A RAPID HEATING PROCESS FOR OUT-OF-AUTOCLAVE CURING OF TOUGHENED EPOXY PREPREGS

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ABSTRACT

Toughened epoxy prepregs are utilized in advanced composite structures on military aircraft. The conventional processing route employs autoclave curing under a pressure of 7 bars (100 psi) and long cycle times to achieve final properties. An out-of-autoclave advanced composite curing technology has been employed that uses a heat transfer fluid (HTF) to apply heat and modest pressure to the uncured epoxy prepreg during processing. The HTF enables precise control of the process temperature throughout the curing process. As this technology is based on rapid heat transfer and the ability to accurately control mold temperature, it offers potential savings on process time, energy, investment, and overall component manufacturing costs. Additionally, a differential vacuum technique has been applied to the laminates during the cure cycle that yields void-free laminates. This paper reviews the progression of the process development and the resulting panel and component qualities. Data showing process parameters, laminate properties, and cured components are presented.

1. INTRODUCTION

For many years, autoclave curing of pre-impregnated (prepreg) materials has been the standard process by which high performance aerospace composite components have been produced. As advanced composites replace metals to a higher degree on new aircraft, there has been, in recent years, an increased emphasis to explore "out-of-autoclave" methods of composite fabrication. This is driven by the high capital costs of autoclaves and their installation, high energy costs, and long processing times.

Out-of-autoclave options include specially developed prepregs that require only vacuum bag processing, as well as resin infusion of dry fiber preforms. The drawback to these methods is the requirement to qualify new materials and develop a new database of design allowables, at considerable expense. An alternate process that is able to utilize existing autoclave-qualified prepregs would reduce greatly any recertification costs, provided it could produce components with quality similar to those manufactured in an autoclave.

Toughened epoxy prepreg systems, such as CYCOM®977-3 from Cytec Engineered Materials, are used in composite structural aircraft components. Typically, these material systems and components require autoclave processing to achieve high quality consolidation and develop the advantageous properties of the resin systems. Industry and Government customers are interested in alternative out-of-autoclave processes to reduce manufacturing costs. Not only could this reduce the need for capital-intensive autoclave equipment and lessen tooling costs, it could also result in faster cure cycles and lower processing costs.

The Quickstep (QS) process, invented in Australia, has demonstrated the ability to produce aerospace-quality advanced composites using autoclave-qualified prepregs, vacuum-only prepregs, and resin infusion techniques. In late 2006, a Quickstep QS20 machine and associated tooling was installed in Dayton, Ohio, to introduce the process in North America. Since then, demonstration and development projects with a number of U.S.-based aerospace and defense companies have been completed. In 2010, Quickstep and Vector Composites, under a funded research project, employed the process to demonstrate the ability to cure CYCOM 977-3 uni directional epoxy prepregs to aerospace standards, the results of which are presented herein.

1.1 The Quickstep Process Overview

The Quickstep process utilizes a fluid-heated, balanced-pressure, floating mold for the curing, partial curing, and joining of composite materials. The process works by rapidly applying heat to an uncured laminate stack that is molded to a rigid (or semi-rigid) tool floating in a Heat Transfer Fluid (HTF). The mold and laminate stack are separated from the circulating HTF by a flexible membrane. The temperature and pressure of the HTF behind the mold and flexible membrane stay the same. The process uses vacuum, combined with optional vibration, to evacuate air and volatiles from the laminate as well as to compact, heat, and cure the part. The laminate may be thermoset, low temperature thermoplastic prepreg, or a wet resin/dry fiber combination. In most cases, following optimization of certain processing parameters, specifically bagging schemes, intermediate and final dwell temperatures, and curing times, the Quickstep process has been able to achieve laminates with aerospace-level void contents and degree of cure (1-3).

The laminate stack is assembled on a single-sided tool using conventional lay-up, sealed in a vacuum bag, then installed in a low-pressure chamber containing a glycol-based HTF. The tool and laminate are supported between two flexible membranes in the pressure chamber (see Figure 1).

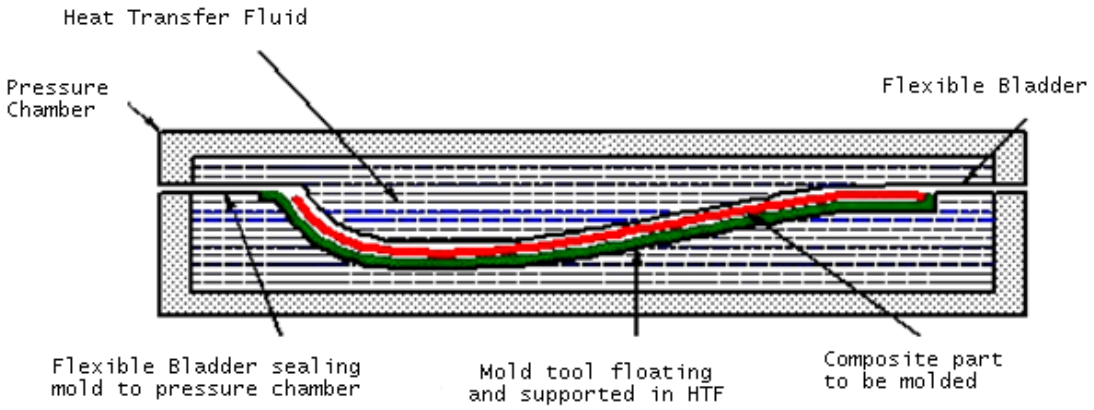


Figure 1. Schematic of the Quickstep Process

Temperature control is maintained by circulating the HTF through the pressure chamber. As fluids have a heat energy per unit volume capacity much greater than that of gas, the heat transfer rate between the HTF and laminate is much higher than that achievable in an oven or autoclave.

This allows rapid heating/cooling rates to be achieved and provides precise control of the resin viscosity, especially during the early consolidation phase of the cure.

The high heat transfer rate allows a lower minimum viscosity to be obtained in the laminate than that observed with a slower autoclave heat-up rate (see Figure 2). This is made possible by the laminate reaching consolidation dwell temperatures with reduced chemical cross-linking having occurred within the matrix. By achieving lower viscosities in the laminate, excellent consolidation is obtainable at low applied pressures, typically vacuum, plus 10 to 30 kPa (1.5 to 4 psi) externally from the fluid. The HTF also acts as a large thermal sink, removing any excess heat generated in a high-rate exothermic reaction, thus a constant cure temperature may be more easily maintained, even for thick laminates (3).

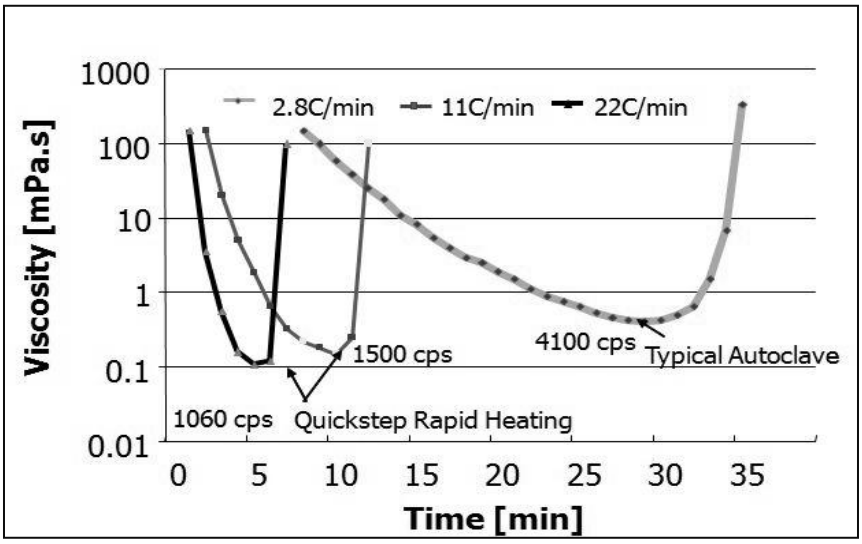


Figure 2. Lower Minimum Viscosity Attained with the QS Process

The HTF is stored in three separate tanks, a hot tank, medium tank, and cold tank (see Figure 3a). Heat energy can be efficiently accumulated over many hours, stored in the tanks, and used repeatedly for many cure cycles, unlike the consumables (e.g., pressurized nitrogen) in autoclave curing. The pumping and recycling of the HTF to the curing chambers can take place over minutes, thus allowing for rapid heat-up and cool-down of the part. With the high level of available heat-energy the cross-linking takes place rapidly and in a fraction of the time achievable within an autoclave.

(a)

(b)

Figure 3. Quickstep QS20 Machine (a) and Curing Chamber (b)

Due to the rapid heating and cooling characteristics and faster cure times, cycle times for the QS process are notably shorter for current generation prepreg materials. Savings of over 50 percent have been realized for several commonly used 175 °C curing aerospace prepregs.

In addition to improved, rapid, uniform temperature control, significant savings are available to industry from reduced scrap rates for interrupted cure cycles, reduced rate tooling requirements, and increased flexibility in part manufacture. Since a part may be cured when lay-up is completed, the mold can be returned to the lay-up area sooner than is typical of batch processing, and lean manufacturing principles, such as "flow processing" can be implemented. This is especially true for part families of similar shape such as spars, fairings and covers, which would be able to share the same pressure chamber. One study completed by a U.K. manufacturer of blocker doors for commercial jet engines estimated a tooling cost savings of approximately 82 %, due to a combination of reduced tool sets and lower costs of a QS tool compared to an autoclave or oven tool (1).

As a result of such rapid curing, the properties of the final laminate can be slightly different from those produced in traditional processes, and higher glass transition temperatures and material properties have been demonstrated for some materials. In the same UK study (1), test panels of woven Hexcel 914 carbon fiber epoxy demonstrated a glass transition temperature 8 ºC higher than the autoclave-cured material from the same batch, and mechanical properties equal or better to the autoclave process (in some cases as high as 10 %). In a separate study with the same resin, using a unidirectional tape material, the glass transition temperature increased by 30 ºC using QS processing versus autoclave. While this would typically indicate a higher degree of crosslinking, and therefore, resin embrittlement, testing of the G_{IC} fracture toughness by the double cantilever beam (DCB) method yielded significantly higher values for the QS-processed material, indicating possible improved matrix-fiber adhesion or more uniform morphology of the matrix resin (4).

2. EXPERIMENTATION

2.1 Cure Cycle Development

The first step in the development of cure cycle for the CYCOM 977-3 epoxy prepreg system was to identify a bagging scheme that would produce a low-bleed system, along with modifications to the cycle using the process variables available in the Quickstep process. These variables include intermediate hold temperatures, time at temperature, fluid pressure, vacuum pressure, spike temperature, and to some extent ramp rate.

Early trials were focused on how to breathe the part but not bleed the part too much. Because the process does not have the ability to compress entrapped air the way an autoclave does, it is essential to remove all air and volatiles from the laminate before gelation of the resin. During the cure cycle development there were 12 major changes made to the bagging scheme before a scheme was found that worked repeatedly. There were a few other schemes that gave low bleed values but were not always repeatable.

The lay up for the test panels in cure cycle development was 16 plies of 457 mm x 330 mm (18 in. x 13 in.) 977-3/IM7 uni directional prepreg. This panel size was chosen as it has enough distance from the breathing strings to provide breathing indication. The 16 plies were chosen due to the mechanical test panels required in the later stages of the project, requiring 12 to 32 plies. It was determined that 16 plies were enough to detect any potential exothermic reactions.

Laminate quality for this effort was based on surface quality, weight loss, cured ply thickness, and internal quality, measured as follows:

- Surface quality was a subjective number on a 1 to 10 scale, taking into account the surface pitting and was directly affected by resin bleed.
- Percentage weight loss was calculated by the weight difference in the panel before and after the cure, also heavily dependent on the amount of resin bleed.
- Cured Ply Thickness was determined by measuring thickness of the cured laminate.
- Internal Quality was a subjective letter grade from A – F, determined by cutting the panel in half and looking at the cross section of the laminate under a 20x/40x microscope.

Based on rheology data provided by the material supplier, minimum viscosity is indicated at or around 130 °C, and initial trials were devised to bring the resin to minimum viscosity, hold for a period of time to allow trapped gasses to be removed, and then ramp to final cure temperature. The first 13 trials were in the range of 130 °C (+20/-10 °C) for intermediate hold temperature. Since the goal of these trials was to obtain a void-free laminate, it was determined that a hold for 6 hours at 190 °C was unnecessary, and a hold for 2 hours was enough to get a good indication if the first part of the cycle was adequate. As a result, the first cure cycle of 130 °C for 20 min, 190 °C for 120 minutes was established. All iterations were based on this starting point.

During the trials, it was a determined that the differential vacuum technique would be employed involving the use of dual vacuum sources and differing levels of vacuum during the gas removal and curing phases of the process. This technique resulted in panels that were judged superior in

finish and void level, meeting the highest level of each of the criteria defined earlier, demonstrated by the panel in Figure 4.

Figure 4. Representative epoxy panel cured using optimized cure cycle and bagging scheme

2.2 Fabrication of Test Panels

The test panel fabrication was based off cure cycle and bagging developed in the cure cycle optimization. The test panels were produced using CYCOM 977-3/IM-7 uni directional prepreg per the customer's specifications. Table 1 depicts the lay-up and bagging schemes used for these panels. Table 2 details the specific cure cycle parameters used, a direct result of the successful process development trials earlier in the program. All physical and mechanical test panels were processed individually in separate cure cycles.

Table 1. Panel Definition / Layup / Bagging

Material	# Plies	Layup	Size (mm)	Bagging
977-3/IM7 Uni CPT = 0.135mm (0.0053 in.)	32	$[(45/0/-45/90)_2(45/90)]_S$	457 x 330	Differential vacuum
	20	$(90/0)_{5S}$		
	12	$(45/-45)_{3S}$		
	8	$(0)_8$		

Table 2. Cure Cycle Details

Dwell 1				**Dwell 2**			
Temp. (°C)	Time (minutes)	Tray Pressure	Vacuum	Temp. (°C)	Time (minutes)	Tray Pressure	Vacuum
137	45	10 kpa (1.5 psi)	Part = Full 2^{nd} < Full	182	180	10 kpa (1.5 psi)	Part = Full 2^{nd} = 0

All seven (7) panels experienced the same cycle identified above in seven (7) separate cures. The thermal profiles are shown in Figure 5, where the effects of using two tools are observed – the

thicker tool heated more slowly and took a little longer to complete the cure cycle. This difference in thermal control was an artifact of the generic curing chamber, whereas it will be seen later that a part-specific tool can provide controlled heating during a cure.

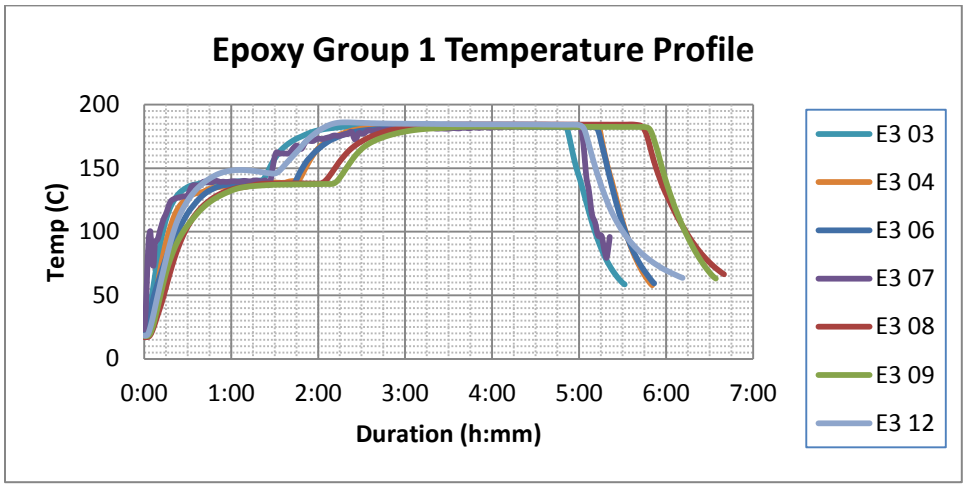


Figure 5. Temperature vs. Elapsed Time for Test Panels

2.3 Test Plan

The laminate buildup (Table 3) and test matrix (Table 4) were developed in coordination with the customer for this project. All of the testing was performed by Integrated Technologies (Intec). The laminate schedule from Table 3 estimated the expected panel thickness using the nominal CPT of 0.13 mm (0.0052 in.) from a reference autoclave process.

Additionally, thickness and weight measurements were taken for all of the duplicate panels produced for the mechanical testing.

Table 3. Ply Schedule and Laminate Definition for Testing

Laminate	% 0	% ±45	% 90	Lay-up	Number of Plies	Target Thickness mm (in)
Basic Quasi-Isotropic	25	50	25	$[(45/0/-45/90)_2(45/90)]_S$	32	4.23 (0.166)
0/90	50	0	50	$(90/0)_{5S}$	20	2.64 (0.104)
+/-45 for In-Plane Shear	0	100	0	$(45/-45)_{3S}$	12	1.58 (0.062)
0 for tensile/compression	100	0	0	$(0)_8$	8	1.06 (0.042)

Table 4. Testing Matrix for Cured Panels

Test	Layup	Thickness (mm)	Method	Specimen (mm x mm)	-65°F dry	RT dry	275°F / wet (water boil)
T_g (DMA, shift storage modulus)			ASTM D7028 @ 1Hz & 5°C/min.				√
Degree of Cure via DSC			ASTM E2160 @ 5°C/min.			√	
0° Tension	0°	1.07	ASTM D3039	12.7x254		5	
0° Compression Modulus	0°	1.07	ASTM D6641	12.7 x 139.7		5	
0°/90° Compression	90°/0°	1.63	ASTM D6641	25.4 x 139.7		5	
+/-45° Unnotched Tension	±45°	1.63	ASTM D3518	25.4 x 254		5	5
0° Interlaminar Shear	QI	4.32	ASTM D2344	6.35 x 24.38	5	5	5
Open Hole Tension	QI	4.32	ASTM D5766	38.1 x 304.8	5	5	
Open Hole Compression	QI	4.32	ASTM D6484	38.1 x 304.8		5	5
						Total:	60

3. RESULTS

Table 5 lists the panels submitted for property evaluations, with summary values for size, weight, number of plies, average Cured Ply Thickness (CPT), and gross panel density.

Table 5. Summary of Attributes of Quickstep Test Panels (3 hr cure)

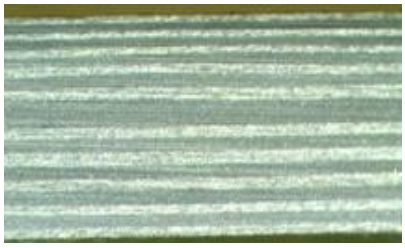
Panel #	Dimensions, mm (in)	Weight, g (lb)	Number of Plies	Average CPT, mm (in)	Density (g/cm^3)
1	457 x 330 (18 x 13)	1019 (2.244)	32	0.135 (0.0053)	1.56
2	457 x 330 (18 x 13)	1018 (2.242)	32	0.135 (0.0053)	1.56

3	457 x 330 (18 x 13)	1015 (2.236)	32	0.135 (0.0053)	1.56
4	457 x 330 (18 x 13)	1014 (2.233)	32	0.135 (0.0053)	1.56
5	457 x 330 (18 x 13)	633 (1.394)	20	0.135 (0.0053)	1.55
6	457 x 330 (18 x 13)	381 (0.839)	12	0.135 (0.0053)	1.56
7	457 x 330 (18 x 13)	253 (0.557)	8	0.137 (0.0054)	1.53

A favorable observation was that the four identical panels (#1, 2, 3, and 4) that were produced via the Quickstep process exhibited nearly identical physical dimensions and weight. This speaks to the repeatability of the process at this stage of development.

3.1 Microscopy and C-scan

Initial microscopy on a couple panels indicated that the panels produced via the Quickstep process were of high quality, as evident in the cross-section shown in Figure 6 at 40X magnification.

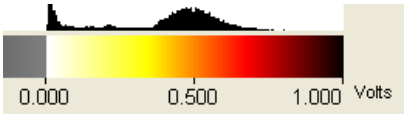


40X Magnification

Figure 6. Representative Image of Cross-Section of 977-3/IM7 Laminates

Nondestructive evaluation (NDE) with c-scan output was performed by the University of Dayton Research Institute (UDRI). The results were categorized as clean, and well within aerospace specifications.

The C-scan for a representative 977-3 cured panel is shown in Figure 7. In interpreting the image colors, the spectrum spans from white (low) to yellow to dark orange to black (high). Low means the reflector plate signal had low amplitude, i.e. sound propagating through the composite was scattered or attenuated. High means the reflector plate signal had large amplitude, i.e. sound propagating through the composite was less scattered or attenuated. As a rule, colors toward the lighter end of the spectrum are preferred.



Color scale bar for NDE c-scan figure

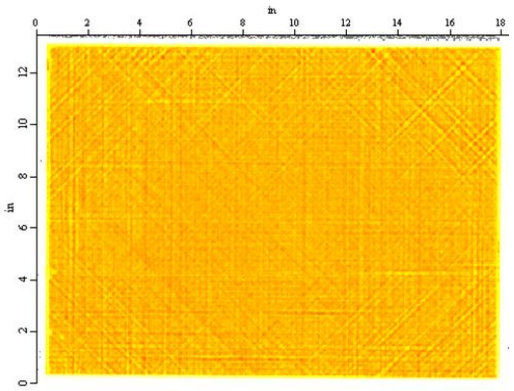


Figure 7. NDE C-Scan of 3 Hour Soak 977-3, QS-Cured 32 Ply Quasi-Isotropic Laminate

3.2 Glass Transition Temperature and Degree of Cure

Table 6 summarizes the results of the DMA measurements (E' and tan δ reported) for glass transition temperature (T_g) and DSC evaluations for degree-of-cure. Samples were tested after the specified cure process of 6-hour hold at 179°C (355°F) with 2.8ºC (5°F)/minute ramp rates for heating and cooling for the autoclave cures. The total autoclave cure cycle, approximated at 8.5 hour from the recommended cure cycle, contains a 6-hour hold at 179°C (355°F) in order to build resin cross-link density to desired levels. The program scope included evaluations that determined that the prescribed 6-hour hold for autoclave processing could be reduced in the Quickstep process to a 3-hour hold without significant compromise on final resin and mechanical properties.

Table 6. Summary of Dry T_g and Degree of Cure

Sample #	Time at 179 ºC (355 °F)	Dry T_g (E') °C (°F)	Dry T_g (tan δ) °C (°F)	Degree of Cure, %
6 hr Autoclave	6	195 (383)	245 (473)	93.6
3 hr Quickstep	3	187 (369)	246 (475)	90.4
Neat Resin (121°C wet T_g)	-	178 (352)	190 (374)	-

The measurements listed in table 6 were representative of the panels that were subsequently tested for mechanical properties. This means that all the panels submitted for mechanical testing were produced using the same cure cycle in which the panels were raised to 127 °C (261 °F), held for 45 minutes, raised to 181 ºC (358 °F), and held at temperature for three hours prior to cooling to room temperature.

3.3 Mechanical Properties

Table 7 lists the results of the mechanical and physical properties for the Quickstep-cured 977-3/IM7 panels.

Table 7. Summary of Screening Test Data for Quickstep-Cured 977-3/IM7 Uni

Test	Conditions	QS 3hr (Average) MPa (ksi)
0° Tensile Strength D3039	RTD	-
Compression Strength D6641	RTD	1186 (172)
OHT D5766	RTD	520 (75.4)
	CTD	530 (76.8)
OHC D484-04	RTD	346 (50.2)
	Hot/wet	278 (40.3)
Compression After Impact (D7136/7)	RTD	168 (24.4)
±45 In-Plane Shear D3518-94	RTD	89.6 (13.0)
	Hot/wet	39.3 (5.7)
SBS D2344	RTD	91.7 (13.3)
	CTD	94.5 (13.7)
	Hot/wet	51.7 (7.5)
T_g via DMA D7028-07, °C(°F)	E'	220 (428)
	E"	260 (500)
	tan δ	265 (509)
Degree of Cure via DSC (ASTM E2160) (%)	5°C/min	92.2%

As a comparison, the above data for Quickstep-cured laminates in Table 8 are compared against autoclave cured laminates in the following graphs, Figure 8-10.

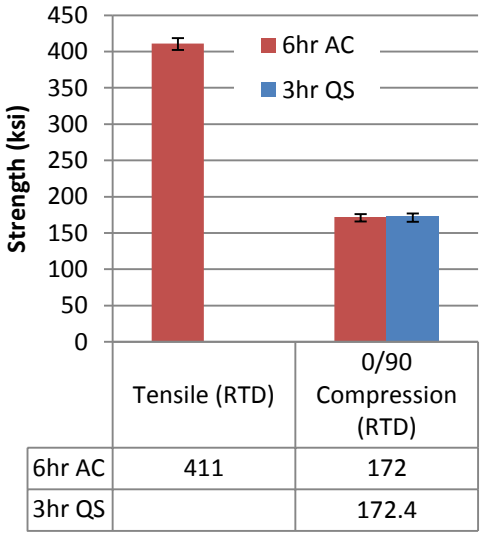
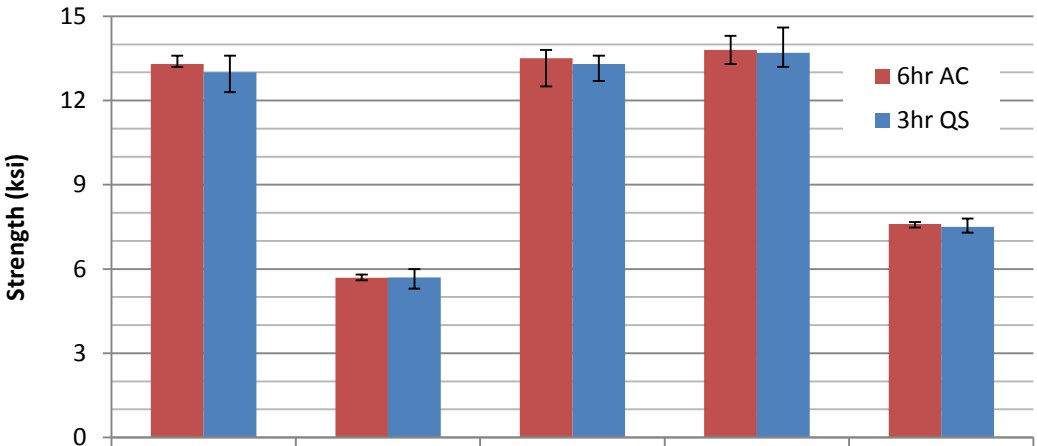
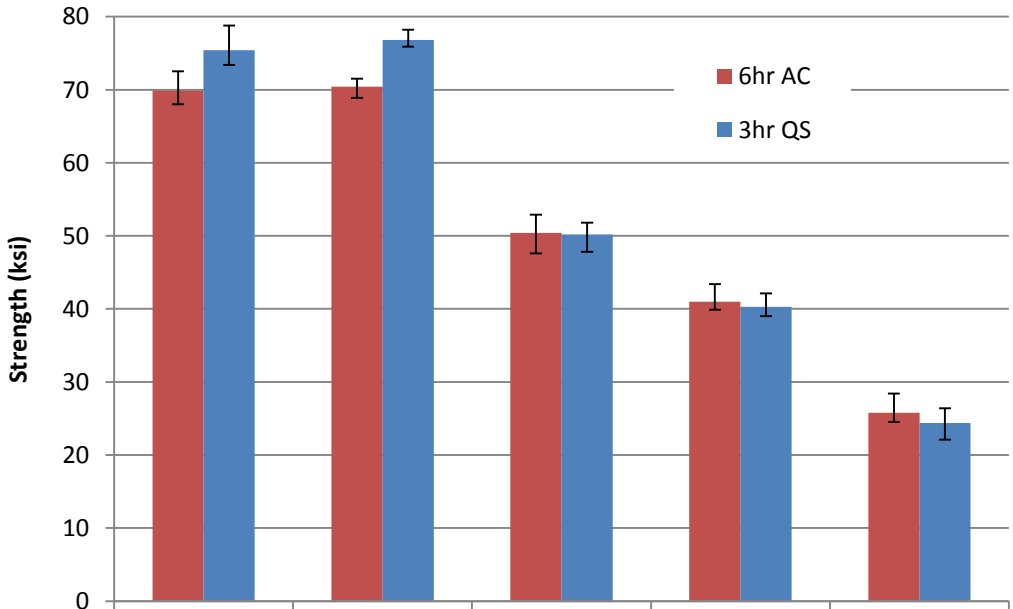


Figure 8. Tensile and Compression Strengths of Standard AC and Optimized QS 977-3/IM7



	±45 In-Plane Shear (RTD)	±45 In-Plane Shear (Hot/wet)	SBS (RTD)	SBS (CTD)	SBS (Hot/wet)
6hr AC	13.3	5.7	13.5	13.8	7.6
3hr QS	13.0	5.7	13.3	13.7	7.5

Figure 9. In-Plane Shear and Short Beam Shear Strengths of Standard AC and Optimized QS 977-3/IM7



	OHT (RTD)	OHT (CTD)	OHC (RTD)	OHC (Hot/wet)	CAI (RTD)
6hr AC	69.9	70.4	50.4	41	25.8
3hr QS	75.4	76.8	50.2	40.3	24.4

Figure 10. Open Hole Tension/Open Hole Compression/CAI Strengths of Standard AC and Optimized QS 977-3/IM7

3.4 C-Spar Fabrication Results

In addition to the test laminates, C-spars were fabricated as demonstration components. Several c-spars were fabricated using a 36 ply schedule at the root end, with approximately 55% of the plies oriented +45°/-45°, 30% oriented 90° and 15% at 0°, with 20 ply drops such that the tip comprises 16 plies, over a length of 1.78 m (70 inches). The debulk schedule used was first ply to the tool, then every 2-3 plies for 2 min/ply.

Figure 11 shows the bagged spar component under bag awaiting cure in the Quickstep chamber. Cure cycle duration for this spar was 4 hours, 11 minutes as shown in Figure 12.

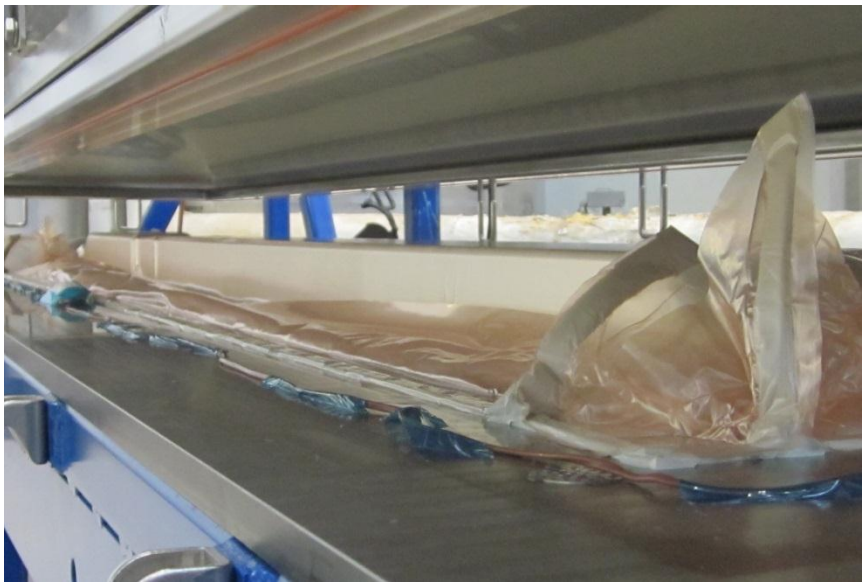


Figure 11. Bagged Spar Ready for Quickstep Cure

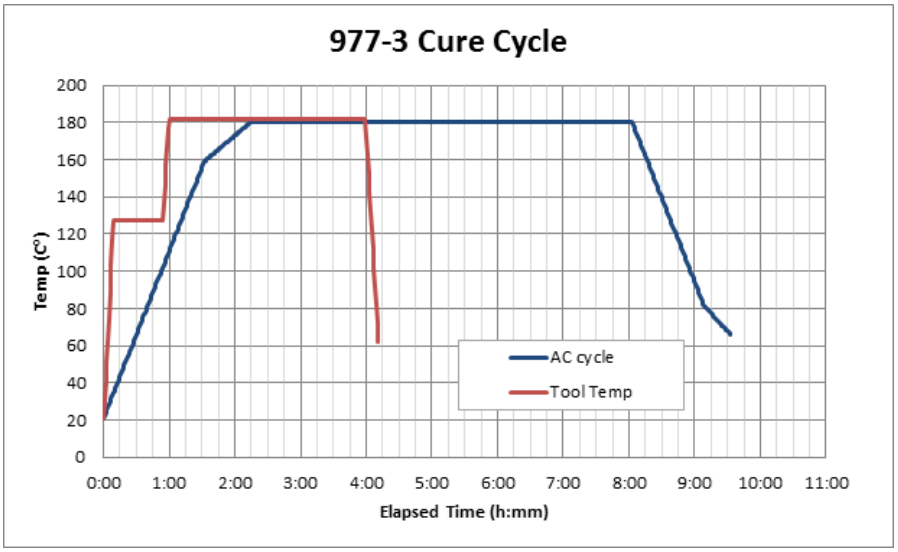


Figure 12. Optimized Quickstep Cure Cycle Comparison to Autoclave Reference

Figure 13 shows the tool side of the cured spar. Average 34 point CPT is 0.135 mm (0.0053 in.) including both flanges, web, and radius, with the CPT in the radius of 0.127 mm (0.0050 in.).

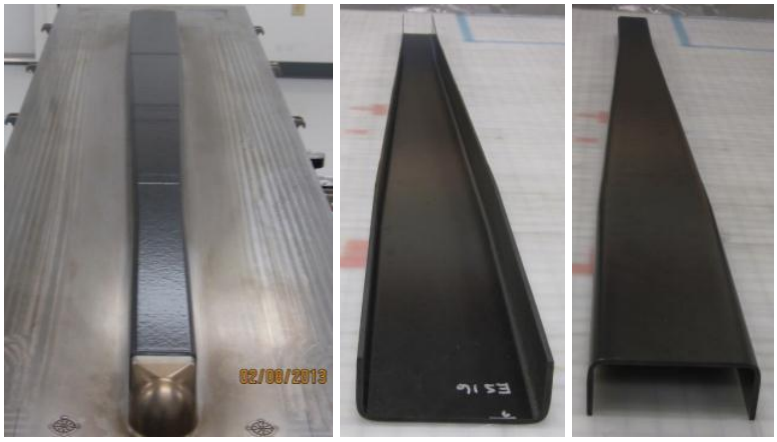


Figure 13. Tapered Spar on Tool After Final Debulk and After Cure

Figure 14 shows key micrographs that document good quality cross-sections in the radius and a ply drop zone.

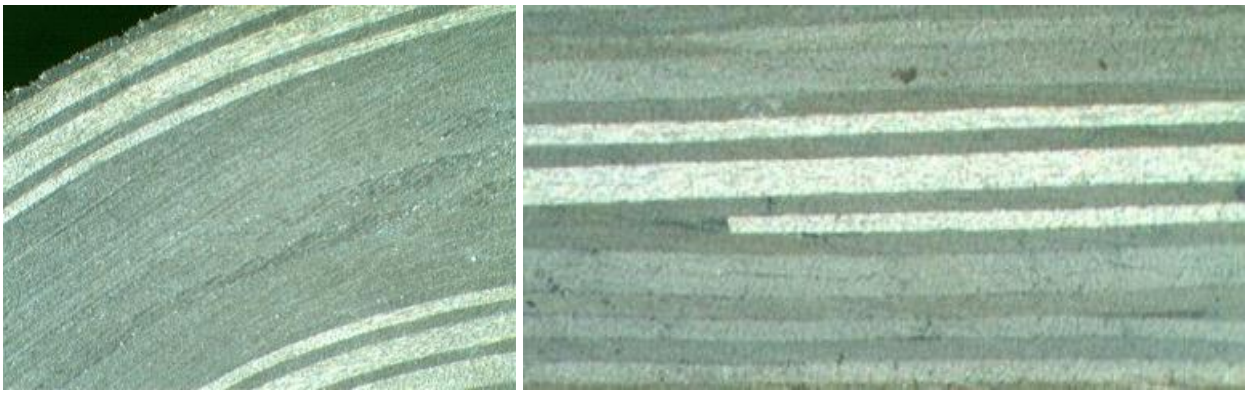


Figure 14. Micrographs of 36 Ply Radius and Tapered Spar Flange at Ply Drop

4. CONCLUSIONS

The overall objectives of this research were: a) to develop a Quickstep cure cycle that would provide high quality laminates from toughened epoxy prepregs; and b) to provide a cycle time reduction for curing of the 977-3/IM7 prepreg, compared to traditional autoclave processing. Both objectives were successfully achieved as the panels exhibited aerospace-level physical qualities, the cycle time was reduced, and cured components were fabricated showing a reduction in the primary curing cycle time to less than 5 hours.

After processing trials to develop the candidate cure cycle for the QS process, the selected final process was subsequently repeated successfully with equivalent output several times, as evident by microscopy and Tg analysis. Mechanical test results compared favorably to equivalent autoclave data. The excellent surface finish, low void content, clean c-scan results, and thermal

test results suggest the mechanical properties are representative of the capabilities of the material. In addition, demonstration c-spars were also fabricated using the same optimized cure developed for the test laminates.

The heating and cooling portions of the cure cycle were reduced from 2.5+ hours estimated for autoclave cure to 1.5 hours in the Quickstep process, a reduction of at least 40 percent. Based on glass transition and degree of cure results, the high temperature dwell was significantly reduced, from six hours down to three hours, resulting in a total cycle time of 4.5 hours, for a total cycle time reduction of approximately 50 percent.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

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