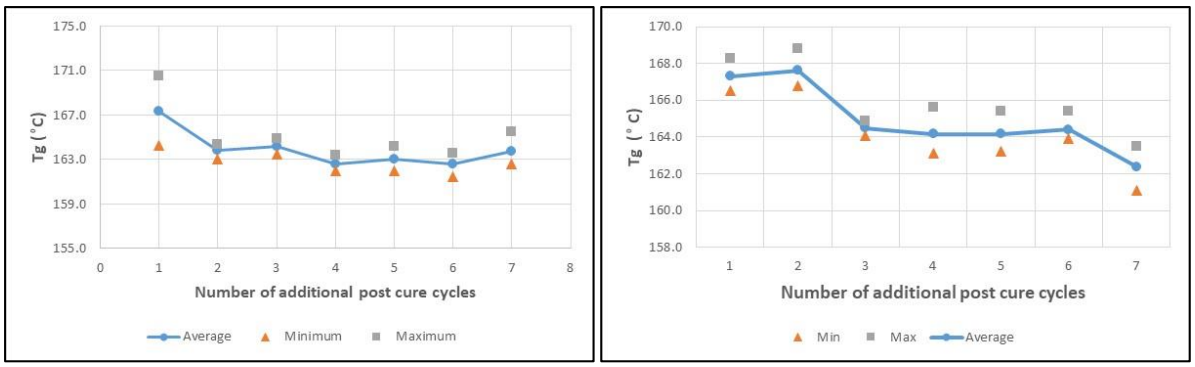
The glass transition temperature is a thermodynamic and thermo-mechanical characteristic. It indicates the softening point at elevated temperatures, the effectiveness of curing agents and the percent of curing [10]. The literature reports that Tg generally increases with the increment of DOC regardless of the cure cycle or cure histories [2].

The graphs presented in Figure 8 show the evolution of the measured Tg values as functions of the number of post cure cycles for the M21 and 8552 test panels. The results indicate that none of the test panels achieved the required value of Tg (190° C) as prescribed in the specifications of each material used. Indeed, the Tg probably cannot exceed the maximum curing temperature (180°C). However, the DOC results presented in section 5.1.1 demonstrate that the step-cure method was so effective in the first post cure cycle with a DOC of 94.5 percent, which is 4.5 percent more than the allowable value. At this stage, further cycles of post curing did not improve the Tg as shown by the curves of the results obtained from two architectures. Indeed, these Tg curves illustrate a downward trend, probably because the panels have almost reached the full curing with complete reaction. This is in contradiction with the conclusions in the works in references [2, 10], which found an increasing trend in Tg with increasing DOC regardless the cure histories. It is surprising to note that even in the range where the tendency of the DOC curve increases, that of Tg on the other hand decreases.

The upward trend in the cure curve of the M21 panels during the first three post cure cycles did not result in an upward trend of the Tg as claimed reference [2]. On the contrary, there is a significant drop in Tg from the second post cure cycle and which continues with a slight downward probably due to the cessation of the curing reaction when the epoxy resin reaches its maximum crosslink density. Thus, it is assumed that the Tg drops because it has reached the full cure when the curing reaction has almost stopped. However, other parameters can also be considered although they were not measured in this study. These include behaviour of carbon fibre due to resin overheating, resin degradation versus decomposition temperature, etc.

The Tg curve of the 8552 test panels shows a slight improvement at the second post cure cycle, likely due to the increase in crosslink density leading to the completion of the reaction as discussed in section 5.1.1. However, there is a significant drop in Tg after the second post cure cycle as the DOC continues to increase. Then, the Tg curve remains almost constant until the sixth post cure cycle and ending up with another significant drop.

In conclusion, the upward trend in Tg with increasing DOC can be justified as long as the curing reaction is not complete. However, Tg measurements performed on samples with different cure cycles have shown that Tg is actually the combined effects of crosslink density, chain segments motion, and decomposition temperature. Thus, overheating the cured resin does not improve the quality of the panels because it results in poor Tg.

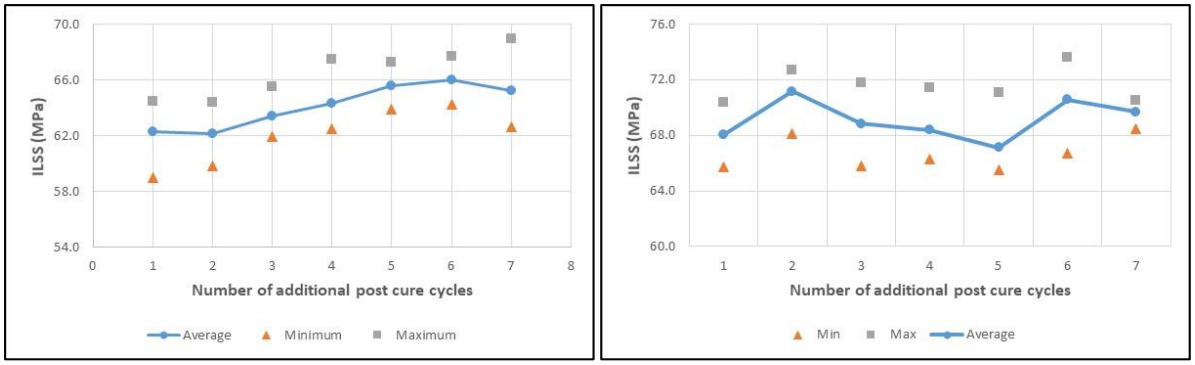


a) b)

Figure 8: Tg results vs additional post cure cycles – a) M21 beams specimens and b) 8552 specimens

5.1.3. Inter-laminar shear strength

The ILS test provides information on the curing quality between the resin and the carbon fibres, [17]. The graphs presented in Figure 9 show the evolution of the calculated ILSS as functions of the number of post cure cycles for the M21 and 8552 test beams. Each point of the graph is the average value of the measured failure load on six specimens and was determined from the load versus displacement curves. The results show that the ILSS values greatly exceed the allowable values of 56 MPa and 62 MPa respectively for the M21 and 8552 materials as specified in Table 1. This demonstrates that the epoxy resin exhibits high crosslink density and good bonding with the carbon fibres. Thus, the ILSS results of the M21 samples show that additional post cure cycles not only increase the pull out strength due to the high crosslink density but also strengthen the bond between prepreg laminates. There is also an improvement in resistance to delamination under shear forces, which justifies the upward growth of ILSS values with increasing number of post cure cycles. Whereas, results from 8552 test beams show mixed effects of multiple post cure cycles on ILSS values, likely due to light crosslink density or the presence of uncured resin. However, after the fifth post cure cycle, the crosslinking between the fibres and the epoxy resin improved with an increase in the resistance to delamination under shear force.



a) b)

Figure 9: ILSS vs additional post cure cycles – a) M21 specimens and b) 8552 specimens

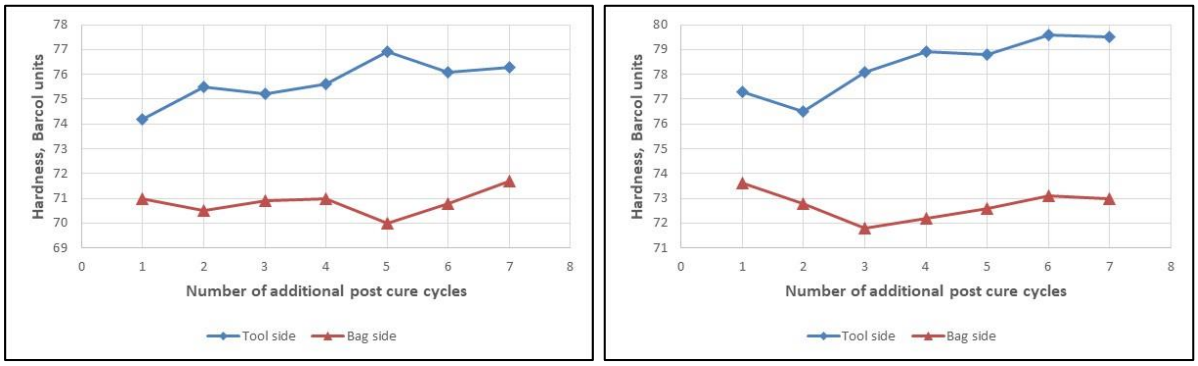
5.2. Indentation hardness

This test determines the indentation hardness of panels cured using a Barcol Impressor. Samples were tested as received and at RT. Barcol hardness was determined on both the bag-side and tool-side surfaces to verify the homogeneity of the manufactured panels as well as to determine the differences in hardness between the various cured panels, which differ in the number of post cure cycles. Each point on the graph is the average of ten Barcol hardness readings. Data was analysed by analysis of covariance to validate Barcol hardness readings. For each post cure batch, the results show that the covariance calculated over ten readings is less than 3 percent.

In Figure 10, Barcol hardness results measured on the bag-side and tool-side are plotted against the number of post cure cycles to illustrate the evolution of surface hardness changes. There is a gap between the two curves, which illustrates the differences in hardness between the bag-side and tool-side surfaces. These results show that the curing process does not guarantee the homogeneity of the cured panels because the tool-side gives higher hardness values compared to those of the bag-side. Indeed, the difference in the mode of transmission of the temperatures to the two surfaces may be the cause of the difference in hardness. The tool-side surface is in direct thermal conduction with the metal tool while the bag-side is in transmission by convection through the atmosphere of the autoclave. The indentation hardness results show that both types of materials respond favourably to scratch and wear resistance since the Barcol values obtained greatly exceed the upper limit recommended by the ICPA by at least 12 units. In addition, the surface of the tool-side has a higher resistance to scratches and wear than that of the bag-side.

The curves show how increasing the number of post cure cycles leads to an increase in tool-side surface, as seen in the curves for samples M21 and 8552, which gradually increase as the number of post cure cycles increases. The exception observed in the second post cure cycle in the hardness measurement of the 8552 specimens could be explained by the presence of uncured resin, which can affect the crosslink density. On the other hand, the hardness measured on the bag-side of the M21 specimens undergoes moderate variations until the fifth post curing and then increases thereafter, whereas that of 8552 specimens begins with a slight drop until the third post cure cycle and then it gradually increases.

The hardness results demonstrate some benefits of performing multiple cycles of post curing on composite parts, namely the improvement in crosslink density that makes these components harder, stiffer and resistant to fracture. However, these advantages are limited because a continuous increase in hardness leads to a loss of homogeneity and embrittlement. For this purpose, the consequences are multiple such as high risks of surface cracking, potential leaks on dry surfaces and lower fatigue resistance.

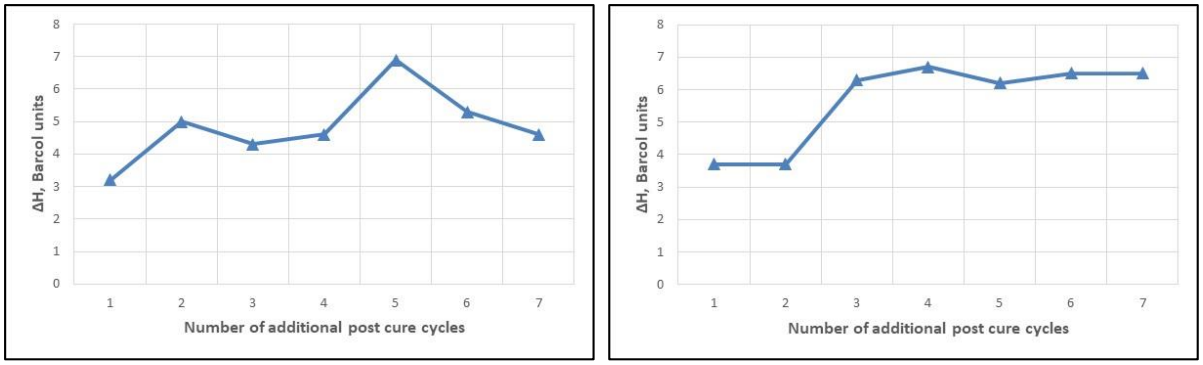


a) b)

Figure 10: Hardness, Barcol units at bag and tool-side vs additional post curing for a). M21 specimens and b). 8552 specimens

Since there is a discrepancy in hardness between the bag-side and the tool-side, it is important to quantify the differences in hardness (ΔH) between the two surfaces. The curves plotted in Figure 11 illustrate these differences in hardness under the different conditions of varying post cure cycles. The ΔH curves show how the two types of composite materials respond differently to Barcol hardness measurements. The ΔH curve of the M21 specimens increase until the fifth post curing due to the gradual increase in tool-side hardness while the bag-side hardness remain almost constant. However, the hardness increase of the bag-side after the fifth post curing leads to a significant drop of the ΔH curve. On the other hand, the ΔH curve of the 8552 specimens shows an increase until the third post cure then it remains almost constant due to the growth of the hardness of the two surfaces in the same proportion.

The ΔH curves of the two materials show that the difference in hardness between the bag-side and the tool-side is greater than 3 Barcol units in the first post cure cycle. It even reaches 7 Barcol units after a few post curing cycles. This number of Barcol units may be a good indication of the acceptable limit beyond which post curing of composite parts should not be allowed. To avoid these differences in hardness, it will be necessary to consider the use of tools, which would attenuate the transmission of heat allowing the equalisation of the level of heat transmitted on both sides.



a) b)

Figure 11: Difference in Barcol hardness versus additional post cure cycles – a). M21 specimens and b). 8552 specimens

5.3. Mechanical properties

The strength results presented include an analytical calculation using classical laminate theory (CLT) and experimental results, which describes the behaviour of composite parts subjected to multiple post cure cycles in compression. The CLT results provide reference allowable strength values without considering multiple post curing processes.

5.3.1. Classical Laminate Theory

This study uses composite application software that applies CLT to determine allowable strength properties. The application used a model based on the stacking sequence of carbon laminates described in section 3, to analyse and calculate the expected strengths of the manufactured composite panels. B-basis values calculated from experimental results using the composite statistical method for small data sets are compared with analytical results obtained from CLT analysis. The analysis uses an (x, y, z) coordinate system with x, y and z in the longitudinal, transverse and thickness directions, respectively, as shown in Figure 12.

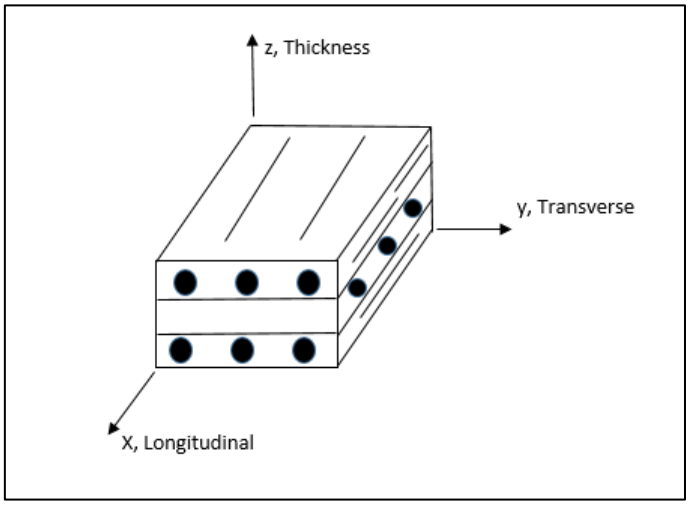


Figure 12: Coordinate system of laminates used for test panels

Knowing the direction of laminates, the number of laminate plies specifying the thickness and the applied load, the CLT uses the matrix of each laminated material to calculate stresses and moments using the stiffness matrix as follows [1]:

$$\{\sigma\} = [\,\overline{Q}\,]\{\varepsilon\} \qquad \begin{bmatrix}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{bmatrix} = \begin{bmatrix}\overline{Q}_{11} & \overline{Q}_{12} & \overline{Q}_{16}\\ \overline{Q}_{21} & \overline{Q}_{22} & \overline{Q}_{26}\\ \overline{Q}_{16} & \overline{Q}_{26} & \overline{Q}_{66}\end{bmatrix}\begin{bmatrix}\varepsilon_x\\ \varepsilon_y\\ \gamma_{xy}\end{bmatrix} \tag{7}$$

where $\overline{Q}$ is the stiffness matrix, σ is the stress and ε is the strain.

Or

$$\{\varepsilon\} = [\overline{S}\,]\{\sigma\} \qquad \begin{bmatrix}\varepsilon_x\\ \varepsilon_y\\ \gamma_{xy}\end{bmatrix} = \begin{bmatrix}\overline{S}_{11} & \overline{S}_{12} & \overline{S}_{16}\\ \overline{S}_{21} & \overline{S}_{22} & \overline{S}_{26}\\ \overline{S}_{16} & \overline{S}_{26} & \overline{S}_{66}\end{bmatrix}\begin{bmatrix}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{bmatrix} \tag{8}$$

where $\overline{S}$ is the compliance matrix.

It is important to note that simulation of resin curing processes was not considered in the CLT analysis. However, the manufacturing processes and all associated process histories were within specifications and standards. Thus, the results of the experimentally determined controlled properties validated the CLT analysis. In addition, the experimental results based on multiple post cure cycles were evaluated by comparison with the results extracted from the first post cure panel considered as the reference panel.

Table 2 presents a summary of the CLT results after analysis of the two types of materials. The stacking sequence of the M21 and 8552 laminates is defined in section 3. These values constitute the allowable strengths for the validation of the experimental results.

Table 2: Properties of composite parts based on the CLT analysis

Properties based on the CLT analysis	M21 Resin	8552 Resin
	Twill weave Panels	Plain weave Panels
	[0/90/±45/0/90/±45/0/90/±45]s	**[0/90/±45/0/90/0/90/±45/0/90/0/90/±45]s**
Compressive Failure Strength, F^{cu}, [MPa]	-357	-377
Compressive Failure Strain, ε^c, [με]	-7773	-7682
Compressive Modulus, E^c, [GPa]	45.962	49.190
Tensile Failure Strength, F^{tu}, [MPa]	392	460
Tensile Failure Strain, ε^t, [με]	8525	9269
Tensile Modulus, E^t, [GPa]	45.962	49.190

5.3.2. Compressive strengths

The section presents the effects of multiple cycles of post cure on the compressive strengths of M21 and 8552 composite beams. It is clear from the thermal analysis performed in section 5.1 that the curing reaction stops when the matrix resin reaches its maximum crosslink density. At this stage, the epoxy resin, which has a higher coefficient of thermal expansion than carbon fibres, tends to shrink on the carbon fibres with a susceptibility to create potential residual tensile and compressive strengths due to the radial and longitudinal forces exerted by the matrix

resin. Thus, pulling out the fibres could be the major failure mechanism in tension and shear while debonding, cracking and delamination are expected to be the source of the failure modes in compression. Indeed, the radial forces may increase the resistance on the fibre pull-out while the longitudinal forces will increase shear, [11]. Thus, the cracking and debonding of fibres are the major failure modes expected in compression. All samples were tested in the as received and RT condition. The specimens exhibited a compressive failure mode in the gauge length area, as shown in the photographs in Figure 13.

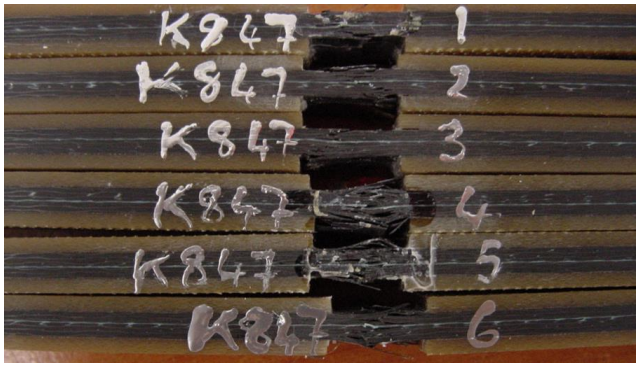


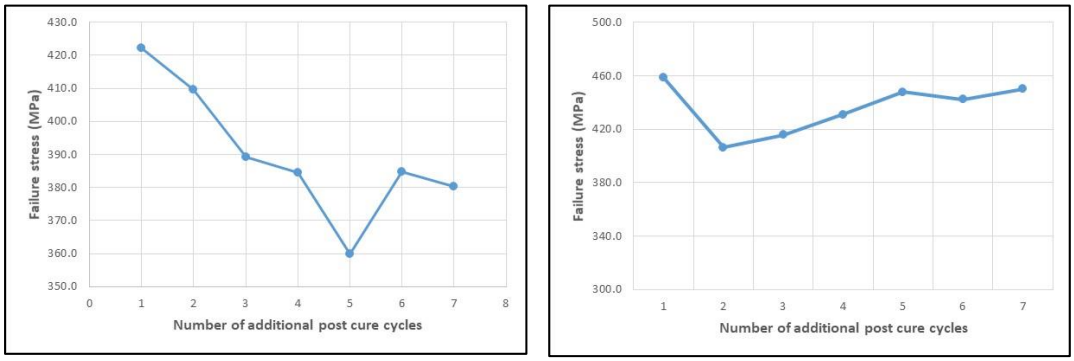
Figure 13: Photographs of typical compressive failed test specimens

Figure 14 to Figure 16 respectively plot the failure values of the stress, the strain and the modulus of elasticity measured in compression. Data analysis was performed using analysis of covariance. The covariance is less than 5 % for the compressive stress, 8 % for the strain and 5 % for the modulus of elasticity measured in compression. Data discrepancies are at six-sigma level including minimum and maximum. These curves highlight the evolution of compressive properties as a function of the additional post cure cycles. Compared to the CLT results presented in section 5.3.1, the experimental strength results of the M21 and 8552 test beams successfully achieved the strength allowable. The compressive strength properties behave very well with strength values at least 18% higher than the allowable. These results are in good agreement with the results presented in reference [11], which illustrate the advantages of using the stepped stage curing method to improve strength results.

The two important factors to consider in determining compression responses are the type of composite materials and the effects of post curing on the crosslink density. Indeed, the strength results show that the M21 and 8552 test beams respond differently to loading while multiple post cure cycles significantly affect the compressive properties.

It is clear that the increase in the number of post cure cycles tends to decrease the compressive breaking strengths of the M21 specimens while those of 8552 specimens, although showing a significant decrease at the second post curing cycle, tends to increase. These results appear in good agreement with the thermal and physical results, which demonstrated the difference between the two architectures regarding the hardening process. Indeed, additional post cure cycles performed after reaching the maximum crosslink density did not improve the mechanical properties of the M21 panels. On the one hand, this means that further post curing cycles insignificantly increase the crosslink between the carbon fibre and the resin. On the other hand, the hardness of the panel surfaces increases continuously as discussed in section 5.2, so that the composite panels become susceptible to compression due to the degradation of the bond between epoxy resin and the carbon fibres. Consequently, the evolution of the curve shows a decrease in strength of 15 percent at the fifth post curing probably due to a failure

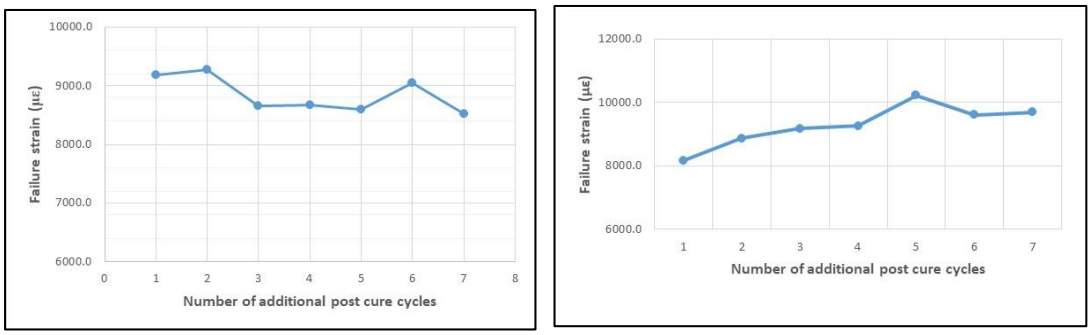
mechanism linked to debonding and delamination. In contrast, the 8552 panels, which showed a gradual curing process, increase their residual compressive strength because the curing reaction is not complete and the crosslink density is still increasing.



a) b)

Figure 14: Compressive failure stress vs additional post curing a) for the M21 specimens and a) 8552 specimens

Statistically, the strains measured at failure in compression for the M21 specimens seem to be less sensitive to the increase in the number of post cure cycles because its variations are insignificant. On the other hand, the strains measured at failure for the 8552 specimens illustrate an upward trend. It appears that gradual curing results in an increased crosslink density, which in turn gradually increases strain until fully cured.

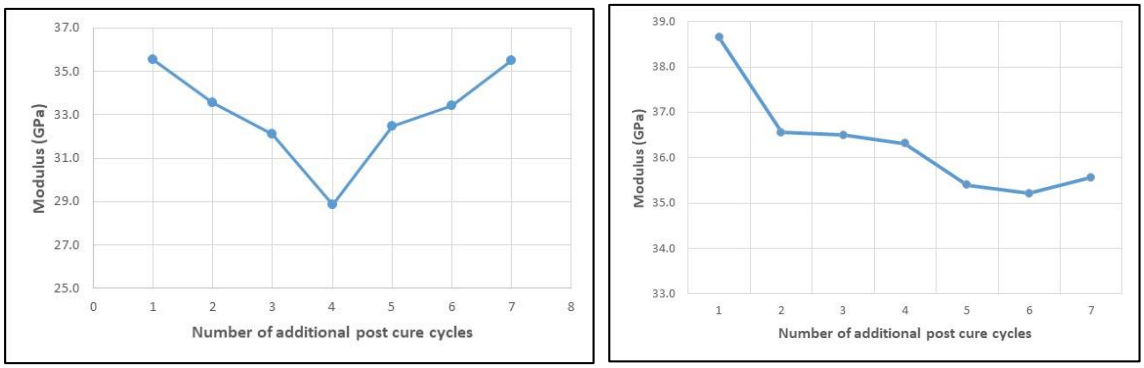


a) b)

Figure 15: Compressive failure strain vs additional post curing for a) M21 and b) 8552 test specimens

Compared to the CLT analysis reported in Table 2, the moduli of elasticity measured in compression on the M21 and 8552 composite beams do not reach the analytical results. However, the trend of the curves clearly shows that multiple cycles of post curing influence the modulus of elasticity measurements. Indeed, the moduli of elasticity measured on the M21 specimens show a decreasing trend of the curve when the DOC and the crosslinking density increase. The modulus of elasticity decreased by 19 percent at the fourth post cure cycle. At this stage, the hardening process is complete and further post curing tends to increase the modulus of elasticity due to the increased stiffness and hardness of the beam. On the other hand, the moduli of elasticity measured on the 8552 specimens tend to decrease with the increase in the number of post cure cycles. In this case, the DOC and the crosslink density gradually increase as the curing reaction progresses further. As noted, there appears to be some

uncured resin distributed throughout the matrix that weakens the composite part before it becomes stiffer upon full cure.



a) b)

Figure 16: Compressive elastic modulus vs additional post cure cycles for a) M21 specimens and b) 8552 specimens

6. Conclusions

This article experimentally investigates the effects of multiple post cure cycles on the thermal, physical and mechanical properties of panels made from two types of carbon/epoxy prepreg laminates. The results show that multiple post cure cycles affect the thermal properties, which in turn are markedly affected by the type of composite materials. Indeed, the experimental results demonstrated changes in thermal properties with increasing number of post cures. These thermal changes did not remain without consequences on the physical and mechanical properties as proven by the results of the hardness and compression tests. The hardness of composite surfaces continuously increases and presents a significant gap between the tool-side and the bag-side. As a result, the M21 test beams are sensitive to compression due to degradation of the epoxy resin while the gradual curing of the 8552 test beams improves its strengths under compressive loading.
Composite structures are brittle and continued post curing of their surfaces can be detrimental to other properties such as Tg. Although Tg is a combined effect of crosslink density, chain segments motion, and decomposition temperature, the results show that overheating the cured resin does not improve the quality of the panels because it results in poor Tg. These results demonstrated that there are limits in terms of the number of allowable post cures. For manufacturing practices, this study recommends no more than five post cure cycles.

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