MECHANICAL AND PHYSICAL EVALUATION OF A NEW CARBON FIBRE/ PEEK COMPOSITE SYSTEM FOR SPACE APPLICATIONS

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ABSTRACT

The European Space Agency is currently examining various composite systems for the fabrication of large composite structures like the liquid hydrogen tanks for Re-usable Launch Vehicles (RLVs). In this body of work, the suitability of carbon fibre/ PEEK, a high performance thermoplastic composite, was examined for space applications. A new form of carbon fibre/ PEEK pre-impregnated tape is now industrially available with mechanical properties expected to equal or surpass those of existing suppliers. The main aim of this project was to thermomechanically characterise the new form of carbon fibre/ PEEK for space applications under pressure formed autoclaved conditions, and to compare against properties achieved using the most suitable out of autoclave technology for large space structures. Thermoplastic in-situ automated tape placement (ATP) was chosen as the out of autoclave technique having most potential for the fabrication of large composite structures. Comprehensive mechanical testing was carried out on the carbon fibre/ PEEK materials processed in order to compare the ATP mechanical properties versus the baseline autoclave properties. Laminates were manufactured using both manufacturing techniques to encompass the lay-ups that are commonly used in the aerospace industry; 0º, 0º/90º, ±45º, and quasi-isotropic configurations. Tests carried out on the materials included; tensile, compression, flexure, in-plane-shear and inter-laminar shear. In order to simulate the temperature differentials present in a space environment, tests were carried out at incremental temperatures over the range of -70ºC to 250ºC. To simulate the affect of impact from space debris, compression after impact tests were carried out on the material. G_{IC} and G_{IIC} tests were carried out in order to characterise the fracture toughness of the carbon fibre/ PEEK. Moisture uptake, which can contaminate and degrade space structures when in the presence of space vacuum was also analysed for both materials. Qualitative tests which were carried out following material processing included fibre volume fraction and DSC analysis. Ultimately, there may be a need to bond large composite sections together for RLV tanks. PEEK is an excellent hot melt adhesive and various bonding procedures have been developed to take advantage of this. Two of these are; resistance welding using metal mesh and amorphous interlayer bonding using PEI film. Laminates were bonded using both procedures and parameters were varied in an effort to establish the optimum method of bonding for the material. Following a trade-off study between the techniques, the bonding procedure of most promise was down-selected and full scale temperature testing followed.

1. INTRODUCTION

At the heart of efforts by The European Space Agency to develop a Re-usable Launch Vehicle (RLV) lies the need to develop a composite tank for storage of the cryogenic fuel. Composites will offer a 20 to 30% weight saving on comparably sized aluminium tanks which are used for cryogenic fuel storage in present day launch vehicles [1]. This will enable the placement of larger payloads in space, thus decreasing launcher costs. Traditionally, high performance composite materials have been autoclave consolidated in order to attain the optimum material properties. However, fuel tanks for RLVs will be very large, with liquid hydrogen tanks measuring possibly up to 40 metres in length and 5 metres in diameter. It would be prohibitively expensive to build an autoclave of this size. If the process was to be used for the manufacture of an RLV tank, it would have to be assembled by joining smaller autoclave-consolidated panels.

Two recent NASA sponsored studies [2, 3] reviewed the potential of out-of-autoclave processes for fabricating very large composite structures like the RLV liquid hydrogen tanks. Both studies have shown thermoplastic in-situ automated tape placement (ATP) to be the most suitable alternative to autoclave manufacturing which will enable large component fabrication and at the same time achieve mechanical properties approaching those of autoclaved structures. Thermoplastic in-situ automated tape placement (ATP) is a manufacturing process where the prepreg is continuously oriented, laid down and consolidated onto the tool surface in a single step. There are no expensive, secondary processing steps required such as autoclave or hot-press consolidation. Nejhad et al [4] explains that conceptually there is no limitation on producing parts with thick cross-sections and large surface areas. Ultimately, there should be no problem scaling up such equipment for the fabrication of RLV cryogenic tank sections. Research [2, 3] into existing thermoplastic ATP technology shows that the biggest challenge facing engineers involved is the development of a conformable compaction system. FIG 1. shows ply overlap which can occur for example on the first ply lay-up. Such an over-lap presents a problem to rigid compactors. The rigid compactor concentrates its force on the high spots and so low spots are not substantially compacted.

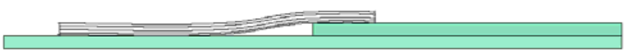

FIG 1. Lack of conformity encountered by rigid compactor [2]

Carbon fibre reinforced PEEK became commercially available in the early 80s, and attracted much interest for its toughness, solvent resistance, wide service temperature range and potential for rapid processing. The most widely used material is APC-2 [5], a high volume fraction, unidirectional prepreg tape, which can be laminated or tape-laid by ATP. The material attracted attention for space applications [6], due to its dimensional stability, low moisture absorption, low level of outgassing in vacuum conditions, resistance to radiation and thermal cycling. Numerous papers have been published on the properties of CF/PEEK under simulated space environment conditions. A new form of CF/PEEK prepreg is now industrially available which has been developed by Gurit SupREM located at Flurlingen in Switzerland. The prepreg manufactured by the company has been produced using a patented aqueous powder impregnation technique. In 1993, Vodermayer [7] and colleagues successfully demonstrated the aqueous powder impregnation technique on a laboratory scale. Today the laboratory equipment has been scaled up to industrial size and the company has the ability to produce highly impregnated thermoplastic tapes with fibre volume fraction contents of up to 65%. The aqueous powder impregnation technique involves fibre tows being impregnated by very fine polymer powder particles with the aid of water assimilation. Research carried out by Vodermayer et al. [7] shows that melt impregnation techniques which are being used to impregnate CF/PEEK up to now are limited to a line speed of about 6m/min. The authors claim that impregnation speeds of up to 50m/min are achievable with the new technology of aqueous powder impregnation. Using the patented technology, the company now produces unidirectional carbon fibre PEEK prepregs with high fibre content and high grade impregnation quality.

Thermoplastic resins flow when heated above their glass transition temperature (amorphous polymers) and above their melting point (semi-crystalline polymers like carbon fibre/ PEEK). Therefore, thermoplastic parts can be welded together by the application of heat and pressure in a process called fusion bonding. Fusion bonding is widely considered to be the ideal joining technique for thermoplastics and research into the area has increased as the use of thermoplastic composites in the aerospace industry has become more widespread. A vast amount of fusion bonding techniques exist and these include; hot tool welding, laser welding, hot-gas welding, resistance welding, ultrasonic welding, linear vibration welding, microwave welding and amorphous interlayer bonding (Thermabond[TM]). Authors such as Yousefpour [8], Ageorges [9] and Silverman and Creise [10] have carried out a great deal of research into the various forms of fusion bonding available. Reviewing published data such as these showed amorphous interlayer bonding using the Thermabond[TM] process and resistance welding using metal mesh as being the techniques with the most potential for bonding large composite sections as would be used in RLV tanks.

2. MANUFACTURING OF LAMINATES

2.1. Autoclave Fabrication of Carbon Fibre/ PEEK Laminates

Autoclave fabrication of the carbon fibre/ PEEK laminates was carried out at ÉireComposites Teoranta, An Cheathrú Rua, Co. Galway, Ireland. The company has significant experience in composite manufacture especially in processing high performance thermoplastics using autoclave technology.

Using a guide frame, the sheets of prepreg were aligned in the required laminate stacking sequence, vacuum bagged and placed in ÉireComposites' 1.5m autoclave. A vacuum was drawn on the vacuum bag of 1 bar (29"Hg). The autoclave door was then sealed and the processing cycle as shown in FIG 2. commenced.

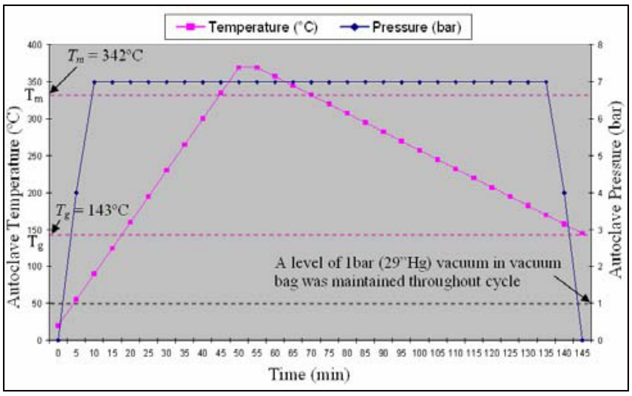

FIG 2. Optimum autoclave processing cycle for Gurit SupREM carbon fibre/ PEEK prepreg

Using the temperature of the mould as the control, the temperature of the material was heated to 370°C at a rate of 7°C per minute. Simultaneously the chamber was pressurized to a pressure of 7 bar (of Nitrogen), at a rate of 1 bar per minute. The level of 1bar (29"Hg) vacuum in vacuum bag was maintained throughout the cycle. Once the mould temperature reached the requisite temperature of 370°C, the temperature was maintained for a dwell time of 5 minutes. Following the dwell period, the heaters were disabled and the system was allowed to cool naturally.

Laminates were autoclaved to encompass the lay-ups that are commonly evaluated in the aerospace industry using conventional laminate stacking sequences. These were; $[0^\circ]_{16}$, $[90^\circ]_{16}$, $[0^\circ/+45^\circ/-45^\circ/90^\circ]_{4S}$, $[0^\circ/+45^\circ/-45^\circ/90^\circ]_{2S}$, $[\pm45^\circ]_{4S}$ and $[0^\circ/90^\circ]_{4S}$.

2.2. Automated Tape Placement (ATP) of carbon fibre/ PEEK

Automated Dynamics located at Schenectady, New York was selected as the company to carry out the in-situ automated tape placement (ATP) of the carbon fibre/ PEEK material. The company was chosen due to its proprietary thermoplastic in-situ processing equipment and expertise, specialising in fabricating high quality thermoplastic composite parts. The incoming prepreg tape is heated instantaneously using ADC's patented hot nitrogen gas torch to above its melt temperature at the nip region with compaction roller which can be actively heated to enhance throughput. The roller, torch, material guidance and compaction force are all located in a compact, lightweight, fibre placement head. High processing speeds of between 2 and 20 inches per second depending on material and part configuration are achievable and the appropriate processing window is achieved by adjusting ADC's processing variables. There are only 5 independent process variables: nitrogen gas temperature, compaction roller temperature, nitrogen gas flow, compaction pressure and lay-down rate. These process variables were set as follows for the Gurit Suprem one inch wide unidirectional carbon fibre/ PEEK prepreg;

Laydown Rate:	3.0 inches per second
N_2 Temp:	925°C
N_2 Flow rate:	90 *slpm/torch
Compaction Load:	300 pounds
Roller temperature:	475°C

**slpm is measure of gas flow; Standard Litres Per Minute*

Manufacturing companies encounter difficulties when trying to fabricate flat unidirectional (0º) laminates using the thermoplastic ATP technique. Conversely, the thermoplastic ATP method is very much suited to the fabrication of 0º pipe sections. Therefore flat laminates were manufactured in the following lay-ups; $[0°/+45°/-45°/90°]_{2S}$, $[0°/90°]_{4S}$ and $[±45°]_{4S}$. Ring sections were ATP processed with a unidirectional $[0°]_{16}$ lay-up.

3. PHYSICAL TESTING AND RESULTS

3.1. DSC Tests to EN ISO 11357

TAB 1. presents the results of DSC testing carried out on autoclaved and ATP processed carbon fibre/ PEEK material according to the test standard EN ISO 11357. Tests were carried out using a Rheometric Scientific DSC analyzer. For both processing techniques, the enthalpy of fusion, melt temperature and percentage crystallinity of the carbon fibre/ PEEK were investigated.

	Autoclaved CF/PEEK	**ATP CF/PEEK**
Enthalpy of fusion (J/g) Mean/ (Std. Dev.)	26.29 (2.86)	48.97 (4.95)
Melt Temperature (°C) Mean/ (Std. Dev.)	342.45 (0.34)	345.62 (0.34)
Crystallinity (%) Mean/ (Std. Dev.)	20.23 (2.20)	27.01 (6.54)

TAB 1. Results of DSC tests on autoclaved and ATP processed carbon fibre/ PEEK

On examination of the DSC results, it can be seen that the melt temperature of the two manufacturing techniques is in the range expected of 343ºC, the melt temperature of PEEK [11]. Understanding the figures achieved for the percentage of crystallinity for the materials is more difficult however. Thermoplastic polymer chemistry shows that the rate at which the melt is cooled to below the Tg is the primary processing variable that controls the level of crystallinity [11]. Research by Corrigan [12] on APC-2 material shows that the slower the rate of cooling from melt leads to a higher percentage crystallinity and that the relationship is close to linear with over 40% crystallinity achievable at a cooling rate of 0.01ºC/s. Conversely, Corrigan shows that rapid cooling in the range of 100ºC/s produces amorphous material. Bearing in mind the cooling rates of the manufacturing techniques, one would therefore expect the crystallinity levels of the autoclave processed material to be higher than the ATP processed material.

3.2. Effects of Moisture Absorption to EN 2823

Specimens were exposed to the affects of a humid atmosphere according to the requirements of prEN 2823. In accordance with the standard, specimens were placed in an environmental chamber at a constant temperature of 70°C and constant exposure of 85% relative humidity for a duration of 1000 hours. Traveller specimens which were conditioned alongside test coupons were weighed regularly in order to calculate the percentage moisture uptake for the batch being conditioned. TAB 2. presents a summary of the moisture uptake analysis after 1000 hours at 70°C and 85% relative humidity for both autoclaved and ATP processed carbon fibre/ PEEK.

	Autoclaved CF/PEEK	**ATP CF/PEEK**
% Moisture Uptake after 1000hrs @ 70°C/85% rh	0.17%	0.20%

TAB 2. Summary of Moisture Uptake Results

Examining the data in TAB 2. shows that the saturated moisture uptake of the material is in the range of 0.17-0.20% by weight. Research carried out by Wang and Springer [13] show an equilibrium water content of about 0.2% by weight for similar tests on APC-2. The figures highlight the excellent resistance of carbon fibre/ PEEK to moisture ingress, especially when one considers the moisture uptake of conventional epoxy systems is in the region of 1% by weight [11].

The figures show that the ATP manufactured carbon fibre/ PEEK is slightly more susceptible to moisture uptake than the autoclaved material (0.03% difference). The reason for this is probably due to the higher percentage void content present in the ATP material as evidenced from microsectional analysis carried out at CTL [14].

3.3. Fibre Volume Fraction measurements to EN 2564

Fibre volume fraction and density measurements were performed according to the requirements of EN 2564. Firstly, the density of each specimen was determined by Archimedes Principle. Fibre weight fraction and fibre volume fraction measurements were performed by the acid digestion method. Concentrated sulphuric acid was chosen as the liquid for matrix digestion because it is one of only two solvents that will chemically attack PEEK (concentrated nitric acid being the other) [15]. Specimens were placed in sulphuric acid, heated to 200ºC and stirred until complete matrix digestion had taken place. Following matrix digestion, hydrogen peroxide was mixed with the solution to neutralise it. The residual fibres were then removed using a sintered glass crucible and dried in an oven before being accurately weighed. TAB 3. presents the results of the tests carried out.

	Autoclaved CF/PEEK	ATP CF/PEEK
Density (kg/m3) Mean/ (Std. Dev.)	1545.36 (12.32)	1479.12 (28.79)
Fibre Weight Fraction Mean/ (Std. Dev.)	0.61 (0.02)	0.62 (0.02)
Fibre Volume Fraction % Mean/ (Std. Dev.)	52.6 (2.3)	51.8 (1.6)

TAB 3. Density, Fibre Weight Fraction and Fibre Volume Fraction Test Results

Examining the data, it can be seen that the density of the autoclaved material is slightly higher than that of the ATP processed material (~4%). The reason for this is probably due to the higher void content of the ATP material as highlighted in a CTL test report [14]. The extra voids would have increased the effect of buoyancy on the specimen and therefore decreased the density figures achieved. This would also explain the larger standard deviation for the ATP material. The results of the fibre volume fraction tests were used in Sections 4.1 and 4.5 to normalise the 0º fibre dominated test results.

4. MECHANICAL TESTING AND RESULTS

4.1. 0º Tensile Tests on Autoclaved and ATP processed carbon fibre/ PEEK

Following trials in order to establish the optimal test procedure for carrying out tensile tests on 0º autoclaved carbon fibre/ PEEK material, the test standard EN 2561 was chosen with tests performed using mechanical wedge action friction grips. The test standard ASTM D-2290-00, often referred to as the tensile split disk method was used in order to carry out tests on the ATP unidirectional disk sections. The test involves the tensile testing of the disk section and yields the apparent 0º tensile strength of the material. FIG 3. shows a comparison of the results achieved and the results presented have been normalised to 55% volume fraction using the results from Section 3.3.

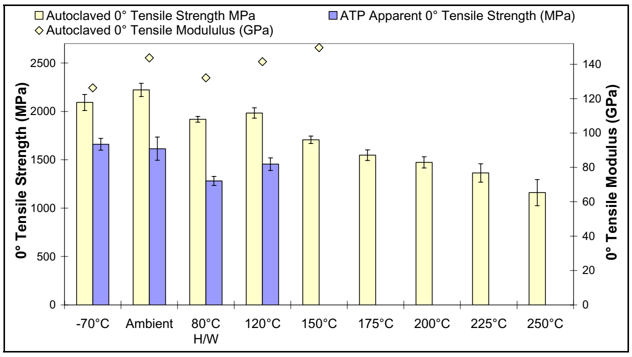

FIG 3. Comparison of 0º Tensile Tests on Autoclaved vs. ATP carbon fibre/PEEK

The 0° tensile test demonstrates the excellent resistance of carbon fibre/ PEEK material to thermal degradation. Examining the autoclaved 0° tensile properties, the material demonstrates a broad temperature range in which the material maintains a high tensile strength and modulus. As expected there was a gradual drop off in strength properties for the material as test temperature was increased. However, at a test temperature of 250°C, the material still retained over 50% of its strength at room temperature.

Comparative analysis of the manufacturing processes shows that the ATP processed material achieved on average, 73% of the autoclaved 0º tensile strengths. The ATP material behaves similarly to the autoclaved material at the various test temperatures with comparable knockdowns in properties from ambient, albeit from a lower starting point. The knockdown in ATP properties demonstrates at first hand, the need for conformable compaction system development to the process as discussed in Section 1.

4.2. 90º Tensile Tests on Autoclaved carbon fibre/ PEEK

90º tensile tests were performed according to the requirements specified in EN 2597. As described in the test method, specimens were extracted from a unidirectional laminate and tensile tested perpendicular to the fibre direction. A summary of the results attained are presented in FIG 4.

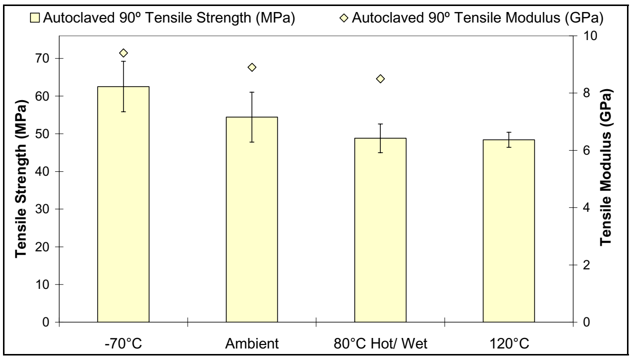

FIG 4. 90º Tensile Tests on Autoclaved carbon fibre/ PEEK material

90º tensile testing is a matrix dominated test which demonstrates the excellent resistance of PEEK material to thermal degradation. The 90° tensile strength test results on autoclaved material are consistently high for all tests carried out. The cryogenic temperature testing of the material shows the suitability of PEEK to sub-zero environments. The 90º tensile strengths achieved at -70ºC are actually higher than the results of testing carried out at ambient. Tests at 80ºC on conditioned specimens and at 120ºC show a small decrease (~10%) in strength and modulus properties from tests carried out at ambient.

4.3. 0º/ 90° Tensile Tests on Autoclave and ATP processed carbon fibre/ PEEK

0º/90º tensile tests were carried out on specimens extracted from $[0°/90°]_{4S}$ laminates in accordance with EN 2561. Similarly to the 0° tensile tests on autoclaved material, the tests were carried out on un-tabbed material using mechanical wedge action friction grips. A summary of the results achieved are presented in FIG 5.

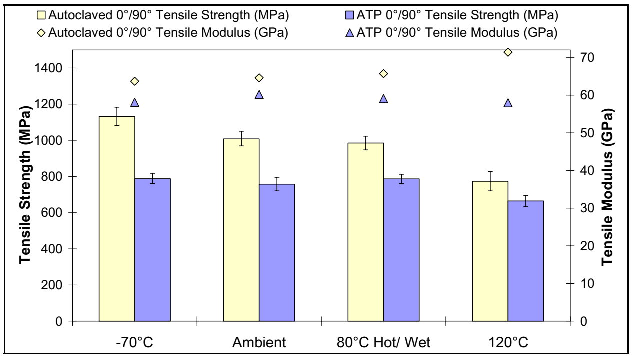

FIG 5. Comparison of 0°/90° Tensile Tests on autoclaved and ATP processed CF/ PEEK

For simple cross-plied laminates in the 0°/90° mode, the tensile strength and modulus values attained are, as expected, approximately half that of the 0° test results. This is true for both autoclaved and ATP material. The average ATP 0°/90° tensile strength of the material for all conditions is 50% of that attained during 0° tensile split disks. This would indicate that the apparent tensile strength values attained during the tensile split disk testing are very close to the true tensile strength for the material. Comparative analysis of 0°/90° tensile tests carried out at the various test temperatures shows that the ATP processed material achieved on average, 78% of the autoclaved 0°/90° tensile strengths. As with the 0° tensile test results, the modulus values for the 0°/90° tests are very consistent and there is no significant drop off in stiffness at the various test conditions from ambient.

4.4. Plain Tensile Tests on Autoclave and ATP processed carbon fibre/ PEEK

Plain tensile tests were carried out on specimens extracted from $[0°/+45°/-45°/90°]_{2S}$ (quasi-isotropic) laminates in accordance with AITM 1.0007. Un-tabbed specimens were tensile loaded to failure and a summary of the results for tests carried out are presented in FIG 6.

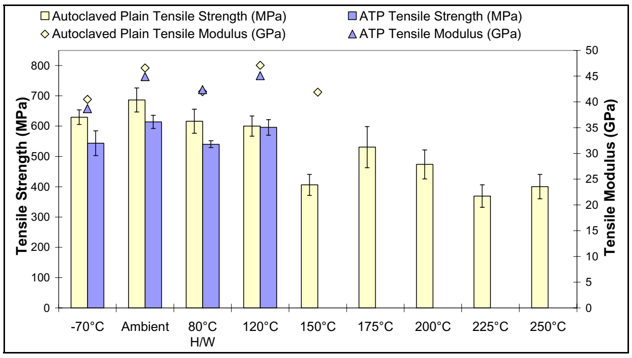

FIG 6. Comparison of Plain Tensile Tests on Autoclaved and ATP processed CF/ PEEK

The results of plain tensile tests on ATP manufactured $[0°/+45°/-45°/90°]_{2S}$ material approach those attained from autoclave processing. The largest difference in strength properties from autoclaved to ATP occurs at -70°C where there is a knockdown of 14%. The average knockdown in strength values is just 9%. Likewise the average knockdown in stiffness values between the two manufacturing techniques is just 3%. The proximity of the results achieved indicate that processing issues associated with ATP manufacturing such as the need for a conformable compaction system have a much smaller effect on the mechanical properties of a quasi-isotropic lay-up than on unidirectional laminates (where there was an average knockdown in tensile properties of 27%). Gripping of the specimens at high temperatures of 150ºC, 225°C and 250°C proved very difficult. The failure modes attained for the specimens tested at these conditions occurred inside or at the gripped area, however their results have been included in the analysis due to the high strength values attained and the comparability of the results. Tensile strength values achieved remained high even for elevated temperature testing. The strengths achieved at 250°C were almost 60% of those achieved at ambient. As seen for the fibre dominated tests earlier, the modulus values for the plain tensile tests are very consistent and there is no significant drop off in stiffness at the various test conditions from ambient.

4.5. 0° Compression Tests on Autoclaved carbon fibre/ PEEK

Following research performed in order to establish the optimal test procedure for carrying out compression tests on 0º autoclaved carbon fibre/ PEEK material, the test standard ASTM 6641 incorporating a CLC fixture was chosen. A summary of the results attained are presented in FIG 7.

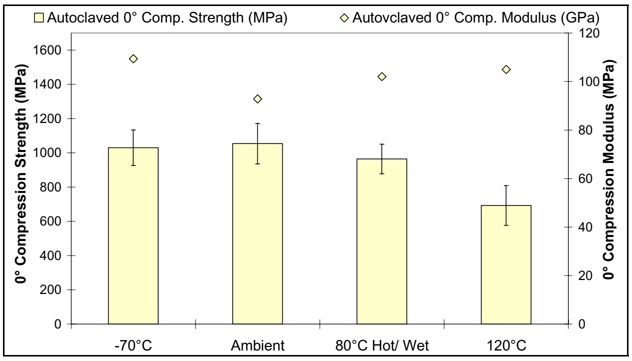

FIG 7. 0° Compression Tests on Autoclaved $[0°]_{16}$ CF/PEEK material

In comparison to the strengths achieved in the 0º tensile tests, these figures are low however and this trend is commonplace among most high performance thermoplastics. For the tests carried out, the 0º compression strengths achieved averaged 50% of the strengths attained for the 0° tensile tests. The largest knockdown in properties occurred at 120°C where the 0° compression results only reached 35% of those reached during 0° tensile testing. This would indicate that the onset of Tg has a more significant affect on the compression results than on tensile results. Modulus values were consistently high for all 0° compression tests carried out and the stiffness values averaged 76% of those attained in tensile tests. 0° compression tests were not carried out on ATP processed material due to the difficulties involved in tape laying flat unidirectional laminates and also the absence of a test standard to compression test specimens of an alternative geometry.

4.6. In-Plane Shear Tests on Autoclave and ATP processed carbon fibre/ PEEK

In-plane shear tests were performed to AITM 1.0002. As part of the test, specimens were extracted from a laminate having a $[\pm 45°]_{4S}$ lay-up and tensile tested to failure. A summary of the results of tests carried out are presented in FIG 8.

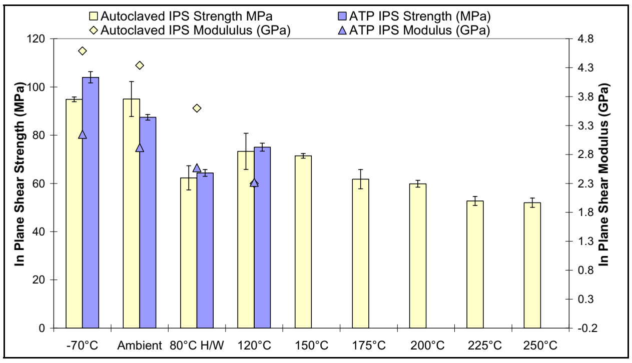

FIG 8. Comparison of In-Plane Shear Tests on autoclaved and ATP processed CF/ PEEK

The comparative in-plane shear tests carried out between the two manufacturing techniques present the unique situation where the ATP properties are greater than the autoclaved properties. ATP in-plane shear strengths are on average 1.8% higher than their autoclaved counterparts. This pattern seems unlikely considering the previous comparative tests examined for 0º, 0º/90º and plain tensile results presented earlier. It could be argued that the lack of a conformable compaction system for the ATP processing technique did not have as significant an effect on in-plane shear properties as it had on 0º tensile tests. There is a possibility that this technology gap affects the in-plane shear properties to an even lesser extent and that the true in plane shear properties of the material are approached by ATP.

As can be seen there is a gradual drop off in in-plane shear strengths as tests were carried out at high temperatures, however at 250°C the autoclaved material still retains 55% of the strength achieved at ambient conditions. Results would indicate that moisture uptake has a more significant effect on in-plane shear results than on tests on fibre dominated coupons. 80ºC Hot/ Wet in-plane shear strength results are in the range of tests carried out at 175ºC, whereas for tests carried out on 0º and 0º/90º tensile, these results are in the range of 120ºC. There is a large drop off in modulus values for the autoclaved material as the Tg is approached. The autoclaved in-plane shear modulus at 120°C is less than half of that achieved at ambient conditions.

4.7. 0º Flexure Tests on Autoclaved CF/ PEEK

0º flexure tests were performed on autoclaved carbon fibre/ PEEK specimens using a 3-point flexure fixture according to the requirements specified in EN 2562. A loading nose of radius 12.5mm was used and the radius of the supports used was 5mm (Type B specimens). The span between the supports was set to 50 mm. The test speed was set to 2mm/min and specimens were loaded until failure occurred. A summary of the results attained are presented in FIG 9.

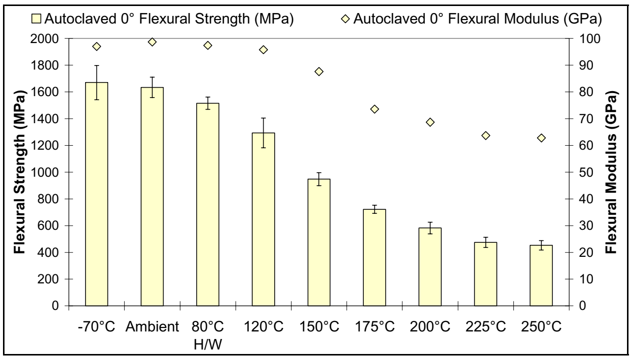

FIG 9. 0° Flexure Tests on Autoclaved CF/ PEEK

The results of 0º flexural testing present a clear trend of how increasing temperature decreases flexural strength in a close to linear fashion over a wide temperature range (from -70ºC to 250ºC). The flexural strength results follow a similar pattern to the results of 0° tensile tests. However the flexural strengths are lower than tensile strengths due to the complex deformation of flexure testing which involves tension, compression and shear loading mechanisms simultaneously. Due to these more complex loading mechanisms, flexural strengths achieved on unidirectional autoclaved material averaged 70% of tensile results. 0° flexure modulus values followed the same trend as the flexural strengths and averaged 57% of the 0º tensile modulus values presented in Section 4.1. Hot/ wet conditioning had a negligible effect on flexural properties. However, an area of concern with 0º flexural testing on carbon fibre/ PEEK material was the rate at which the strength of the material decreased with increasing temperature. For example, the flexural strength of the material at 250°C was only 28% of the material strength at ambient. Conversely, the 0° tensile strength of the material at 250°C is 52% of its ambient value.

4.8. 90º Flexure Tests on Autoclaved carbon fibre/ PEEK

90º flexure tests were carried out on autoclaved carbon fibre/ PEEK using a 3-point flexure fixture according to the requirements specified in ISO 178. As described in the test method, specimens were extracted from a unidirectional laminate and tested perpendicular to the fibre direction. A summary of the results achieved are presented in FIG 10.

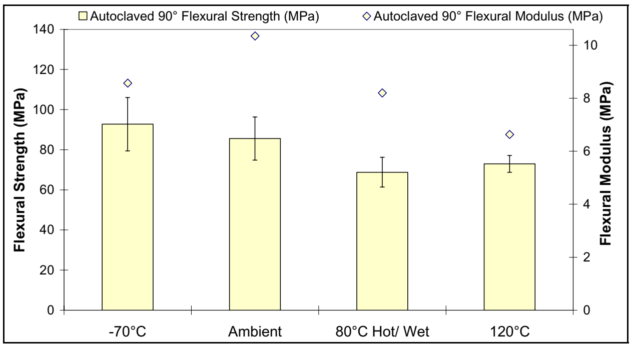

FIG 10. 90° Flexure Tests on Autoclaved CF/ PEEK

The pattern of the 90° flexural strength results presented for tests on unidirectional carbon fibre/ PEEK are almost identical to the pattern of results for the 90º tensile tests presented in Section 7.3. This is hardly surprising since both tests are resin sensitive type tests. 90° flexure results are on average 49% higher than the results achieved for 90º tensile tests. This trend is the opposite to that found for the 0° flexure testing in Section 5.7, where the 0º tensile strength was found to out-perform the 0º flexure strength of the material by a similar figure. Based on the results for all conditions examined, it is fair to say when unidirectional carbon fibre/ PEEK is loaded in the longitudinal direction, its strength is higher for tension tests than for flexure but when loaded in the transverse direction, the flexural strength of the material outperforms the tensile strength. Research by Cogswell [11] on Cytec APC-2 agrees with these trends.

4.9. Inter-laminar Shear Tests on Autoclaved and ATP processed CF/PEEK

Inter-laminar shear strength (ILSS) tests on autoclaved $[0º]_{16}$ carbon fibre/ PEEK were performed according to the requirements given in EN 2563. The radius of the loading nose used was 3mm and the radius of the supports was 3mm. The span between the supports was set to 5 times the average thickness of the batch of specimens tested.

In order to carry out inter-laminar shear tests on $[0º]_{16}$ carbon fibre/ PEEK ATP processed material, tests were performed to ASTM D2344. Specimens were extracted from a unidirectional ATP disk and loaded in a test arrangement as shown in FIG 11. The radius of the loading nose used was 3mm with the ends of the specimen supported by flat platforms set to a span of 4 times the specimen thickness. The surfaces of the flat supports were polished in order to simulate a free moving slide. The test speed was set to 1 mm/min crosshead displacement and specimens were loaded until failure occurred. FIG 12. shows a comparison of the results achieved for tests carried out.

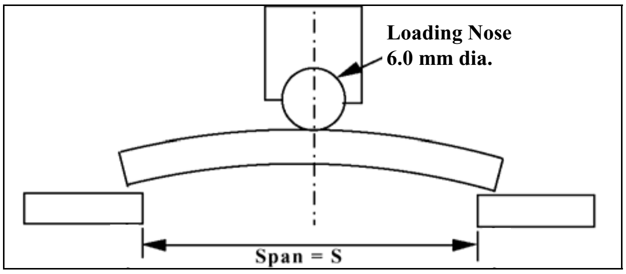

FIG 11. Interlaminar shear ring test set-up for ATP $[0º]_{16}$ carbon fibre/ PEEK

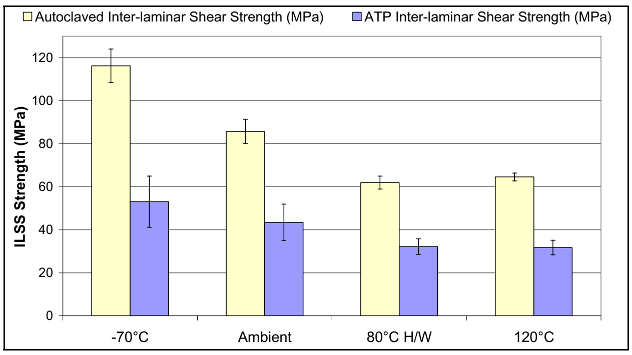

FIG 12. Comparison of 0º ILSS Tests on Autoclaved vs. ATP carbon fibre/PEEK

The comparative interlaminar shear tests carried out between the two manufacturing techniques show the largest knockdown in properties from autoclaved to ATP for all tests carried out. On average, the results of ILSS tests on ATP material reached only 49% of those achieved on autoclaved material. In composites, the interlaminar shear strength test is often used as a qualitative test as it gives a good indication of the fibre/ matrix adhesion achieved during processing and is representative of the general quality of the lamina properties. However, in light of the results of the comparative tests carried out previously; 0° tensile, 0°/90° tensile, plain tensile and in-plane shear, the interlaminar shear test results do not give an accurate indication of the ATP properties achievable. It could be argued that these tests are not directly comparable bearing in mind that the autoclaved specimens were extracted from 0° flat laminates and the ATP specimens were extracted from 0° circular disks.

4.10. Fracture Toughness Tests on CF/ PEEK

As part of fracture toughness tests on autoclaved carbon fibre/ PEEK, G_{IC} and G_{IIC} tests were carried out. G_{IC} is defined as the critical value of strain energy release rate in a crack opening mode (I) and G_{IIC} is the critical value of strain energy release rate in crack sliding mode (II).

A $[0º]_{16}$ carbon fibre/ PEEK laminate was autoclaved with a double layer of release film with dimensions according to AITM 1.0005 incorporated at the mid-plane of the laminate. Specimens were extracted according to the standard and tested in a double cantilever beam (DCB) arrangement with the function of the film being to introduce the initial crack. In the double cantilever configuration, the ends of the sample were pulled apart at a rate of 10mm/min through hinges mounted on the specimen until a total propagated crack length of 100 mm had been achieved. G_{IC}, the interlaminar fracture toughness energy was calculated from the propagated crack length and the energy applied from the load–crosshead displacement diagram. As part of the G_{IIC} test procedure, the same specimen as used for G_{IC} examination was trimmed to produce a flexure specimen of 110mm total length, 40mm of which was pre-cracked. The pre-cracked specimen was then loaded according to AITM 1.0006 in a three point bend fixture until crack propagation onset. The total fracture toughness energy was calculated from the initial crack length and load-displacement diagram.

	Ambient
G_{IC} **(J/m^2)** **Mean/ (Std. Dev.)**	1062.7 (60.17)
G_{IIC} **(J/m^2)** **Mean/ (Std. Dev.)**	999.87 (114.56)

TAB 4. Mode I and Mode II Fracture Tests on Autoclaved $[0°]_{16}$ CF/PEEK material

In carrying out the G_{IC} tests summarised in TAB 4. the stability of crack propagation in the carbon fibre/ PEEK material was clear as the crack-opening moved slowly and in a controllable manner and little crack movement was observed when crosshead movement was ceased. The influence of high fracture stability in a material is to increase its fracture toughness and this was reflected in the high G_{IC} values generated.

The results of G_{IIC} fracture toughness tests carried out indicate that a high shear force in the region of 1000 J/m^2 is required to initiate interlaminar crack sliding in a carbon fibre/ PEEK laminate. In work carried out by Cogswell [11] on carbon fibre/ PEEK, the author explains that the high fracture toughness of the material is due to the good interface and tough resin which promotes a significant toughening mechanism by deflecting crack growth from the resin rich interlayers into the body of the material.

4.11. Compression After Impact Tests

Compression after impact tests were performed on autoclaved carbon fibre/ PEEK $[0°/+45°/-45°/90°]_{4S}$ material according to AITM 1.0010. Impacts were performed at the required energies using a drop weight impactor and specimens were subsequently compression tested using a Boeing compression after impact test fixture. FIG 13. shows a graphical comparison of the compression after impact strengths achieved on tests carried out at ambient conditions and at -70ºC.

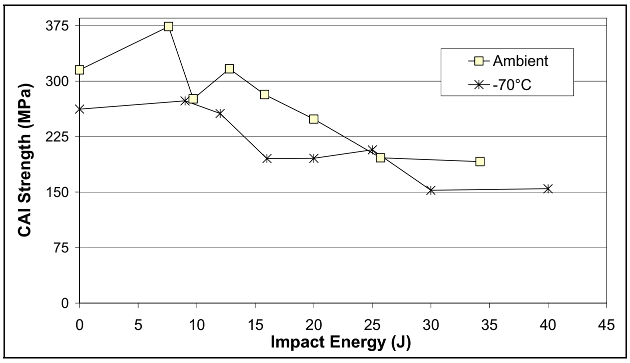

FIG 13. CAI tests on autoclaved carbon fibre/ PEEK at -70°C and ambient

As can be seen, compression after impact strength results achieved are consistently high at both conditions and there is no significant drop off in strength as the impact energy is increased. Residual compression strength tests carried out at sub zero temperatures show only slight change from ambient conditions. The knockdown in residual compression strength for the specimens impacted at maximum energy (~ 40 joules) and tested at ambient is only 40% less than the results of tests on un-impacted specimens.

5. BONDING TRADE-OFF STUDY

5.1. Amorphous Inter-layer bonding - Thermabond™ process

In 1989, Smiley and co-workers [16, 17] at ICI Composite Structures developed an amorphous interlayer bonding procedure for thermoplastic composites called the Thermabond™ process. The Thermabond™ process is a fusion bonding procedure where an interlayer polymer with different characteristics than the reinforced polymer in the composite is used. The Thermabond™ system can be used very successfully to bond carbon fibre/ PEEK components when amorphous polyetherimide (PEI) resin is used as the thermoplastic interlayer. How the physical characteristics of the two polymers compare is shown in FIG 14. The amorphous PEI has a glass transition temperature of 210°C. Semi-crystalline carbon fibre/ PEEK on the other hand, has a glass transition temperature of 143°C and a melting point of 343°C. The two resins are compatible on a molecular level and the physical behaviour of the materials enables a processing window in the temperature range from 260°C to 315°C. Work by Smiley et al. [18] has shown that below 260°C, the PEI interlayer does not flow sufficiently and that above 315°C softening of the PEEK composite occurs through the structure.

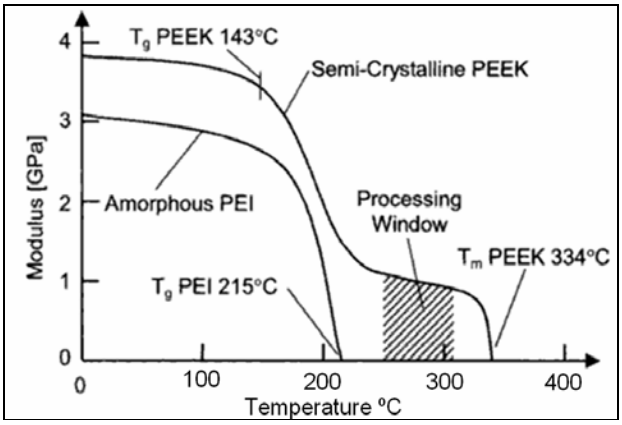

FIG 14. Physical characteristics of PEEK and PEI for Thermabond™ process [9]

The laminates employed in this study consisted of 16 ply 0° Gurit Suprem carbon fibre/ PEEK material. During the autoclaving procedure, a layer of PEI film (thickness 250 micron) was placed over the top surface of the prepreg and the laminate was autoclave processed as shown in FIG 2. The fully consolidated panels were then trimmed, cleaned with acetone, dried and then aligned in a specially constructed aluminium fixture as sketched in FIG 15. The fixture was designed to produce an even pressure distribution over the overlap region and allow a 12.5mm overlap length as required by AITM 1.0019. The composites were aligned so that PEI coated faces of the carbon fibre laminates were facing each other as shown and an extra layer of PEI film was placed at the interface in order to promote adhesion mechanisms such as molecular diffusion, mechanical keying and fibre migration. Using torque screws located at the regions highlighted, the pressure at the overlap region could be accurately simulated. Once assembled, the jig was placed in a preheated oven. Variations in clamping pressures and processing temperatures which were within the processing window presented in FIG 14. were examined in order to optimise the bonding process for Gurit Suprem carbon fibre/ PEEK material.

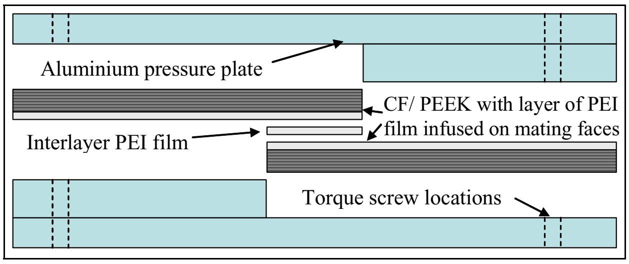

FIG 15. Exaggerated sketch showing amorphous inter-layer bonding assembly

In all trials carried out, the temperature of the composite was measured using a thermocouple and was maintained at the required temperature for half an hour before the assembly was removed and allowed to cool to room temperature. Lap shear strength tests were subsequently carried out. Examining the results achieved, the highest lap shear strength averages were achieved using a clamping pressure of 0.6MPa ± 0.1MPa at a processing temperature range of 275° - 290ºC. These results are presented in TAB 5.

	PEI Bonding
Lap Shear Strength (MPa) Mean/ (Std. Dev.)	28.19 (8.3)

TAB 5. Results of amorphous interlayer trials

5.2. Resistance welding using metal mesh as the resistive element

Resistance welding trials were carried out using metal mesh as the heating element. Yousefpour et al [19] performed experiments to establish the optimum heating element mesh size to bond APC-2 carbon fibre/ PEEK. The authors carried out trials using various mesh sizes in order to establish which mesh configuration would provide the most uniform heat distribution at the weld interface and the best mechanical performance. The authors found that a stainless steel mesh with the properties detailed in TAB 6. provided the ultimate mechanical properties of any mesh configuration examined. Resistance welding trials on the Gurit SupREM carbon fibre/ PEEK material were carried out on mesh with identical characteristics.

Wire Diameter (mm)	Mesh Thickness (mm)	Open Gap (mm)
0.04	0.08	0.089

TAB 6. Metal mesh properties for resistance welding

Specimens with dimensions 100mm x 25mm were extracted from $[0°]_{16}$ laminates and placed in grooves machined in metal plates to AITM 1.0019 configuration as shown in FIG 16. A layer of neat PEEK with thickness 0.15mm was placed on both surfaces of the area to be bonded as shown with dimensions 12.5mm x 25mm.

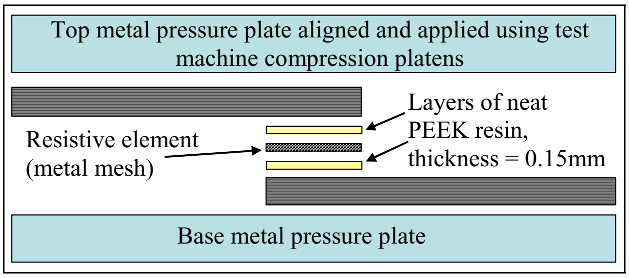

FIG 16. Sketch showing resistance welding assembly (metal mesh)

The function of the neat PEEK polymer films is to act as insulators, and facilitate melt flow in the bondline, preventing current leakage, preferential heating and consequently providing a better quality of weld [8]. The wire mesh heating element was then placed between the layers of neat PEEK to be bonded. The ends of the heating elements were clamped between copper connectors. The function of the copper connectors was to provide an even voltage distribution through the wire mesh and help prevent localised heating problems along the heating element. Special care was taken to ensure that the edges of the metal mesh close to the copper connectors, were not directly exposed to air. The metal top plate was then placed on top of system, sandwiching the heating element between the two layers of neat PEEK polymer film.

A 10kN Zwick screw driven test machine was used to apply homogenous pressure of 1 MPa to the welding assembly and all welding was conducted under displacement control. A DC power supply was used to apply 18.5 Amps of electrical current and 4.5 Volts to the heating element during welding. The temperature at the weld interface was monitored using a thermocouple which was placed between the neat PEEK and the wire mesh. The welding process was stopped when the temperature at the interface reached 430°C. This took about 90 seconds and the material was then allowed to cool to room temperature (approx 120 seconds) before being removed and lap shear tested. TAB 7. presents the results of the lap shear tests carried out at ambient conditions on the materials.

	Resistance Welding
Lap Shear Strength (MPa) Mean/ (Std. Dev.)	30.87 (0.87)

TAB 7. Results of resistance welding trials

5.3. The Effect of Temperature on Metal Mesh Resistance Welded CF/ PEEK

As can be seen from the results in TAB 5. and TAB 7. the lap shear strengths attained from the resistance welding are more consistent and controllable than that attained from the PEI bonding. Also the time involved to bond the material is much shorter for the resistance welding. For these reasons, the resistance welding method with metal mesh was selected as the most promising of the bonding techniques and full matrix testing was carried out.

FIG 17. presents the results of lap shear tests carried out on the carbon fibre/ PEEK material bonded using a metal mesh resistive element and tested at various temperatures.

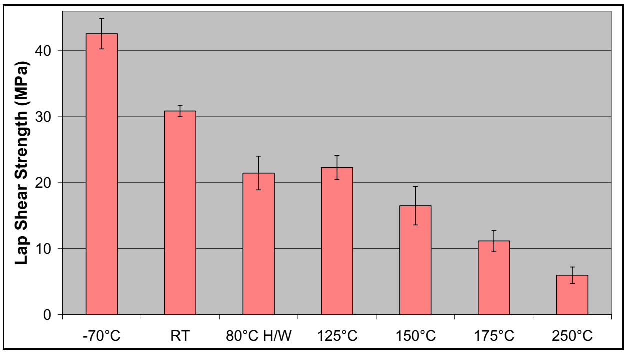

FIG 17. Metal mesh resistance welding lap shear results

Examining the data, the affect of increasing temperature on the lap shear strengths achieved is clear. The lap shear strength results decrease significantly with temperature and at 250°C, only 20% of the strength achieved at ambient conditions was reached. Interestingly, the lap shear strength results at -70°C represented a 38% increase from ambient.

6. SUMMARY AND CONCLUSIONS

A new form of carbon fibre/ PEEK pre-impregnated tape is now industrially available in powder processed material from Gurit Suprem, of Switzerland. The main aim of this project was to thermomechanically characterise the new form of CF/PEEK for space applications under pressure formed autoclaved conditions, and to compare against properties achieved using the most suitable out of autoclave technology for large space structures. Automated tape placement (ATP) was chosen as the out of autoclave technique having most potential for the fabrication of large composite structures like the liquid hydrogen tanks for the Re-usable Launch Vehicle (RLV). The second aim was to evaluate joining and bonding processes with the new carbon fibre/ PEEK material.

Comprehensive mechanical testing was carried out on the carbon fibre/ PEEK materials processed in order to compare the ATP mechanical properties to the baseline autoclave properties. Tensile tests carried out on various lay-ups (unidirectional, 0º/90º and quasi-isotropic) showed that tensile strengths of the ATP processed material averaged 85% of those achieved on the autoclaved material. Comparative in-plane shear tests showed a negligible difference in mechanical properties between the two technologies and 100% of autoclave properties were approached using ATP. The largest knockdown in properties was found in inter-laminar shear results where ATP processed material achieved only 52% of autoclaved strengths. Differences in the loading configurations between the two materials for the inter-laminar shear tests make comparisons difficult. However, where direct comparative tests were carried out between the two technologies, the results of testing on the ATP material approached those achieved on autoclaved material and the suitability of ATP processing to carbon fibre/ PEEK prepreg was shown. TAB 8. shows a comparison of the strength results achieved for tests on ATP processed carbon fibre/ PEEK versus tests on autoclaved material where comparative tests were performed.

	-70°C	RT	80°C H/W	120°C
0° Tensile	79%	73%	67%	73%
0°/90° Tension	70%	75%	80%	86%
Plain Tension	86%	89%	88%	99%
In-Plane Shear	110%	92%	103%	102%
ILSS	46%	51%	52%	49%

TAB 8. Comparison of ATP strength ratios vs. autoclaved for comparative tests

Tests carried out on the carbon fibre/ PEEK material at conditions simulating a space environment demonstrated a suitability to space applications. The material exhibited low moisture absorption, damage tolerance even at high impact loads (40 joules). The material also demonstrated excellent resistance following exposure to cryogenic temperatures (-70°C) and showed little change in mechanical properties from ambient conditions. High temperature testing tests on the material demonstrated the high service temperature available with the new carbon fibre/ PEEK material.

Ultimately, there may be a need to bond large composite sections together for RLV tanks. PEEK is an excellent hot melt adhesive and various bonding procedures have been developed to take advantage of this. Two promising procedures are: resistance welding using metal mesh; and amorphous interlayer bonding using PEI film. A trade off study was carried out between both procedures in an effort to establish the optimum bonding procedure for the Gurit Suprem carbon fibre/ PEEK material. Resistance welding was successfully carried out using stainless steel metal mesh as the resistive element and lap shear strengths in the region of 31MPa were achieved. The Thermabond^{TM} fusion bonding mechanism was also successfully applied to the carbon fibre/ PEEK material where polyetherimide (PEI) was incorporated as the thermoplastic interlayer resin. Using this bonding technique, lap-shear strengths in excess of 28MPa were achieved at the optimum processing conditions. Because the results of tests carried out on resistance welded specimens were found to be generally higher and more consistent than those achieved with PEI bonding and that the bond time for resistance welding was significantly shorter, resistance welding was chosen as the bonding method of most promise and full scale temperature testing was carried out. The affect of increasing test temperature on the lap shear strengths was highlighted as an area of concern for the resistance welded material. At a test temperature of 250°C, only 20% of the strength achieved at ambient conditions was reached.

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