EFFECT OF CURE CYCLE ON THE PROPERTIES OF THICK CARBON/EPOXY LAMINATES

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SUMMARY

This paper presents research on the effect of cure cycle on material properties of thick (~20 mm) unidirectional carbon/epoxy laminates. The paper compares the results of a standard cure cycle for thin laminates (~2 mm) with an optimized cure cycle developed for thick laminates to replicate thin–section cure conditions.

Keywords: cure optimisation, thick laminates, exotherm, DSC, incremental slitting, mechanical and physical characterisation

INTRODUCTION

The complexity and physical magnitude of many engineering structures used in transportation (road, sea and air), civil infrastructure (building and bridges), nuclear and chemical plant, and off-shore applications requires versatile materials that can be tailored to meet demanding service conditions [1]. Polymer matrix composites (PMCs) offer the user/designer the flexibility and range of mechanical and physical properties to meet these requirements. These materials have tended to be used for their weight reduction and corrosion resistance qualities. The use of PMCs has primarily involved thin membrane structures, but in recent years their use in large, thick structures (i.e. thickness in excess of 10 mm), often complex in shape, has expanded. The wide range of processing routes, fibre types and formats (two- and three-dimensional architecture), and resin matrices provides the means of producing thick complex engineering structures suitable for use in safety critical applications and hostile environments, such as bridges, wind turbines, commercial aircraft and off-shore drilling platforms.

It has been suggested that variations in material properties (particularly strength) due to laminate thickness can partially be attributed to differences in processing conditions [2]. Thicker laminates require longer curing cycles in order to achieve complete cure. Increasing the rate of cure may reduce the cure cycle time, but at the expense of material performance. Fabrication of thick composite laminates (10 mm or greater) is often difficult, with process-induced (i.e. residual) stresses becoming increasingly important as the thickness is increased. Residual stresses can have a significant effect on the engineering properties of laminated structures by inducing warpage, fibre buckling, matrix micro-cracking and delaminations. These stresses arise from resin chemical shrinkage, as a result of curing, and differences in thermal contraction between adjacent plies on cooling the laminate from the cure temperature. The net effect is that the mechanical loads required to induce failure may be reduced.

Heat generation caused by exothermic chemical reaction of the matrix may also result in material degradation [3]. If dissipation of liberated heat through thermal conduction is slow, then the internal temperature may be elevated to levels that induce irreversible thermal damage. The risk of heat damage through exothermic reaction to the matrix increases with laminate thickness. A second concern relates to the complex temperature and degree of cure gradients that develop in thick-sections during the curing process. These gradients may induce a non-uniform state of cure through the laminate thickness, which can result in poor laminate consolidation, leading to undesirable fibre volume fractions and entrapped volatiles or voids.

This paper details the formulation of an 'optimised' cure cycle for the autoclave manufacture of ~20 mm thick unidirectional (UD) carbon fibre-reinforced (CFRP) laminates. The optimised cure cycle was designed to ensure an equivalent degree of cure to that of a thin laminate cured using the material supplier's standard cure cycle. The paper also details an assessment of the effects on the physical, mechanical and thermal properties of thick laminates when processed (autoclave) using the standard and optimised cure cycles.

EXPERIMENTAL

The material system used in this study was SE84 LV UD carbon fibre-reinforced epoxy and was supplied by Gurit Holdings AG. The nominal cured ply thickness was ~0.3 mm.

Development of Optimised Cure Cycle for Thick Laminates

The autoclave cure cycle for thin (<5 mm thick) SE84 LV laminates, as per the material supplier's recommendation, is shown schematically in Figure 1. The temperature ramp rate is 3 ºC/min and there is a temperature dwell at 75 ºC at a viscosity of 150 poise, at which point pressure is applied. This is followed by a further dwell for 60 minutes at the 120 ºC cure temperature. The vacuum is released at a pressure of 1.7 bar.

Previous work by Gurit [4] investigated curing panels up to 28 mm thick and used lower cure temperatures (up to 85 ºC) and longer cure dwell times (up to 10 hours). In

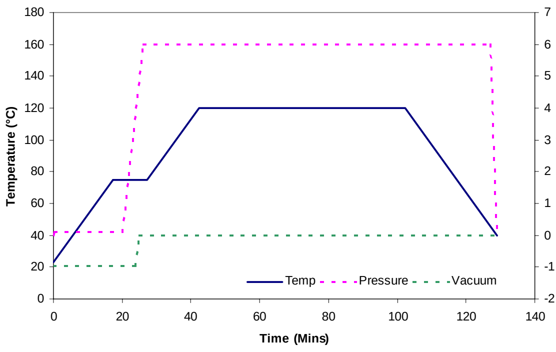


Figure 1 Standard autoclave cure cycle for thin (≤ 5 mm) laminates

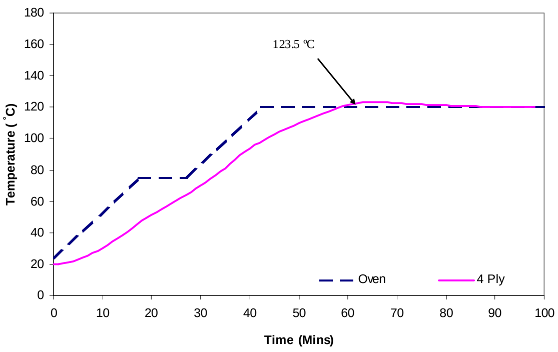


Figure 2 Oven and panel temperature for a standard cure 8 ply laminate

formulating an optimised cure cycle for thick sections, a similar approach was followed in order to quantify the degree of exotherm in thick sections and how potentially damaging levels of exotherm could be minimised to the levels seen during the cure of thin sections.

Initial cure optimisation trials were performed in a Climatic Systems programmable fan oven. All panels were rectangular in shape (203 mm x 152 mm) and were vacuum bag cured. No pressure was applied during cure. Initially, a thin 8 ply laminate was layed-up and vacuum bag consolidated for 10 minutes prior to cure. A ‘K’ type thermocouple was centrally positioned in the panel at mid-thickness and a multi-channel Picolog was used to record the panel temperature every minute. Figure 2 shows the oven and panel temperature throughout the cure cycle. It can be seen that a peak temperature of 123.5 ºC was recorded approximately 20 minutes after the oven had achieved the cure temperature of 120 ºC. Thus the exotherm that occurred within the panel was seen to cause a 3.5 ºC temperature overshoot.

Following the thin laminate trial, a 64 ply, ~20 mm thick panel was layed-up. In order to obtain equivalent consolidation as for the thin 8 ply laminate, the thick laminate was prepared by laying-up 4 plies and then vacuum bag consolidating for 10 minutes, followed by adding a further 4 plies and again consolidating for 10 minutes. This process was followed until 64 plies had been layed-up to form the complete panel. In order to obtain as much information as possible with regard to the temperature distribution and gradients throughout the panel during cure, seven ’K’ type thermocouples were incorporated at various positions and depths (Figure 3). The 64 ply laminate was then cured using the standard, thin laminate cure cycle in order to investigate the degree of exotherm within the panel.

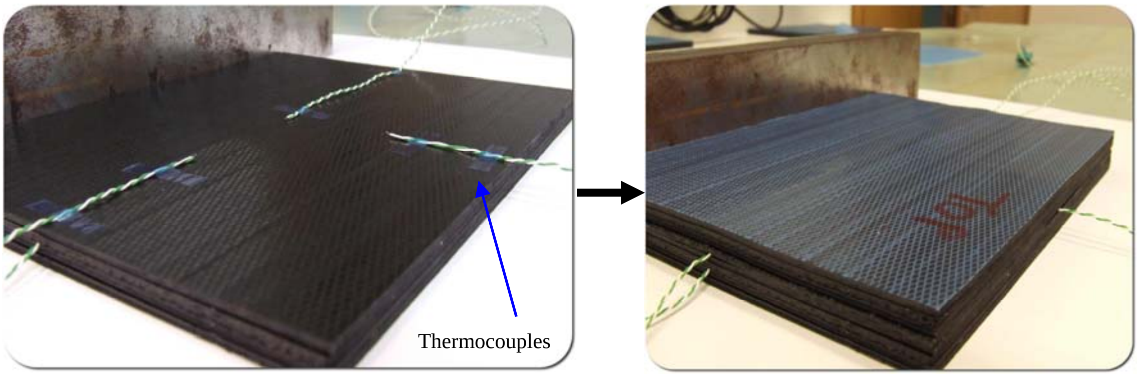
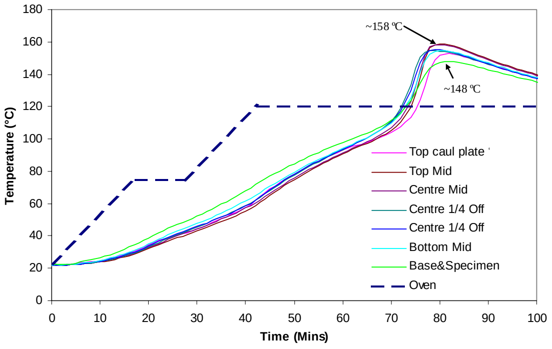


Figure 3 Thermocouple inclusion and placement in a 64 ply laminate

Figure 4 shows the oven and panel temperatures recorded throughout the cure cycle. It can be seen that there is a substantial increase in temperature (maximum ~158 ºC) above the recommended cure temperature of 120 ºC in the laminate due to a large degree of exotherm. It was observed that the temperature difference between the top and bottom caul plate positions in the panel was ~10 ºC and the mid-thickness panel temperature was 154.5 ºC. A comparison of the ‘thin’ and ‘thick’ panel mid-thickness maximum temperatures is shown in Figure 5.



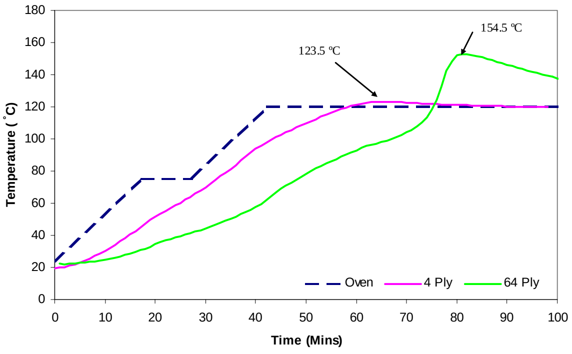
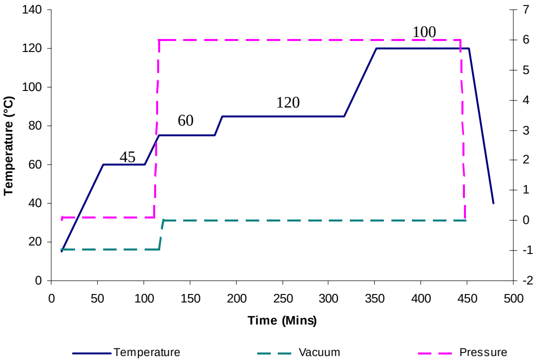


Figure 4 Oven and panel temperature distribution for a 64 ply laminate cured using the standard cure cycle

Figure 5 Mid-thickness temperature for 8 and 64 ply thick panels (standard cure)

Using the standard 'thin' cure cycle to cure a 64 ply thick panel resulted in a temperature overshoot which was deemed to be unacceptable due to the risk of thermal damage to the material. Therefore, the standard cure cycle was modified by undertaking a further series of cure cycle trials where the number of temperature ramps and dwell periods were altered to minimise the degree of exotherm. The general approach was to employ additional temperature steps, at a slower ramp rate of 1 ºC/min, in conjunction with longer dwell periods in order to stagger the exothermic reaction associated with cure so that the maximum panel temperature was similar to that seen for the 8 ply thick panel. The optimised cure cycle formulated for thick panels, after a number of experimental iterations is shown in Figure 6. It is noted that the total cycle time has increased by a factor of ~4 compared to the standard cycle.



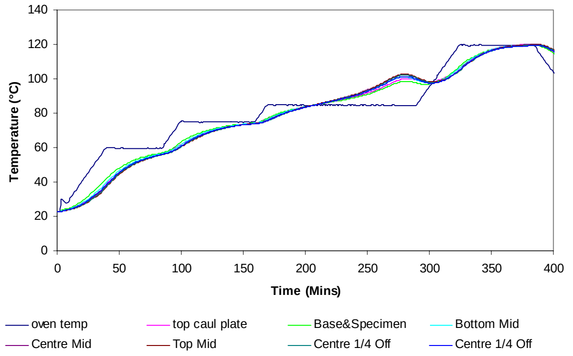
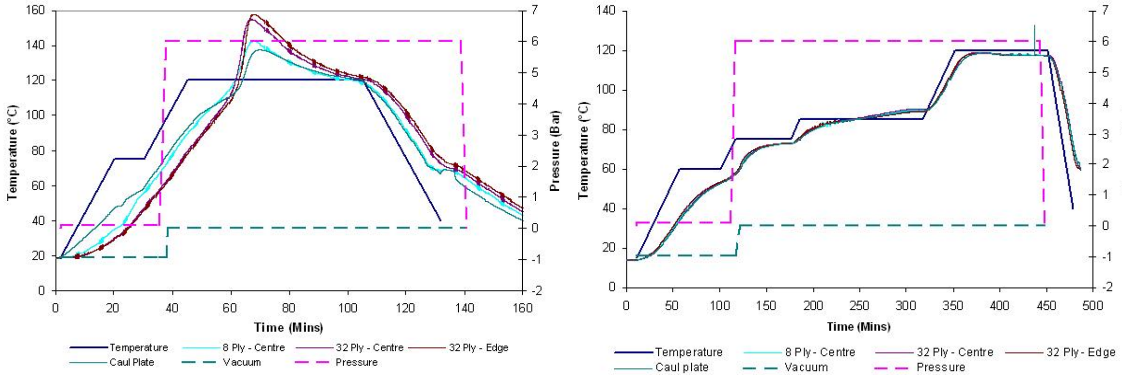


Figure 6 Standard (thin) and optimised (thick) cure cycles

Figure 7 Oven and panel temperature distribution for a 64 ply laminate cured using the optimised cure cycle

The optimised cure cycle is split into 4 stages. The 1st and 2nd dwells allow the panel to reach the oven temperature, the 3rd dwell reduces the rate of cure limiting the exotherm and the 4th dwell is at the required final cure temperature. Figure 7 shows the recorded temperatures (oven and thermocouples) for a 64 ply laminate cured using the optimised cure cycle. It was observed that the maximum panel temperature no longer shows the large increase observed when using the standard cure cycle and is close to the recommended cure temperature of 120 ºC. Also, much less variation in temperature was observed throughout the panel thickness.



(a) **(b)**

Figure 8 Autoclave and panel temperature distributions for a 64 ply laminate cured using (a) standard and (b) optimised cure cycles

Following optimisation of the cure cycle for thick laminates via a series of oven trials, thick panels were produced in the NPL autoclave facility. The panels (64 ply) were made using the standard and optimised cure cycles so that the effects of exotherm on the laminate's physical, mechanical and thermal properties could be determined. For both the standard and optimised autoclave cure processes, thermocouples were used to monitor the panel temperature during cure. The temperature profiles are shown in Figure 8. A large degree of exotherm and variation of temperature throughout the panel thickness was seen for the standard cure. For the optimised cure, the temperature distribution throughout the panel was uniform and there was no excessive exotherm.

Assessment of Physical, Mechanical and Thermal Properties

To assess the effects of the standard and optimised cure cycles on the properties of cured laminates, several physical, mechanical and thermal tests were undertaken. The tests undertaken and their rationale are detailed in Table 1.

The specimens for these tests (with the exception of the residual strain measurements) were milled to size from the ~20 mm thick cured panels. Where appropriate and possible, specimens were extracted from top, middle and bottom through-thickness panel locations to ascertain whether there were any property variations through the panel thickness (Figure 9). Care was taken to ensure that the specimen mid-thickness plane coincided with the mid-thickness plane of the top, middle or bottom sections of the panel. Due to the panel sizes made in these cure trials and the presence of embedded thermocouples within the panels, for some of the tests it was possible to obtain specimens from both oven and autoclave manufactured panels, but for other tests it was only possible to obtain specimens from the autoclave panels. It is noted here that the results of most importance and significance were those obtained for the autoclave panels; hence subsequent work towards the development of thick section test methods was based on autoclave manufactured material. Oven cured material data were produced for comparison to the autoclave data and to assess how sensitive the SE84LV material system was to processing route.

Optical microscopy in conjunction with image analysis was used for the void volume fraction measurements. For comparison to the acid digestion measurements, V_f was

Table 1 Selection of physical, mechanical and thermal tests

Property	Method/Standard	Reason
Fibre and void volume fractions, V_f and V_v	ASTM D 3171 (Procedure A - acid digestion) [5] - image analysis	Physical characterisation of laminate microstructure
Through-thickness shear strength, τ_{13}	NPL Draft V.01 method [6]	Sensitivity to matrix properties i.e. degree of cure
In-plane compression properties, E_{11c}, σ_{11c}	ISO 14126 [7]	Sensitivity to matrix and fibre/matrix interfacial properties
In-plane shear properties, G_{12}, τ_{12}	ASTM D 5379 [8]	Sensitivity to matrix properties
Glass transition temperature, T_g	ISO 11357 Part 2 [9]	Degree of matrix cure
Residual strain, ε_{xx}, ε_{yy}	Incremental slotting [10]	Indication of presence of residual strains and stresses within cured panels

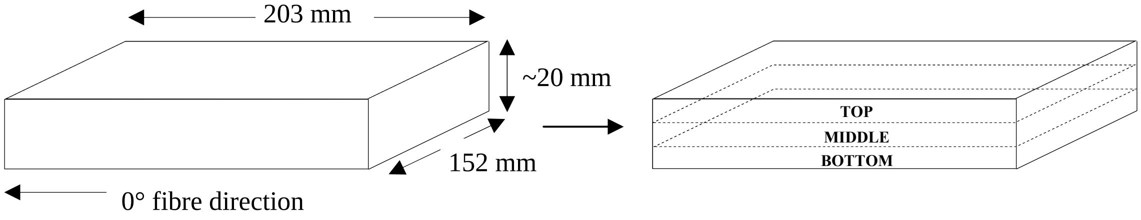


Figure 9 Specimen extraction from ~20 mm thick oven and autoclave, standard and optimised cure panels

also measured using optical microscopy and image analysis. For V_f and V_v by optical microscopy a series of 20 images per laminate section were analysed using a Nikon MM-60 measuring microscope and x10 objective. Image-Pro Plus image analysis software was used to analyse the images.

For the in-plane shear properties, measured according to ASTM D 5379 [8] only a limited number of specimens were extracted and tested for the standard and optimised, autoclaved cure panels.

For the glass transition temperature (T_g) measurements, specimens were heated at 20° C/minute to 190°C followed by a repeat scan on the same sample. All DSC results were normalised with respect to sample weight. In addition, DSC tests were undertaken on a sample of previously manufactured 2 mm thick material, cured in the autoclave using the material supplier’s recommended standard cure cycle. This was carried out to compare the degree of cure in previously manufactured (autoclave) thin laminates to that seen in the two thick laminates via the standard and optimised cure processes.

A compliance technique [10] was used to evaluate the degree of residual strain in cured panels. The method is based on the principle that if a slot is incrementally machined into a thick section then any residual stresses will be progressively released in the material along the plane of the slot. Release of residual stresses will result in deformation of the material. By bonding a strain gauge onto the back face of the specimen this deformation can be measured and can provide an indication of the degree and polarity of the residual strains within the material. For both standard and optimised, autoclave cured panels, incremental slotting tests were performed on two specimens (60 mm x 20 mm x 20 mm); one specimen was slotted transverse to the fibre direction and the other slotted parallel to the fibre direction. A 5 mm gauge-length strain gauge was bonded to the back face of the specimen coincident with the specimen longitudinal axis perpendicular to the slot direction. Specimens were clamped along their length and slotted using a 2 mm diameter 3 Flute slot-drill. Each slot increment was 0.25 mm in depth. After each slot increment had been machined the specimen was unclamped and left to relax for 10 minutes before a strain gauge reading was recorded. The specimen was then re-clamped in identical fashion, before the next increment was machined. This process was repeated until a slot depth of ~12 mm (maximum possible with slot-drill used) had been machined.

RESULTS

The V_f and V_v results (Table 2) for the standard and optimised oven cured laminates were in good agreement and were ~3% higher than for the autoclaved panel which were also in good agreement. It was expected that the V_f results for the autoclave panels would be higher than the oven cured panels as pressure was applied during cure. A possible reason for the oven V_f results being higher than those for the autoclave panels may be due to differences in pre-preg roll fibre volume fractions. The V_v results for the oven cured laminates were 1.2-1.6% higher than for the autoclaved panels which is as expected as the oven cured panels were not cured under pressure. For both standard and optimised cure cycle panels it was observed that there were no variations in V_f and V_v with regard to panel thickness location.

The double-notch shear strength results are shown in Table 3. In general there were no significant differences in mean values observed between the two cure cycles and

Table 2 Fibre and void volume fraction results

Position	V_f by Acid Digestion [5] (%)				V_f and V_v by Image Analysis (%)			
	Standard Cure		Optimised Cure		Standard Cure		Optimised Cure	
	Oven	Auto	Oven	Auto	Oven	Auto	Oven	Auto
Top	58.2 (0.5%)	55.0 (0.7%)	59.2 (0.4%)	54.3 (0.9%)	V_f =57.4 (3.0%) V_v = 2.3 (26%)	V_f =55.6 (4.5%) V_v = 0.7 (43%)	V_f =53.4 (2.8%) V_v = 2.7 (22%)	V_f =55.3 (3.8%) V_v = 1.5 (27%)
Middle	57.4 (0.5%)	55.1 (0.5%)	57.7 (0.5%)	54.4 (0.8%)				
Bottom	57.1 (1.1%)	54.3 (1.5%)	57.2 (1.4%)	54.6 (0%)				
Mean (CoV)	57.6 (1.1%)	54.8 (1.1%)	58.0 (1.8%)	54.4 (0.7%)				

Vf = fibre volume fraction, Vv = void volume fraction
Auto - autoclave processing
CoV—coefficient of variation

process methods. No significant trends were observed in the strength values measured from specimens cut from different locations through the panel thickness.

Table 3 Double-notch shear results [6]

Position	Shear Strength, τ_{13}, MPa			
	Standard Cure		Optimised Cure	
	Oven	Auto	Oven	Auto
Top	59.7 (9.1 %)	61.6 (3.9 %)	56.0 (4.9%)	56.4 (4.8 %)
Middle	58.1 (4.1 %)	56.6 (6.7 %)	51.2 (8.3%)	56.2 (9.6 %)
Bottom	59.2 (1.7 %)	-	52.6 (1.8%)	
Mean (CoV)	58.9 (5.5 %)	59.1 (6.8 %)	53.3 (6.5 %)	56.3 (7.0 %)

The compression results are detailed in Table 4. The modulus results for the standard and optimised cure cycles are all of similar magnitude and show no significant trends with regard to position through the thickness of the panel. The strength results were in good agreement, although for the oven, optimised cure specimens the strength results were slightly higher than for the other panels. This was a somewhat surprising result as the void volume fraction, V_v for this panel was the highest value measured of all the panels at 2.7%. Strength values were also normalised with respect to the V_f of the optimised, autoclave panel, however, the strength results for the optimised, oven panel were still the highest. It is noted that the coefficient of variation for this panel was twice that of the optimised, autoclaved panel.

Table 4 Compression results [7]

Position	Standard Cure				Optimised Cure			
	Oven		Auto		Oven		Auto	
	E_{11c} (GPa)	S_{11C} (MPa)	E_{11c} (GPa)	S_{11C} (MPa)	E_{11c} (GPa)	S_{11C} (MPa)	E_{11c} (GPa)	S_{11C} (MPa)
Top	109.6 (2.2%)	1053 (7.1%)	1009 (25%)	1009 (25%)	110.5 (1.7%)	1295 (8.2%)	-	1086 (0.8%)
Middle	112.6 (1.3%)	1038 (3.5%)	1120 (8.4%)	113.3 (0.6%)	114.6 (1.3 %)	1218 (4.7%)	110.7 (1.7%)	1013 (0.3%)
Bottom	109.6 (1.8%)	906 (15.9%)	-	112.2 (0.5%)	116.1 (1.6 %)	1314 (8.4%)	-	-
Mean (CoV)	110.6 (2.1%)	999 (11.2%)	1064 (17%)	112.8 (0.7%)	113.7 (2.6%)	1276 (7.7%)	111.9 (2.1%)	1050 (3.8%)

The in-plane shear strength and modulus results for the autoclave panels are detailed in Table 5. No significant differences between the standard and optimised panel results for either in-plane modulus or strength were observed.

From the DSC tests, the standard cure panel showed that little or no additional cure occurred at temperatures in excess of the final cure temperature (Figure 10(a)) indicating that the panel was almost fully cured. However this degree of cure was only obtained at the expense of potentially damaging effects of significant exotherm,

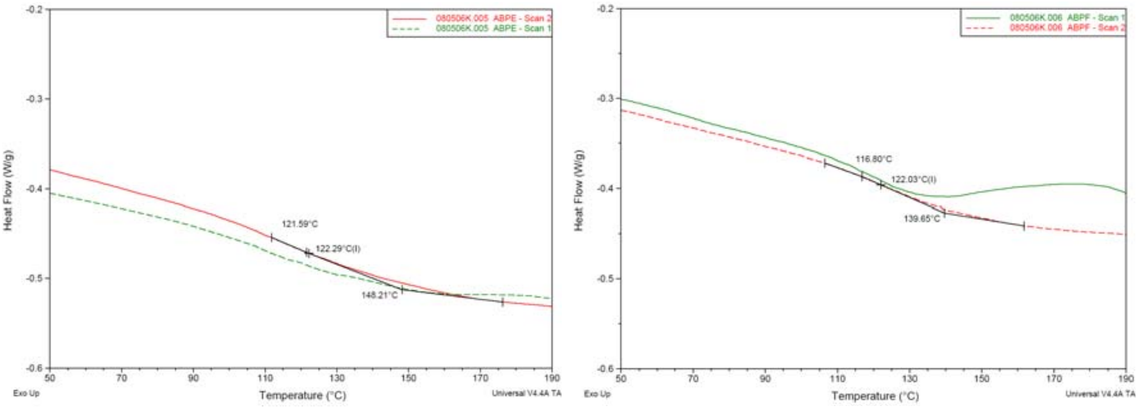
Table 5 In-plane shear results (autoclave only) [8]

Position	Standard Cure		Optimised Cure	
	G_{12} (GPa)	τ_{12} (MPa)	G_{12} (GPa)	τ_{12} (MPa)
Mean (CoV)	4.68 (1.2%)	101.5 (2.7%)	4.76 (1.5%)	96.7 (1.6%)

temperature variation throughout the panel thickness and over-shoot in temperature above 120°C. For the optimised cure cycle panel, a degree of additional cure was observed (Figure 10(b)) indicating that full cure had not been achieved. However, the optimised cure cycle has the advantages that the panel temperature does not exceed the recommended cure temperature and there were minimal differences between thermocouple readings throughout the panel thickness. The glass transition temperature, T_g values from the repeat scans for the standard and optimised cure cycles were in close agreement at 122.29°C and 122.03°C, respectively.

From Figure 11 it can be seen that the degree of cure in a 2 mm thick panel is similar to that seen in the optimised cure, thick panel. Therefore, although the material may not be fully cured using the optimised cure cycle, the similarity in degree of cure allows valid comparison of ‘thick’ and ‘thin’ laminate mechanical properties i.e. any differences in mechanical properties will be as a result of either scaling effects, specimen geometry and/or mechanical test design rather than as a result of cure effects. Although the DSC results indicate differences in cure between the standard and optimised cure cycles, there is little evidence to suggest that this affects the mechanical performance of the material.

Figure 12 shows the results of the incremental slotting tests for measurement of residual strain. The first observation to be made is that the residual strains in the transverse slot direction i.e. across the fibres, were much lower than for the parallel direction. This is as expected as residual strains/stresses are predominantly present in the resin, hence cutting parallel to the fibres will result in a larger degree of residual strain/stress being released than if cut across the fibres. The second observation is that



(a) (b)

Figure 10 DSC results for (a) standard cure, autoclaved material and (b) optimised cure, autoclaved material

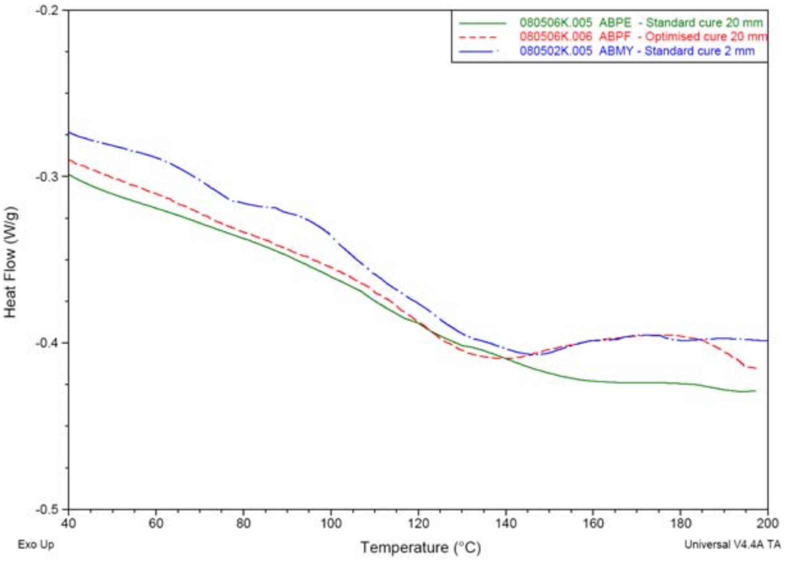


Figure 11 Comparison of DSC results for standard cure thick (20 mm) and thin (2 mm) panels, and optimised cure thick (20 mm) panel.

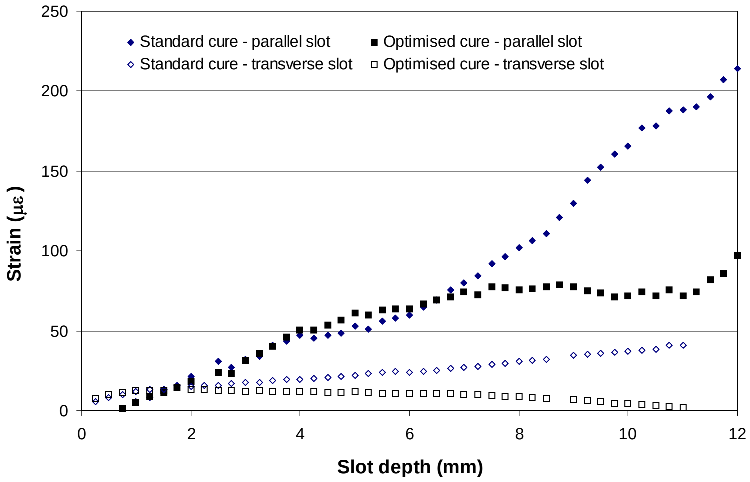


Figure 12 Transverse and parallel (to fibres) incremental slotting results for measurement of residual strain

a larger degree of residual strain release was seen in the standard cure panel than for the optimised cured panel. The compliance method [10] provides a method by which the residual stresses can be derived from the measured strains, however this has not been undertaken here due to the complexity of the analysis and the time available within the project.

CONCLUSIONS

The optimised cure cycle resulted in no temperature overshoot and little or no intra-panel temperature variation. No significant differences were observed in the physical and mechanical properties between the standard and optimised cure cycle panels. This was reasoned to be due to the ‘forgiving’ nature of the material system used and it’s lack of susceptibility to cure temperatures in excess of 30 °C above the recommended cure temperature. DSC results showed that little additional cure occurred in the standard cure panel, but a degree of additional cure was observed in the optimised cure laminate. Although the optimised cure panel was not completely cured, the cure cycle has the advantages that large degrees of exotherm and panel temperature variations are avoided. The degree of cure in a sample of 2 mm thick material cured using the standard cure cycle is similar to that observed for the optimised cure thick panel. This equivalence in degree of cure should allow valid comparisons of 'thick' and 'thin' laminate mechanical properties to be undertaken in future work. Residual strain measurements showed that the degree of residual strain (and therefore stress) in the standard cure panel was higher than for the optimised cure panel. This may be due to the optimised cure panel not being fully cured, but is more likely to be as a result of the larger difference between peak cure and room temperature (ΔT) seen by the standard cure panel as a result of excessive exotherm.

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