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Bonding and Sealing Evaluations for Cryogenic Tanks

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Abstract

Several different cryogenic tank concepts are being considered for reusable launch vehicles (RLV's). Though different tank concepts are being considered, many will require that the cryogenic insulation be evacuated and be bonded to a structure. In this work, an attempt was made to evaluate the effectiveness of maintaining a vacuum on a specimen where foam or honeycomb core was encased within Gr/Ep. In addition to these tests, flatwise adhesion pull off tests were performed at room temperature with PR 1664, EA 9394, FM-300, Crest 3170, and HT 435 adhesives. The materials bonded included Gr/Ep, Gr/BMI, Al, and stainless steel facesheets, and Ti honeycomb, Hexcel honeycomb, and Rohacell foam core materials.

Introduction

Reusable launch vehicles (RLV's) will use cryogenic hydrogen and oxygen as the fuel. The fuel will be stored in tanks at cryogenic temperatures. Numerous designs have been evaluated for the liquid hydrogen (LH2) and liquid oxygen (LOX) tanks. The designs include sandwich panels with a foam or honeycomb core between two facesheets. The foam or honeycomb core serves as a portion of the cryogenic insulation and as a structural member. Tank concepts where the cryogenic insulation is located on the inside or the outside of the tank structure have also been considered. Regardless of the tank design, adhesives will be used to attach the cryogenic insulation to the tank wall.

Studies have been performed on the evaluation of adhesives for cryogenic applications. Goeders and Perry [1] evaluated 24 adhesives for bonding PEEK/IM-6, a potential cryogenic tank material. They considered various surface preparations and measured the mean shear strength. The specimens were exposed to thermal and mechanical cycling, as well as humidity exposure. They also tested the PEEK/IM-6 bonded to titanium and IM-7/8551-7 (Gr/Ep) and titanium bonded to itself and to IM-7/8551-7. Elevated temperature shear tests were performed as well as room temperature tests. As a result of their tests, they recommended FM 300 and EA 9394 adhesives.

McDonnell Douglas Aerospace performed adhesive tests at both cryogenic and elevated temperatures [2]. Two sets of tests were performed: one in the temperature range -100°F to 400°F, and the other -200°F to 250°F. In the higher temperature range, EA 9395.5 was the best for shear strength, while EA 9394 provided the best peel strength. In the lower temperature range, the EA 9394 was the overall best performing adhesive.

In this report, two different types of tests that support cryogenic tank development efforts are discussed. The first involved fabricating “ravioli” specimens, where a honeycomb or foam core was encased in Gr/Ep. The ravioli specimens were cooled to cryogenic temperatures while a vacuum was pulled on the inside of the specimens. The intent was to evaluate the ability to fabricate a specimen that could maintain a vacuum when cooled to cryogenic temperatures. The second type of test evaluated adhesives for use on the cryogenic tank (cryotank) by performing flatwise tension tests on thermally cycled specimens of different construction.

Composite Fabrication

The Gr/Ep used for the experimental analysis was IM7/977-2 from Fiberite while the Gr/BMI was IM7/5260. Two in-house shops were used to layup and cure the composite. Both, however, used the same layup and cure procedures. The cure cycle used for the Gr/Ep is given in Table 1. The composites were nominally 0.040-in. thick, which required eight plys of the lamina.

Table 1: Cycle Used for Cure of IM7/977-2

Pressure
Apply 22 inches Hg vacuum to bag
Apply 100 psi to laminate when temperature reaches 200°F
Vent vacuum when pressure reaches 20 psig
Temperature
Heat from room temperature to 210°F at a rate of 2-5°F/minute
Hold at 210°F for 1 hour
Heat from 210°F to 350°F at a rate of 1-5°F/minute
Hold at 350°F for 3 hours
Cool down to 140°F at 5-10°F/minute
Below 140°F, release pressure and remove part

Prior to bonding materials to Gr/Ep or Gr/BMI, the composite must be grit blasted to prepare the surface for bonding. Previously No 5 grit at 90 psi was used to prepare the surface. Due to the large size of several of the samples, a different grit blaster was sought. The grit blaster with a larger stream size used 120 grit. Representative sections of Gr/Ep were prepared for bonding with both the No. 5 grit blaster at 90 psi and the 120 grit blaster at 40 psi. After the grit blasting, the specimens were cut, mounted, polished, and examined under a microscope. Photomicrographs were taken of the first ply cross-section for each facesheet at 500X magnification. In addition, photomicrographs were taken of the surface of each facesheet at 100X. No cracking was observed in either facesheet, and significant abrasion was noted on the face of both facesheets. There was no evidence of any damage to the samples by the larger 120 grit. As a result of the above analysis, the 120 grit at 40 psi was used for all subsequent bonding preparation.

Ravioli Specimens

An important aspect of fabricating a cryotank is the ability to both monitor the health of the system and fabricate a structure that can be sealed. One way to monitor the health of a sandwich tank structure is to continuously monitor gases that may be present between the inner and outer facesheets, i.e. in the core material. To determine the feasibility of health monitoring of the cryotank, several small specimens were fabricated with Rohacell foam or honeycomb core embedded inside Gr/Ep. The specimens were evacuated and cooled down to cryogenic temperatures, attempting to maintain the vacuum. The ability to evacuate a representative tank specimen and maintain a near vacuum at cryogenic temperatures relates to the health monitoring of the tank.

Pre-ravioli Tests

Prior to embedding Rohacell foam in a ravioli specimen with a stainless steel port for pulling a vacuum, it was decided to evaluate the effects of the CTE mismatch between the stainless steel tube with a flange, the foam, and the Gr/Ep. To evaluate the effects of the CTE mismatch, a specimen was fabricated as shown in Figure 1. A 2 in. x 2 in. Rohacell 110WF foam specimen was bonded to a 2 in. x 2 in. piece of Gr/Ep. A stainless steel tube with a flange was inserted through the Gr/Ep and a recession was cut in the foam for the flange. The specimen was bonded together with EA9394 room temperature cure adhesive.

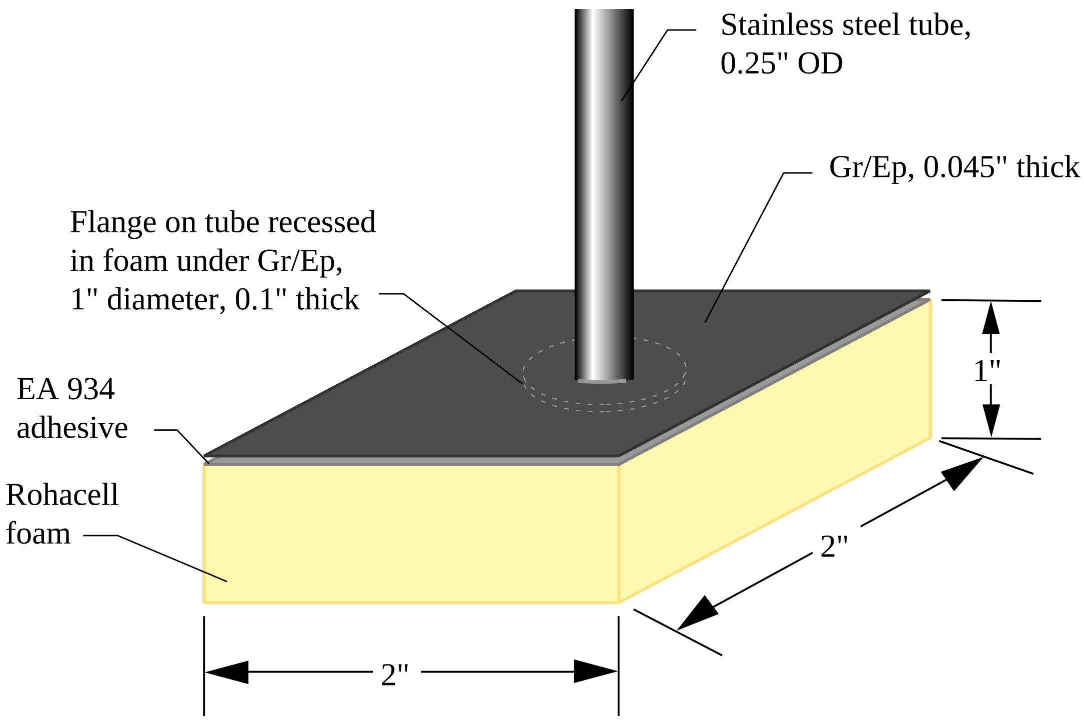

Figure 1: Schematic diagram of test specimen with stainless steel tube embedded between Gr/Ep and Rohacell foam.

The specimen was immersed in LN2, and though cracking and popping sounds were heard during the initial immersion, no structural damage was noticed. During subsequent immersions, no popping sounds were heard. A few days later, a He leak test was performed on the specimen, and no He was detected penetrating the foam or bondline. The specimen was immersed in LN2 while pulling a vacuum on the tube. The system was overloaded and shut down due to the rapid increase in pressure. The specimen was then removed and He gas was again introduced on the outside of the specimen. This time, He was detected through the foam or the bondline, but it was not known which. The bondline between the foam and the Gr/Ep was later coated with PR

1664, a two-part room temperature cure polyurethane adhesive, to reduce the influx of gas at the bondline. The specimen was then inserted in LHe. It took about 5-10 sec. before the pressure began to rise (from 10^{-6} - 10^{-7} to 10^{-3} - 10^{-4}). The rise in pressure was significantly less than during the previous test when the specimen was inserted in LN2. The pressure remained constant for approximately 5 min, and then began to rise. The specimen was then removed from the LHe, and cracks were noticed in the PR 1664 adhesive used to seal the bondline. After the specimen dried for two days, it was then connected to a vacuum pump for several hours. Helium appeared to be inside the specimen, i.e. a specimen saturated with He. The next day, the specimen was connected to the He leak detector. The specimen was able to hold a vacuum on the order of 10^{-6} - 10^{-7}. When He gas was introduced to the specimen, the pressure quickly rose, indicating a leak. The tests were informative but inconclusive.

Specimen 1

The first ravioli specimen fabricated consisted of Rohacell 110 WF foam encased in 0.040-in-thick facesheets of Gr/Ep. Specimen 1 was constructed based on an existing tool that had been used for a Gr/Ep sandwich construction for the SR71. The tool is 1 in. thick with a base 7.5 in. x 7.5 in. The top of the tool is 5 in. x 5 in., with the sides of the specimen sloping at 45° angles from the bottom to the top. The core material for the sandwich construction was first machined to the shape of the tool. The tool was then used as a male mold to form the top (“hat”) portion of the Gr/Ep specimen. A 12 in. x 12 in. flat piece of Gr/Ep was made for the bottom portion of the Gr/Ep specimen. Prior to testing, the ravioli specimen was examined by several NDE techniques, including C-scan and shearography. The results were qualitative in nature, but showed no problems existed. The C-scans showed no anomalies, so the ravioli specimen was then bonded together using FM-300 film adhesive.

The specimen was tested by inserting it into a dewar of liquid nitrogen. The specimen was inserted into the liquid nitrogen for a period of approximately 5 min., and then removed. The specimen floated in the liquid nitrogen, and was held under manually. During the first immersion, cracking and popping sounds were heard nearly the entire time. The specimen was removed after approximately 5 min. and allowed to warm. During this time, the specimen was behind a plexiglas shield. As expected, the specimen frosted as it warmed. During the second immersion, no cracking and popping sounds were heard. However, during the second warm up cycle, the frost pattern on the bottom of the specimen was non-uniform on the Gr/Ep section that was bonded to the foam. The non-uniformity, which looked about half heavily frosted and half lightly frosted, was not noticed during the first warm up cycle. The specimen was then immersed in LN2 and removed for ten cycles of five minutes in, five minutes out. The non-uniform frost pattern on the bottom of the specimen noticed after cycle 2 was not noticed during subsequent immersion.

The specimen was then immersed in LHe. Due to the dewar size, the sides of the panel had to be trimmed prior to insertion in the LHe. When the panel was trimmed, tiny cracks were noticed in the bondline between the hat section and the facesheet. The specimen was immersed in the LHe and held for several minutes. After the LHe boiloff ceased, the specimen was removed from the LHe, but was kept in the dewar (above the liquid level) for several minutes. Popping and cracking sounds were heard, and finally, a loud pop was heard. Upon inspection, it was determined that the top and bottom sheets had disbonded on one of the sides. One possible scenario is that during bonding, air escaped from inside the ravioli specimen at the bondline, and formed tiny channels in doing so. Trimming the specimens opened up the channels for the LHe to enter. When the specimen was immersed in the LHe, cryopumping of the LHe occurred. When the specimen was removed from the LHe, the LHe vaporized and the specimen could not contain the increased pressure, and thus disbonded.

Specimen 2-4

Two more specimens were fabricated with Rohacell foam encased in the Gr/Ep. Channels were drilled in the foam so that a vacuum could be pulled during testing. One specimen was made with Nomex honeycomb core in the Gr/Ep. Table 2 lists the different types of core material used for the specimens.

Table 2: Core Material Specimens Used for Ravioli Specimens 2-4

Specimen no.	Core material	Adhesive
2	Rohacell WF 51	FM 300
3	Rohacell WF 71	PR 1664
4	Nomex honeycomb	Crest 3170

The hat portion of the second specimen did not visually appear to be as good quality as the first hat specimen. Bridging was observed on the flat part of the hat specimen at the base of the sloped side. The bridging is attributed to a lack of pressure over that portion.

With a 0.25-in-diameter stainless steel tube sticking through the Gr/Ep, it was difficult to bond the specimen in an autoclave with an elevated temperature film adhesive. Thus, a room temperature cure EA 9394 epoxy adhesive was used. The top and sides of the ravioli specimen were dead weighted for 24 hours on the sides and top of the specimen. Upon removing the weights, it was obvious that the specimen had not bonded properly. The flat facesheet of the specimen was removed, the mating surfaces were cleaned, and the specimen was rebonded using PR 1664 adhesive. A double vacuum bag was used to apply pressure on the specimen during bonding.

Specimen 5

An attempt was also made to co-cure a specimen rather than secondary bonding two facesheets. For this specimen, Rohacell WF 71 foam was co-cured between Gr/Ep. Eight plies of Gr/Ep were used for the bottom (flat) portion, and eight plies for the top (hat) portion. The picture frame region around the foam was thus composed of 16 plies of co-cured Gr/Ep. No adhesive was used between the foam and the Gr/Ep - only the resin from the composite. The Gr/Ep was cured with 50 psi at 350°F in an autoclave. The specimen was in a vacuum bag during the cure. A 0.25-in-diameter stainless steel tube protruded through the Gr/Ep to enable the foam core to be actively evacuated. A flange on the end of the tube was bonded to the foam just below the Gr/Ep surface with EA 9394 adhesive. The co-curing process (50 psi at 350°F) caused no noticeable deformation of the Rohacell foam. During testing, this specimen was unable to maintain a vacuum at cryogenic temperatures.

Specimen 6

Two major changes were made to the final ravioli specimen fabrication process attempted. The first change was an increase in the thickness of the hat section from 8 plies to 12 plies. Twelve plies is considered to be closer to an actual cryotank thickness.

The second change was a modification to the ply layup. The original layup was one that had been designed for a structural panel test for the SR 71 aircraft. The layup was designed to provide the necessary structural support but was not required to maintain a vacuum. The layup was such that on the top hat panel, the four corners of the top surface were not covered by any plies of fabric. Instead, the plies butted up against each other, with different lamina at different angles. Thus, there were four points that were covered only by resin, and not by the fabric.

During initial testing at room temperature, the specimen maintained a high vacuum. The specimen was then cooled down, attempting to maintain a vacuum during cooldown. The cooldown history of the specimen is shown in Table 3. After 40 minutes, the vacuum shut off due to leakage into the specimen. The system was restarted, but would not pump down below 80 mtorr. The specimen was then allowed to warm back to room temperature, warming back to 15.7°C after 94 minutes.

Table 3: Cooldown and Vacuum History of Specimen 6

Time, min	Temperature, °C	Hi vac, torr
0	24.2	4.5×10^{-5}
9	3.8	4.5×10^{-5}
11	2.2	4.5×10^{-5}
14	-9.0	4.5×10^{-5}
16	-14.5	4.5×10^{-5}
18	-32.2	4.5×10^{-5}
21	-41.4	4.5×10^{-5}
24	-46.6	4.5×10^{-5}
26	-60.0	4.5×10^{-5}
29	-75.6	4.5×10^{-5}
34	-79.2	4.5×10^{-5}
37	-105.3	4.5×10^{-5}
39	-117.7	4.5×10^{-5}
40	-119.0	$> 80 \times 10^{-3}$

A second test was later performed, and the results are shown in Table 4. The specimen recovered after being warmed back to room temperature and was able to maintain a high vacuum. The specimen was cooled down, with the high vacuum kicking off at -26.1°C. The leak detector would not stay on, and the system was turned off and the specimen allowed to warm.

Table 4: Cooldown and Vacuum History of Specimen 6 During Second Test

Time, min	Temperature, °C	Hi vac, torr
0	22.3	3×10^{-5}
3	6.0	3×10^{-5}
15	2.7	1×10^{-5}
17	-19.1	2×10^{-5}
21	-26.1	shut off
32		leak detector wouldn't stay on
64	9.3	1×10^{-4}

A test was then performed on the specimen where it continued to be cooled down even if the pressure began to rise. Figure 2 is a plot of pressure versus temperature for specimen #6. The data for the first test is shown by the squares in the figure, while the data for a second test is shown by the circles. The total elapsed time was 90 minutes, and several days elapsed between the tests. Though a hard vacuum could not be maintained at the cryogenic temperatures, it appears that the specimen was able to recover its ability to hold a vacuum after warming back to room temperature. The reduced pressure of 10 torr is not low enough to significantly decrease the gas thermal conductivity, but may assist in vehicle health monitoring.

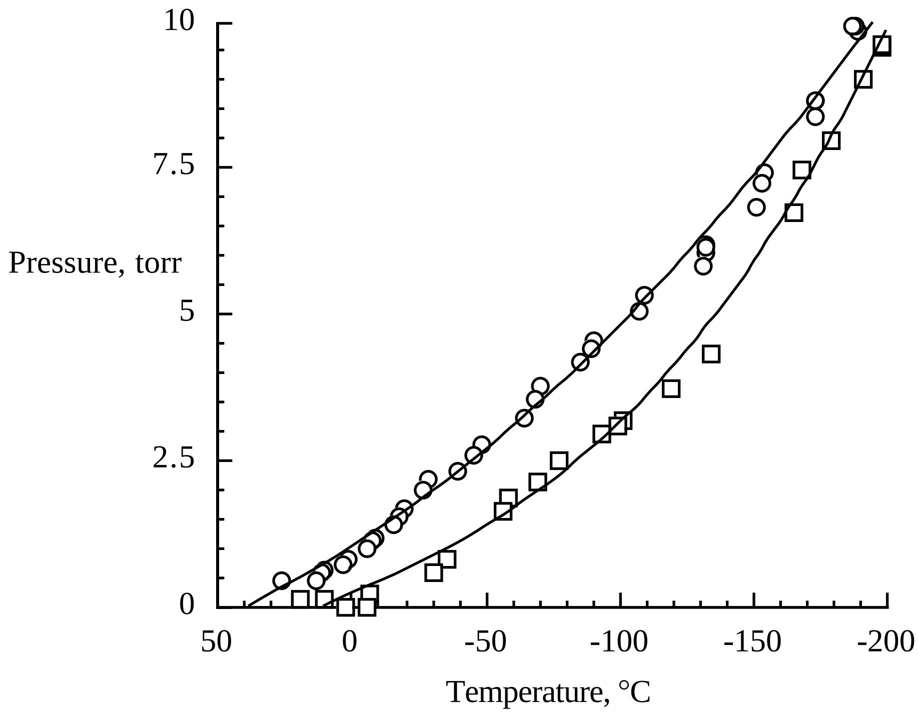

Figure 2: Pressure versus temperature for specimen #6.

Flatwise Tension Tests

The ultimate tensile stress of a sandwich construction was determined by performing flatwise tension tests of different core materials bonded to various facesheet materials. Flatwise tension specimens were constructed to evaluate several different adhesives. The adhesives evaluated were PR 1664, EA 9394, Crest 3170, FM 300, and HT 435 and are shown in Table 5. The PR 1664 is a polyurethane adhesive and the EA 9394 is an epoxy, and both are room temperature cure adhesives. The Crest 3170 adhesive is an epoxy adhesive that can be cured at room temperature or elevated temperature if a shorter cure time is desired. An elevated temperature post cure of the Crest 3170 can also increase the strength of the bond. FM-300, an epoxy adhesive, can be obtained for curing at 250°F or 350°F. The FM-300 used here is the 250°F cure adhesive. HT 435 is a higher use temperature adhesive and is a modified epoxy-phenolic that is cured at 340°F. Composite facesheets co-cured to honeycomb core specimens were also fabricated and tested.

The bonding procedures for each type of adhesive are different and are given in

Table 6. Prior to bonding to the composite surfaces, the surface was first grit blasted with 120 grit Al_2O_3 at 40 psi and then cleaned with ethyl alcohol. The bonding with the Crest 3170 was performed by mixing the adhesive in a 2:1 weight ratio. However, after much of the testing was complete, it was discovered that the instructions with the adhesive were incorrect, and the two parts should be mixed in a 1:1 weight ratio. Once discovered, the procedure was modified for subsequent tests.

Table 5: Adhesives Evaluated for Bonding Cryotank Specimens

Adhesive	Type	Cure Temp., °F
PR 1664	polyurethane	RT
EA 9394	epoxy	RT
Crest 3170	epoxy	RT-212
FM-300	epoxy	250
HT 435	modified epoxy-phenolic	340
Co-cure	resin	

Bonding the Gr/Ep or Gr/BMI to Rohacell foam can be performed after the composite has been cured or as a co-curing process. Both room temperature and elevated temperature cure adhesives are available. The elevated temperature cure can be performed in an autoclave or in a heated press. Difficulties are present with both. During an autoclave cure, the corners of the foam tend to get compressed. An autoclave cure at 250°F compressed Rohacell WF71 foam with both 40 psi and 20 psi. In both cases, the corners were excessively compressed. A tool on top of the Gr/Ep would prevent the corner compression from occurring. A third specimen was bonded in a heated press. The foam was compressed slightly, but the compression was uniform.

Table 6: Bonding Procedures

Composite surface
- Lightly grit blast surfaces with 120 grit Al_2O_3 at 40 psi
- Clean surface with ethyl alcohol

HRP-3/8-2.5 drill core
- Heat for 1 hour at 220°F in air
- Clean surface by blowing air across it
- During elevated temperature cure, drop pressure to zero for approximately 15 sec after attaining maximum temperature and pressure

PR 1664
- Heat the catalyst to 120°F
- Place adhesive in a vacuum to eliminate air
- Cure at room temperature with 10 psi for 24 hours

EA 9394
- Mix 100 units of part A and 17 units of part B by weight at room temperature
- Total weight should be less than 450 g to reduce heat buildup
- Pot life is approximately 90 minutes (450 g)
- Cure at room temperature for 8 hours with 15 psi

Crest 3170

- Mix equal parts by weight of constituents A and B
- Total weight should be less than 450 g to ensure pot life
- Mix until entire quantity is uniformly creamy
- Average working life is 2 hours at room temperature
- Apply adhesive to both surfaces approximately 5 mils thick
- Cure for 1 hour at 100°C with 10 psi
- Post cure for 1 hour at 100°C

FM-300

- Ramp temperature to 250°F in 30 min. while maintaining 40 psi
- Cure at 250°F for 90 min with 40 psi
- Use thermocouple to monitor bondline temperature

HT-435

- Cut patterns of the adhesive before removal of the protective covering
- Apply adhesive film smoothly to the surface
- Ramp temperature to 340°F in 40 minutes while maintaining 40 psi
- Hold for 40 minutes at 340°F and 40 psi
- Use thermocouple to monitor bondline temperature

Multiple combinations of facesheets and core material were studied. The different facesheets used were Gr/Ep (IM7/977-2), Gr/BMI (IM7/5260) stainless steel (SS), and Al. In the case of the composite materials, the material was 8 plies thick with a $[+45/0/-45/90]_s$ layup. The core materials considered were Ti honeycomb, Hexcel HRP-3/8-2.5 honeycomb, Nomex paper honeycomb, and Rohacell foam. The Hexcel HRP-3/8-2.5 honeycomb (3/8 in. cell size and 2.5 lb/ft^3 density) is referred to as "drill core" since 0.09-in-diameter holes were drilled into each cell prior to expanding the honeycomb. The different adhesives, facesheets, and core materials are listed in Table 7, with a check mark indicating the combinations that were tested.

Table 7: Adhesives, Facesheets, and Core Materials Used in Adhesive Study

Facesheet/Core	EA 9394	PR 1664	Crest 3170	FM 300	HT 435	Co-cure
Gr/Ep						
Ti		√	√		√	
HRP	√	√	√	√	√	
WF71	√	√		√	√	
Nomex	√	√		√		
Gr/BMI						
Ti		√	√		√	
HRP						√
Nomex	√			√	√	
WF71	√			√	√	
Al						
Ti	√	√	√		√	
SS						
WF71	√	√	√			

The flatwise tension tests were conducted in accordance with ASTM C 297-61

(Reapproved 1988), "Standard Test Method for Tensile Strength of Flat Sandwich Constructions in Flatwise Plane". All the specimens were 2 in. x 2 in., which is larger than the minimum size required. ASTM C 297 states that all dimensions shall be in error no more than 0.5%, i.e. 0.01 in. on a 2 in. length. Unfortunately, the tolerances for the specimens and fixtures were not recorded, though visual inspections indicated square corners and a close fit between the fixtures and the specimens. The suggested load rate is such that the maximum load is reached between three and six minutes. A load rate of 200-400 lb/min was used, which depending on the bond strength, resulted in average failures of three to six minutes.

Gr/Ep Facesheets with Rohacell Foam Core

Rohacell WF 71 foam was sandwiched between two 7 in. x 7 in. sheets of Gr/Ep for use in the specimens. The foam was dried according to the manufacturer's specifications prior to bonding. The weights of the foam, facesheets, and final 7 in. x 7 in. piece are shown in Table 8. The two specimens with the room temperature cure adhesives (PR 1664 and EA 9394) were bonded using dead weights. The two specimens with elevated temperature cure adhesives (FM 300 and HT 435) were bonded in a press between heated platens, using 15 psi.

As an additional test, an optical fiber was inserted between one of the facesheets and the foam to determine the survivability of the fiber during later testing. The section with the fiber embedded between the facesheet and the foam was first cut off, and then nine 2 in. x 2 in. specimens were cut from the remaining portion of the sample. The total weight also includes the weight of the optical fiber.

Table 8: Weights of Specimen Components Used for Adhesive Comparison

	PR 1664	EA 9394	FM 300	HT 435
Foam before drying, g	72.98	70.88	68.25	74.89
Foam after drying, g	71.80	69.73	67.03	73.56
Facesheet 1, g	49.34	50.12	50.49	49.82
Facesheet 2, g	49.63	49.79	49.45	49.62
Total weight after bonding, g	205.64	209.02	190.80	196.44
Thickness prior to bonding, in.			1.125	1.125
Thickness after bonding, in.			1.082	1.083
Applied pressure, psi			15	15

Nine 2 in. x 2 in. specimens were cut from each 7 in. x 7 in. specimen. Three foam Gr/Ep specimens with each adhesive were first cooled with LHe. The specimens were placed in a dewar and cooled with gaseous helium/frozen air. After the air evaporated, the specimens were covered with LHe. After the LHe evaporated and the specimens warmed back to room temperature, the specimens were cooled with gaseous helium, and later with LN2. A second set of twelve specimens was heated for ten 20 min. cycles from room temperature to 250°F. A third set of twelve samples was not heated, and served as controls. After the thermal conditioning, the Gr/Ep Rohacell foam specimens were bonded to 2 in. x 2 in. Al fixtures with EA9394 adhesive.

After the specimens were bonded, they were stored in plastic zip-lock bags with moisture absorbing desiccant to keep the foam from absorbing moisture. Prior to testing, the specimens were placed in an oven at 140°F for two days to ensure no moisture was present in the foam.

The specimens were tested in the 22 kip machine in the Thermal Structures Lab at NASA Langley Research Center at room temperature. Universal joints were used on both ends of the specimens to help ensure a normal force to the bonded surfaces. The load was increased at a rate of 200 lb/sec, and the specimens were pulled until failure.

The ultimate flatwise tensile stress of each specimen is shown in Figure 3 for each adhesive and each thermal conditioning. The adhesives are displayed in the order EA9394, FM300, PR1664, and HT435. The adhesive designation is indicated above the middle of the three values for each adhesive. In each case, ovals are drawn grouping the data from each adhesive. One of the PR1664 specimens with no pre-conditioning disbonded between the Gr/Ep and the Al fixture, and thus no data was obtained for that specimen.

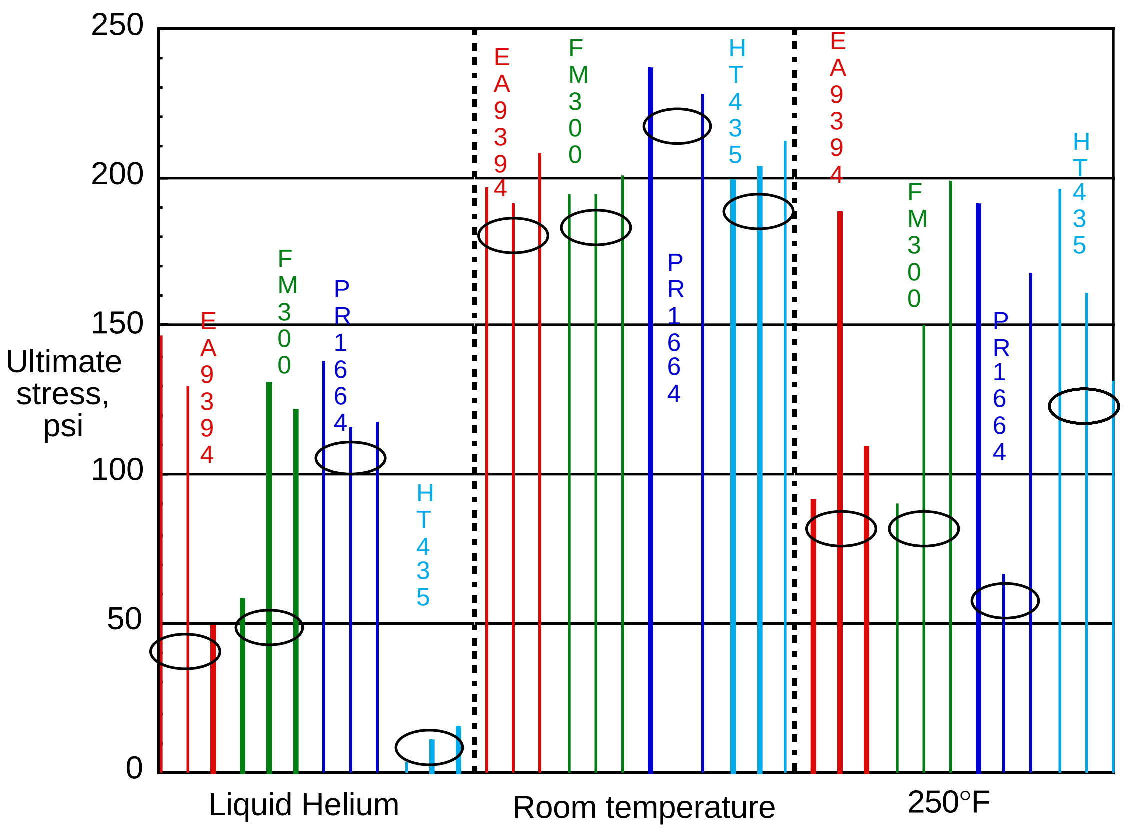

Figure 3: Ultimate stress of Rohacell WF71 foam bonded to Gr/Ep with four different adhesives and three different pre-conditionings tested at room temperature.

The most significant result from the tests is that the HT435 adhesive appeared to be very weak after exposure to LHe. Each of the adhesives performed best with no thermal conditioning. The second best performance was obtained with the 250°F pre-conditioning. The LHe pre-conditioning had the most effect on the ultimate stress of the bonds. In none of the cases did the specimens fail only in the interior of the foam. In all cases, there was failure at the interface of the foam and the adhesive. This seems to indicate an adhesive failure rather than a foam failure.

The failure mechanism for the LHe pre-conditioned HT435 specimens was quite different from the other specimens. The failure was very slow, as the adhesive seemed to "stretch" prior to failure. All the other specimens failed very quickly, in a brittle failure mode. The foam also failed differently in different types of specimens. It is anticipated that the foam failed after the adhesive failed. In some specimens, the foam failure was in a plane nearly perpendicular to the applied load. In other specimens, there was not one single plane of failure for the foam.

The tensile strength of the Rohacell 71WF foam is stated by the manufacturer to be approximately 400 psi. The highest results obtained here were around 200 psi. The tensile strength of the adhesives should be greater than the 400 psi of the foam. The tensile strength of the FM-300 adhesive is given as 1240 psi at room temperature. However, when the FM-300 is used to bond honeycomb, a peel strength rather than a tensile strength is used and it is stated to be 17 in-lb/in. The tensile strength for bonding Rohacell foam, since it is a closed cell porous material, should fall somewhere between the 1240 psi for solid materials and the reduced values (peel strength) for honeycomb material.

Gr/BMI Facesheets with Rohacell Foam Core

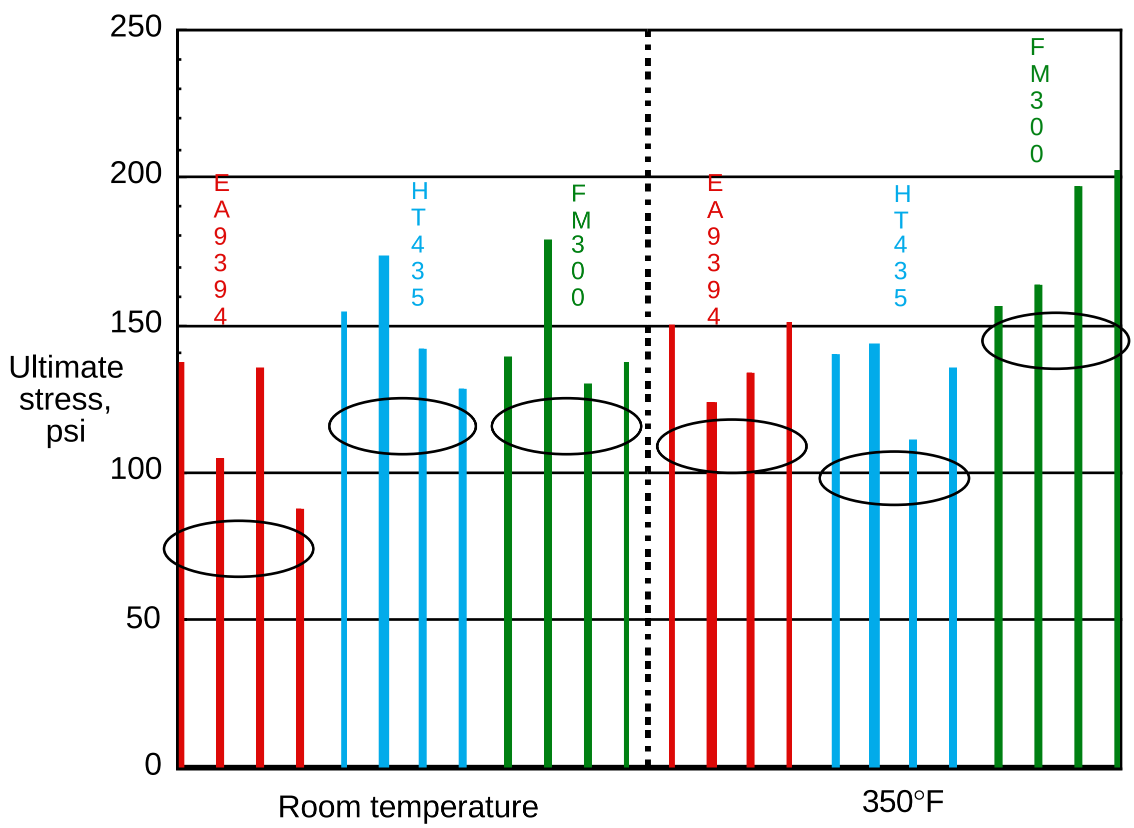

Figure 4: Ultimate stress of Rohacell WF71 foam bonded to Gr/BMI with four different adhesives and two different pre-conditionings tested at room temperature.

Flatwise tension tests were also performed with the Rohacell foam bonded to Gr/BMI facesheets. The BMI matrix has a higher use temperature than the epoxy, and thus may be used for the outer facesheet of the cryotank. As with the Gr/Ep Rohacell foam specimens, each 2 in. x 2 in. specimen was cut from a larger panel. All of the specimens with one kind of adhesive were cut from the same panel. Due to the higher use temperature of the BMI, these specimens were heated to 350°F prior to testing, compared with the 250°F pre-heating of the Gr/Ep specimens. The PR 1664 adhesive has an upper use temperature limit below the use temperature of the Gr/BMI, and thus they would not be used together. Therefore, no tests were performed using the PR 1664 adhesive with the Gr/BMI. The ultimate stress is shown in Figure 4 where the EA 9394, FM 300, and HT 435 adhesives are used. One third of the specimens were heated from room temperature to 350°F and held for 20 min. for a total of 10 cycles prior to testing. One third of the specimens were dunked in LHe prior to testing. The remaining third received no thermal conditioning prior to testing. All the thermal conditioning was performed prior to bonding the specimens to the Al fixtures using the EA 9394 adhesive.

The ultimate stress of the Rohacell foam bonded to the composite facesheets was less effected by the elevated temperature pre-conditioning with the Gr/BMI (Figure 4) than with the Gr/Ep (Figure 3). In Figure 4, the EA 9394 and FM 300 adhesives appear to be slightly stronger after exposure to 350°F, and the HT 435 appears to be slightly weaker after exposure to 350°F. However, the variation between the heated samples and controls is not as significant as with the Gr/Ep facesheets.

Gr/Ep and Gr/BMI Facesheets with Nomex Honeycomb Core

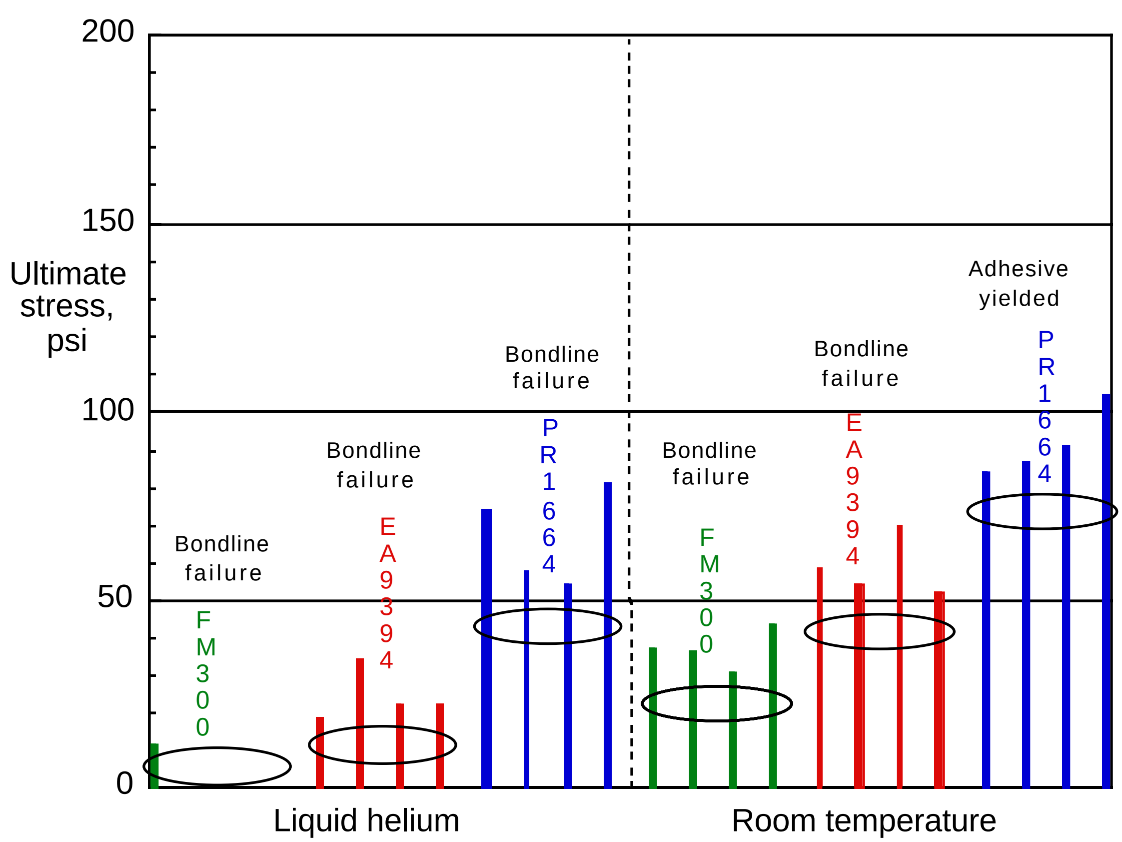

Figure 5: Ultimate stress of Nomex paper honeycomb bonded to Gr/Ep with three different adhesives and two different pre-conditionings tested at room temperature.

Flatwise tension tests were also performed using a Nomex paper honeycomb. The honeycomb is produced by Hexcel and has an upper use temperature of approximately 300°F. As with the Rohacell foam core, both Gr/Ep and Gr/BMI facesheets were used for the tests. For the Gr/Ep facesheets, the HT 435 adhesive was not evaluated since it had previously been shown to be very weak after exposure to LHe temperatures. For the Gr/BMI tests, the PR 1664 adhesive was not tested due to its reduced temperature capability compared to the Gr/BMI. As before, a portion of the specimens were thermally conditioned prior to testing at room temperature. Figure 5 shows the ultimate stress for each adhesive with the Nomex honeycomb core and Gr/Ep facesheets, while Figure 6 shows the ultimate stress for each adhesive with the Nomex honeycomb core and Gr/BMI facesheets.

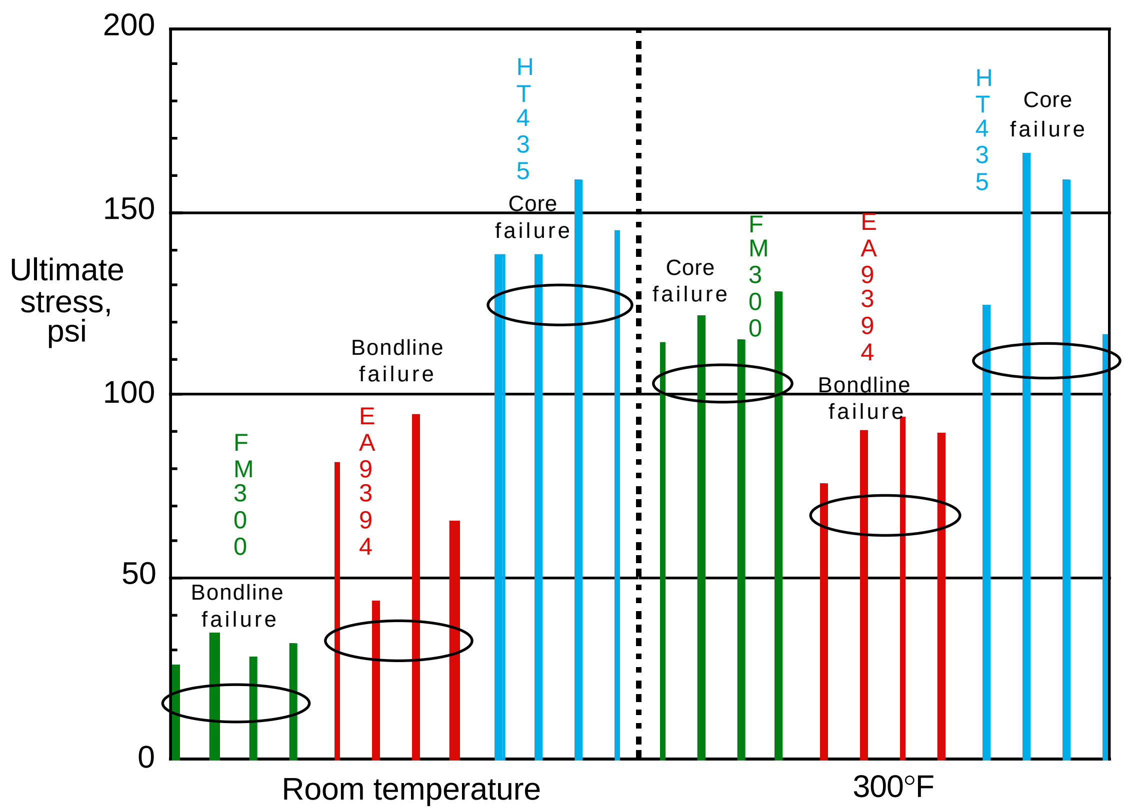

Figure 6: Ultimate stress of Nomex paper honeycomb bonded to Gr/BMI with three different adhesives and two different pre-conditionings tested at room temperature.

In the testing with the Rohacell foam, it was difficult to determine whether the failure was a core failure or an adhesive failure since the failure included both the bondline and the foam in nearly all cases. However, with the honeycomb, it was quite obvious whether the failure was a core or bondline failure. The PR 1664 adhesive, which was tested with Gr/Ep but not Gr/BMI, yielded in the tests shown in Figure 5. As shown in both Figure 5 and Figure 6, the FM 300 adhesive that was not heat treated, i.e., room temperature controls, had a very low strength. The FM 300 adhesive was cured by placing the sandwich material between heated surfaces of a press. The samples that had been pre-conditioned by heating to 300°F had a bondline stronger than the core. The room temperature and 300°F specimens in Figure 6 both were cut out of the same panel. It is suspected that the FM 300 was not cured at the correct temperature, and the thermal cycling prior to testing helped complete the cure of the adhesive, resulting in the higher bond strength. The HT 435 adhesive, bonded to the Gr/BMI, was stronger than the honeycomb core for both the room temperature controls and the specimens that were pre-heated for 10 cycles to 300°F. Even though the contact surface area for the honeycomb is much less than the Rohacell foam, the strength of the HT 435 with the honeycomb is in the same range as with the Rohacell foam.

Gr/Ep Facesheets with HRP Drill Core

Gr/Ep facesheets were also evaluated with Hexcel HRP-3/8-2.5 drill core. The core was obtained with 0.09-in. diameter holes drilled in the cells of the core. The drill core was fabricated for a commercial company on a special order, and some of the excess core was obtained for this testing.

Four samples were tested for each adhesive at each thermal conditioning. The adhesives were room temperature cure EA 9394, PR 1664, and Crest 3170, and elevated temperature cure FM 300 and HT 435. One third of the specimens were dunked in LHe four times and held for approximately 5 minutes. After each dunking, the samples were allowed to warm back to room temperature. Another third of the samples were cycled between room temperature and 250°F ten times. The remaining samples were not pre-conditioned and served as the controls.

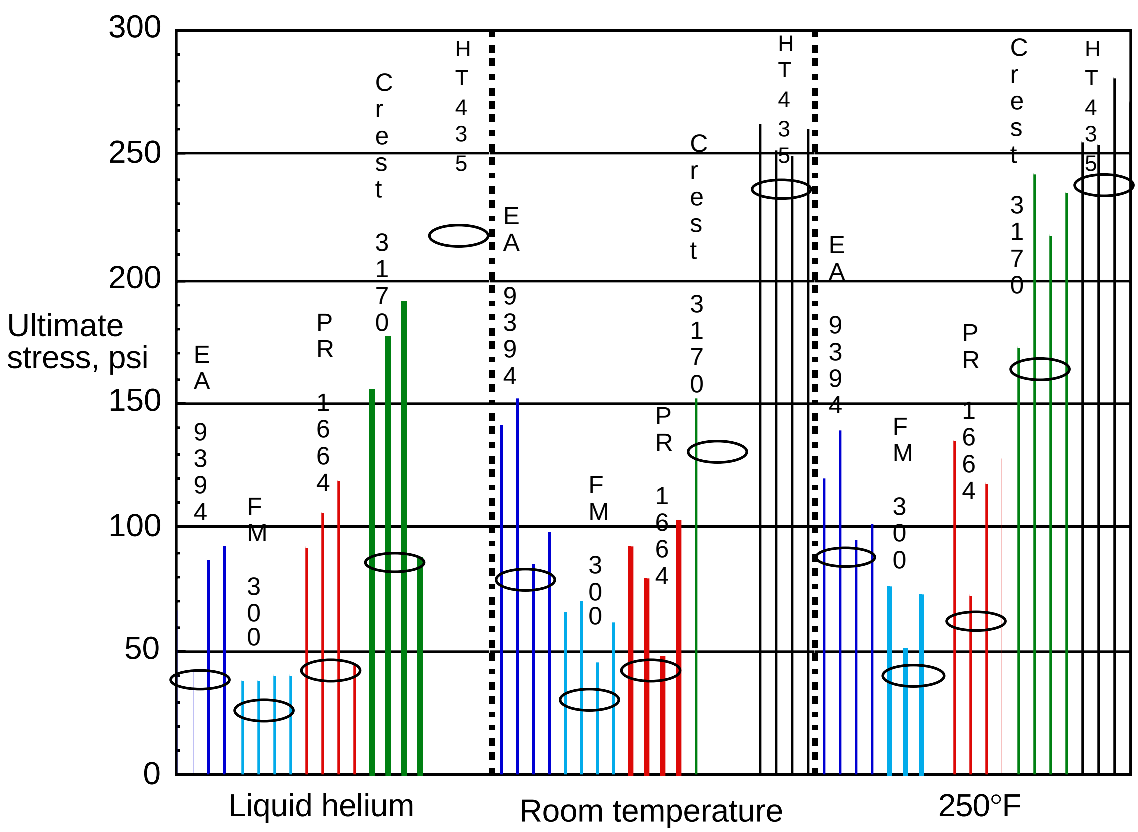

Figure 7: Ultimate stress of HRP honeycomb drill core bonded to Gr/Ep with five different adhesives and three different pre-conditionings tested at room temperature.

Figure 7 shows the ultimate stress of the HRP honeycomb drill core bonded to Gr/Ep with the five different adhesives and three different pre-conditionings. The load rate in all the tests was 3.33 lb/s. From the figure, it is apparent that the Crest 3170 and the HT 435 adhesives performed the best over the range of temperatures. Here, the HT 435 performed very well after thermal cycling in LHe. In earlier tests with Rohacell foam after LHe cycling, the HT 435 adhesive performed very poorly. It is suspected that in the earlier tests, the HT 435 was not cured correctly.

It should be pointed out again that the incorrect mixing ratio, per Crest instructions, was used for the Crest 3170 adhesive. As a result, the adhesive remained tacky after the 24 hour room temperature cure. The adhesive was cured for 1 hour at 100°C with 10 psi and post cured for 1 hour at 100°C. Heat treating the adhesive after the cure eliminated the tackiness of the adhesive, and as can be seen in Figure 7, increased the ultimate stress. It is suspected that using the correct mixing ratio could only help the ultimate stress.

The total displacement prior to failure corresponding to each of the samples is shown in Figure 8. In general, the adhesives that resulted in the highest ultimate stress also showed the highest displacement. The exception is the PR 1664, which is a polyurethane adhesive. One sample with the HT 435 adhesive that was dunked in LHe exhibited a much larger displacement than any of the other samples. The cause of this large displacement is uncertain.

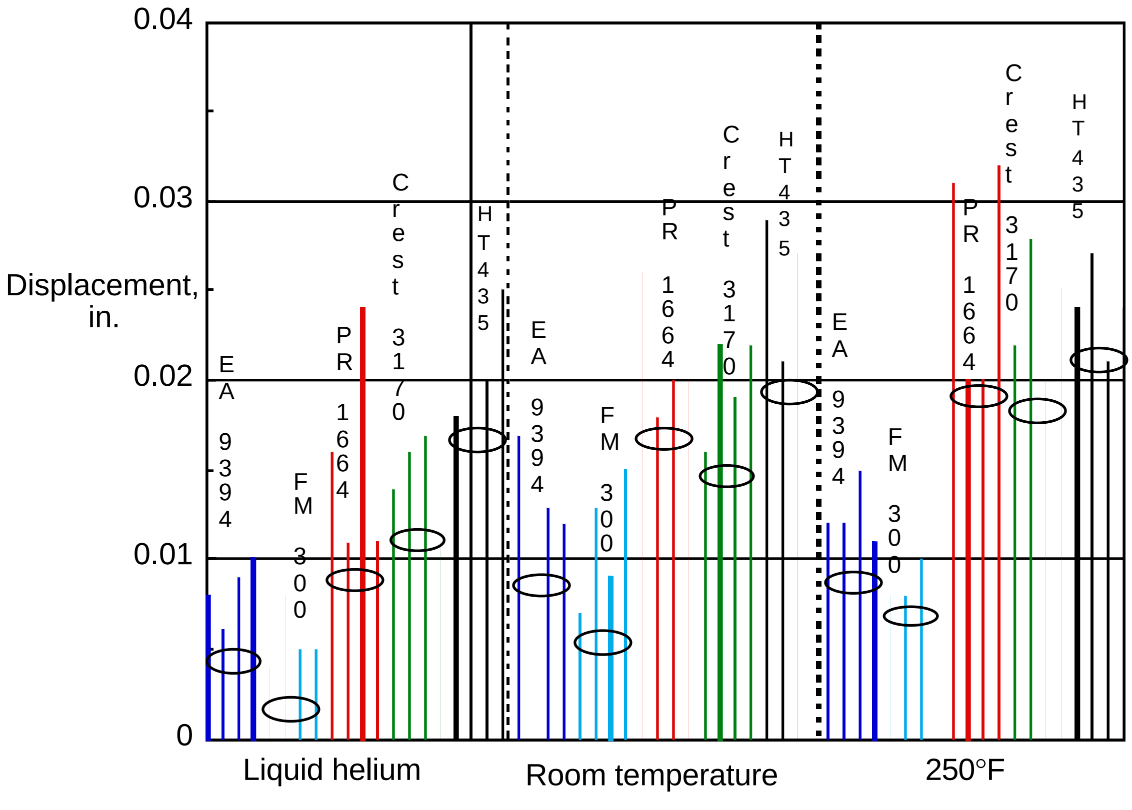

Figure 8: Displacement at failure of HRP honeycomb drill core bonded to Gr/Ep with five different adhesives and three different pre-conditionings tested at room temperature.

Gr/BMI Facesheets with HRP Drill Core

An attempt was made to co-cure Gr/BMI facesheets with HRP drill core. Sixteen 2 in. x 2 in. specimens were obtained. The twelve best specimens were used for the evaluation. On several of the specimens, the Gr/BMI did not appear to be consolidated properly, as delaminations could be seen with the naked eye. In addition, on several specimens, the honeycomb core did not extend to the edges of the samples. The twelve samples that were used for testing were selected such that the above named problems were minimized.

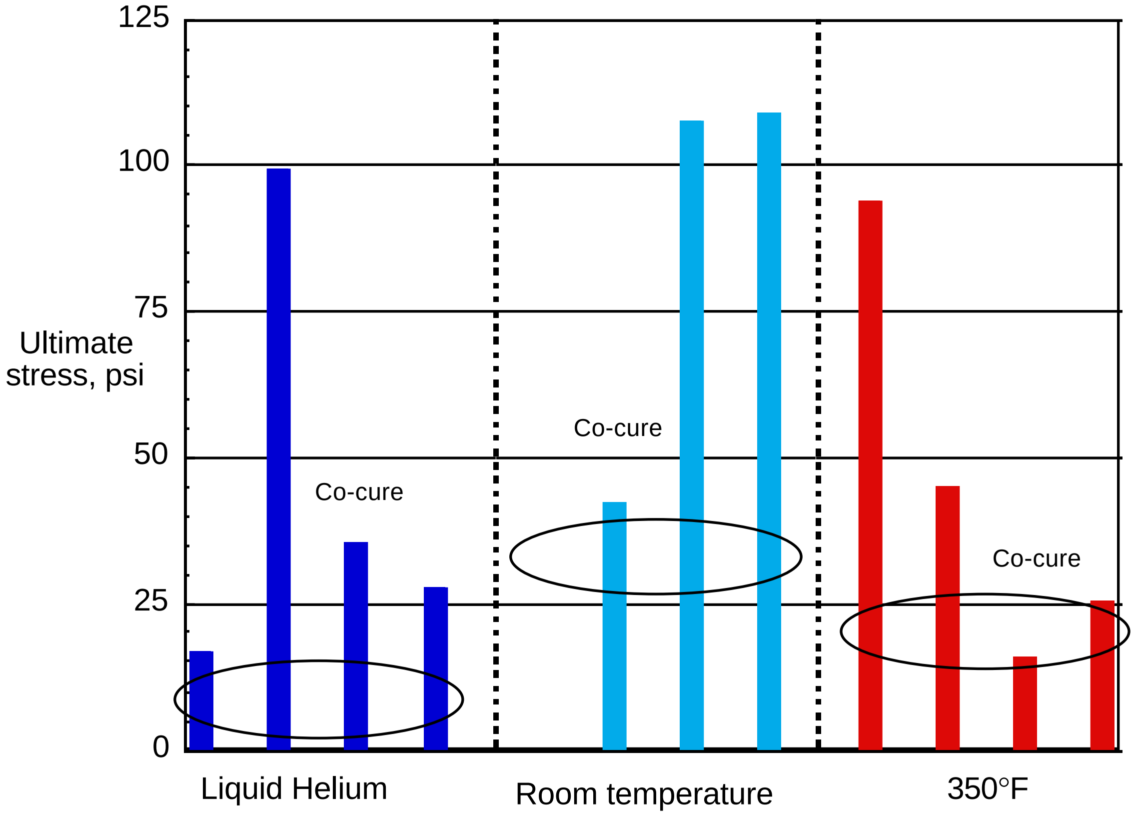

Figure 9: Ultimate stress of HRP honeycomb drill core co-cured with Gr/BMI with three different pre-conditionings tested at room temperature.

Four of the samples were cycled between room temperature and LHe for five 5 min. cycles, four of the samples were cycled between room temperature and 350°F ten times, and the remaining four samples were used as controls. The times for the heating at 350°F are shown in Table 9.

After the specimens were thermally conditioned, they were bonded to Al fixtures with EA 9394 adhesive and tested. One of the room temperature control specimens experienced a disbond between the facesheet and honeycomb core prior to testing. The results of the testing are shown in Figure 9.

Table 9: Heating Times at 350°F for Gr/BMI Facesheets with HRP Drill Core

Cycle	Time, min.
1	20
2	20
3	20
4	30
5	21
6	36
7	48
8	39
9	20
10	25

Gr/Ep Facesheets with Titanium Core

Several adhesives were evaluated for bonding Gr/Ep facesheets to titanium honeycomb core. The Ti honeycomb core consisted of rectangular cells with a 3/8 in. cell size. The adhesives that were tested were EA 9394, Crest 3170, PR 1664, and HT 435. The FM 300 was not tested due to its low performance in previous tests.

The Ti honeycomb core must be cleaned prior to bonding. The procedure for cleaning the Ti is shown in Table 10. After cleaning, the Ti must be bonded very quickly (within several hours) or a primer must be put on the bonding surfaces. All of the specimens here were bonded within a few hours of cleaning. However, to also evaluate the primers, a primer was put on several of the samples.

Table 10: Procedure for Cleaning Titanium

1. Preclean with acetone and general purpose cleaner and rinse.
2. Rinse 10-20 sec. in a solution of
   - H_2O 50%
   - HNO_3 45%
   - HF 5%
3. Rinse in water
4. Dip in either ethyl or isopropyl alcohol
5. Dry with forced hot air
6. Package in brown paper

One third of the specimens were dunked in LHe for five 5 min cycles, warming up in a room temperature environment for 5 minutes between dunks in LHe, one third of the samples were cycled between room temperature and 250°F ten times, and the remaining samples were used as controls. The heating cycle times at 250°F are given in Table 11.

After the specimens were thermally conditioned, they were bonded to Al fixtures with EA 9394 adhesive and tested. The testing was performed at a load rate of 400 lb/min and the results are shown in Figure 10. The PR 1664 adhesive performed the worst of the adhesives tested. The HT 435 adhesive produced, on average, the highest strengths. The Crest 3170, though not a strong as the HT 435, consistently outperformed the PR 1664.

Table 11: Heating Times at 250°F for Gr/Ep Facesheets with Titanium Core

Cycle	Time, min.
1	20
2	202
3	20
4	20
5	20
6	20
7	70
8	20
9	20
10	20

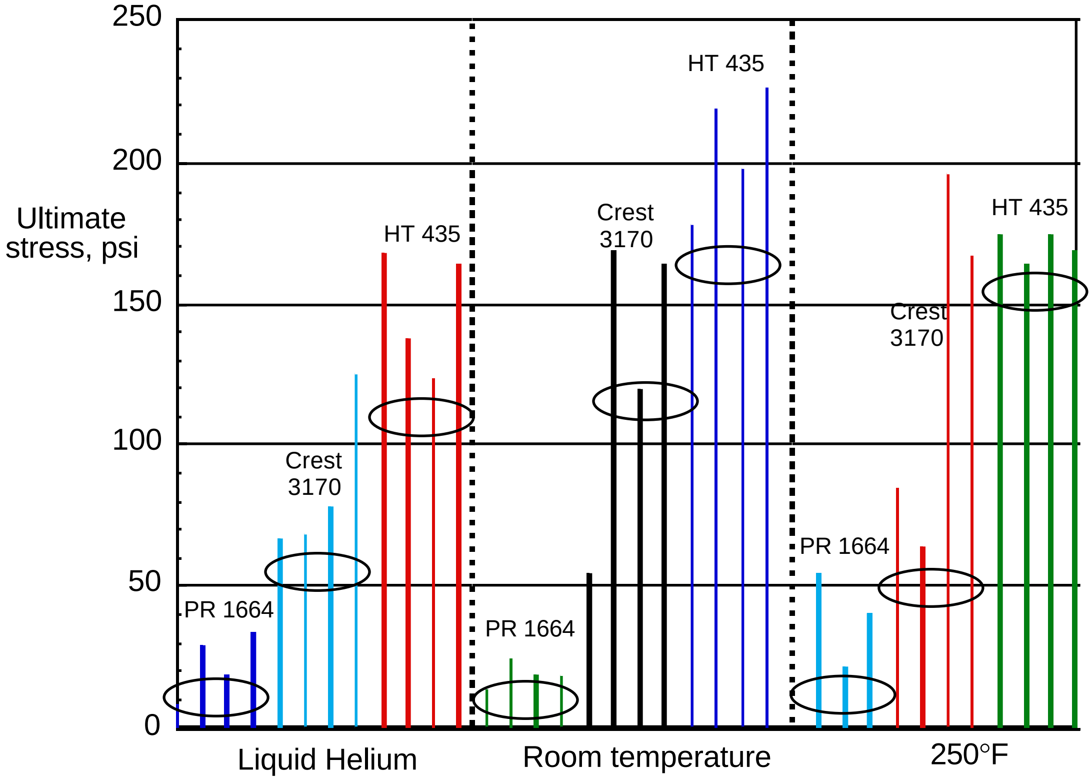

Figure 10: Ultimate stress of Ti core bonded to Gr/Ep with three different adhesives and three different pre-conditionings tested at room temperature.

Gr/BMI Facesheets with Titanium Core

Several adhesives were evaluated for bonding Gr/BMI facesheets to titanium honeycomb core. For these tests, a Hysol primer was used on the Ti prior to bonding with the HT 435. The purpose of the primer was to protect the Ti after it had been cleaned. Though the use of the primer would relax the necessity of bonding the Ti within a few hours of cleaning, it was bonded within a few hours. The Ti honeycomb core consisted of rectangular cells with a 3/8 in. cell size. One third of the specimens were dunked in LHe for five 5 min cycles, warming up in a room temperature environment for

5 minutes between dunks in LHe, one third of the samples were cycled between room temperature and 350°F ten times, and the remaining samples were used as controls. The heating times at 350°F are the same as those given in Table 9.

After the specimens were thermally conditioned, they were bonded to Al fixtures with EA 9394 adhesive and tested. The specimens were tested with a load rate of 400 lb/min, and the results are shown in Figure 11. As in many of the previous tests, the HT 435 adhesive resulted in the highest ultimate stress. The PR 1664 strength was far below the other two adhesives for all temperature cases.

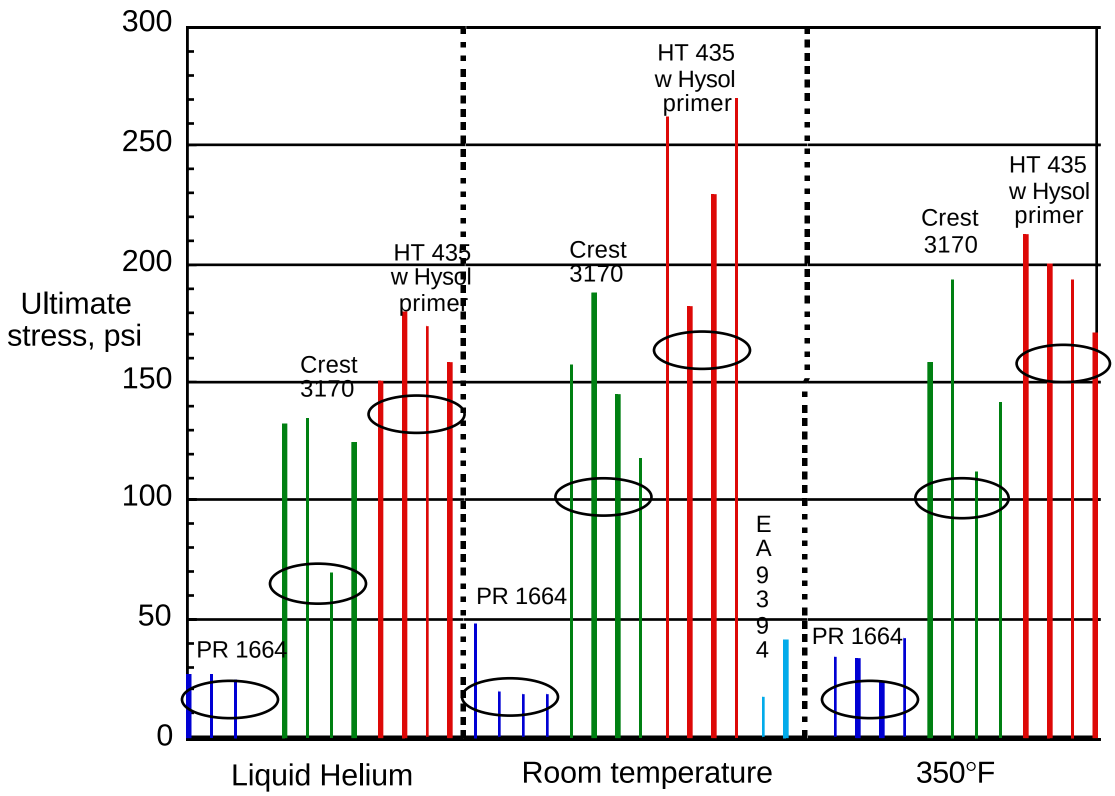

Figure 11: Ultimate stress of Ti core bonded to Gr/BMI with three different adhesives and three different pre-conditionings tested at room temperature.

Aluminum Facesheets with Titanium Core

Several adhesives were evaluated for bonding aluminum facesheets to titanium honeycomb core. The Ti honeycomb core consisted of rectangular cells with a 3/8 in. cell size. Four pieces of honeycomb core and eight Al facesheets were cut into 7 in. x 9 in. sections. The Al and Ti were cleaned prior to bonding according to the procedures given in Table 10 and Table 12. After the cleaning, the sandwich panels were bonded together within a few hours. No primer was used in the bonding. Due to the need to bond the specimens quickly, the Crest 3170 was cured at 212°F for 1 hour instead of at room temperature. The EA 9394 adhesive was cured at 125°F for 2.5 hours in order to meet the time constraints. Both of these elevated temperature cures are recommended by the manufacturers for faster curing.

Table 12: Procedure for Cleaning Aluminum

1. Preclean with acetone and general purpose cleaner and rinse.
2. Rinse 1-2 min. in Aluminetch #2 (7 oz/gal), followed by 10 sec immersion in

H_2O	50%
HNO_3	45%
HF	5%

3. Rinse in water
4. Dip in either ethyl or isopropyl alcohol
5. Dry with forced hot air
6. Package in brown paper

One third of the specimens were dunked in LHe for five 5 min cycles, warming up in a room temperature environment for 5 minutes between dunks in LHe, one third of the samples were cycled between room temperature and 350°F ten times, and the remaining samples were used as controls. The time at LHe temperatures varied somewhat due to the difficulty in dunking specimens in LHe. In most of the five cycles, the specimens were cooled to LHe temperatures and then slowly allowed to warm. In general, after approximately 5 minutes, the samples had warmed up to the LN2 temperature range. The heating cycle times at 350°F are given in Table 13**.**

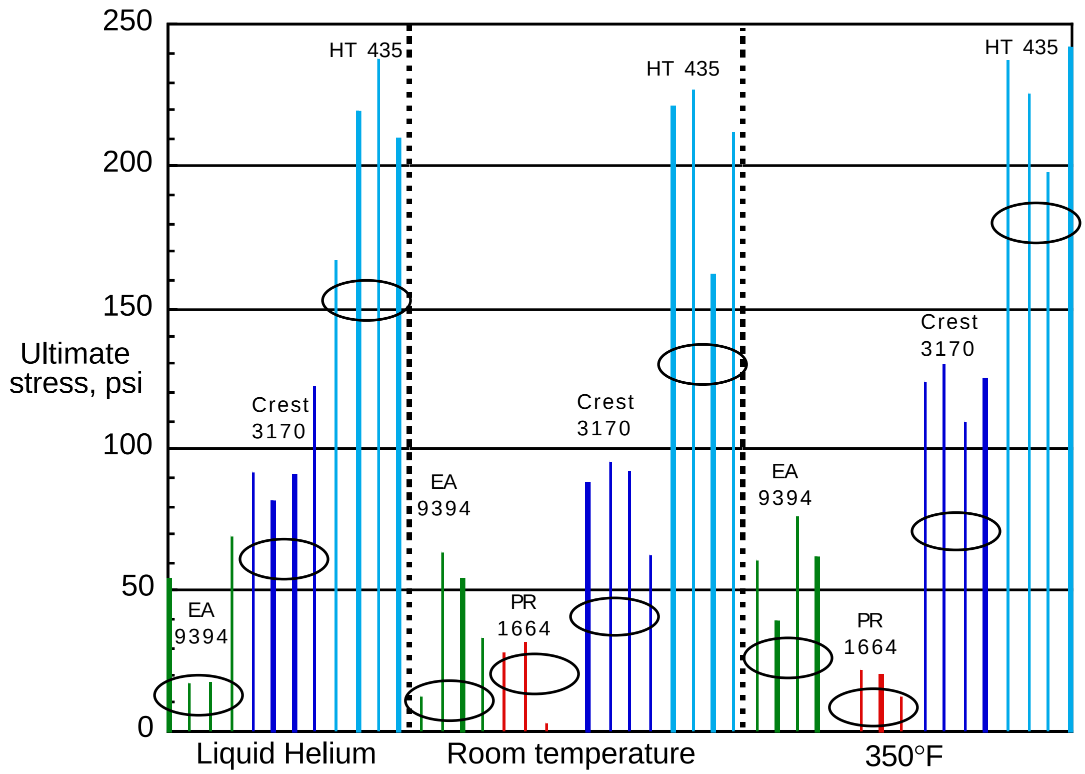

Figure 12: Ultimate stress of Ti core bonded to Al with three different adhesives and three different pre-conditionings tested at room temperature.

After the specimens were thermally conditioned, they were bonded to Al fixtures with EA 9394 adhesive and tested. Again the HT 435 produced the strongest bonds, with the Crest 3170 next, followed by EA 9394 and PR 1664. In many of the samples, the PR

1664 bondline failed at the Al interface, and not the honeycomb. A film of the PR 1664 remained attached to the Ti core. After the specimens were dunked in LHe, the PR 1664 bonded specimens all failed prior to bonding to the fixtures. The adhesive remained bonded to the Ti core, but disbonded from the Al facesheet.

Table 13: Heating Times at 350°F for Aluminum Facesheets with Titanium Core

Cycle	Time, min.
1	33
2	38
3	27
4	23
5	21
6	35
7	34
8	26
9	25
10	30

Stainless Steel Facesheets with Rohacell Foam Core

Several adhesives were evaluated for bonding stainless steel (SS) facesheets to Rohacell foam core. Three pieces of Rohacell foam core and six SS facesheets were cut into 7 in. x 9 in. sections. Only three adhesives were studied since the application is for bonding the Rohacell foam on the outside of a SS test panel and a room temperature cure adhesive is desired. The adhesives that were tested were EA 9394, Crest 3170, and PR 1664. The correct ratio of 1:1 was used for the two parts of the Crest 3170 for this test. The SS was cleaned prior to bonding according to the procedure given in Table 14. After the cleaning, the sandwich panels were bonded together within a few hours. No primer was used in the bonding.

Table 14: Procedure for Cleaning Stainless Steel

1. Preclean with acetone and general purpose cleaner and rinse.
2. Rinse 30 sec. in a solution of
   - H_2O 50%
   - HCl 50%
3. Rinse in water
4. Dip in either ethyl or isopropyl alcohol
5. Dry with forced hot air
6. Package in brown paper

Rohacell WF 71 foam was used for the testing. The foam was not heat treated or dried and no attempt was made to keep the foam dry. Heat treating the foam increases its compressive strength. The application for the foam here is as a cryogenic insulation on the external surface of a SS test panel. Since the compressive strength is unimportant in this application, and since keeping the foam dry during the entire fabrication process greatly increases the complexity, no attempt was made to keep the foam in the specimens dry.

One third of the specimens were dunked in LHe for five 5 min cycles, warming up in a room temperature environment for 5 minutes between dunks in LHe, one third of the samples were cycled between room temperature and 350°F ten times, and the remaining samples were used as controls. The time at LHe temperatures varied somewhat due to the difficulty in dunking specimens in LHe. In most of the five cycles, the specimens were cooled to LHe temperatures and then slowly allowed to warm. In general, after approximately 5 minutes, the samples had warmed up to the LN2 temperature range. The heating cycle times at 350°F are the same as those given in Table 13.

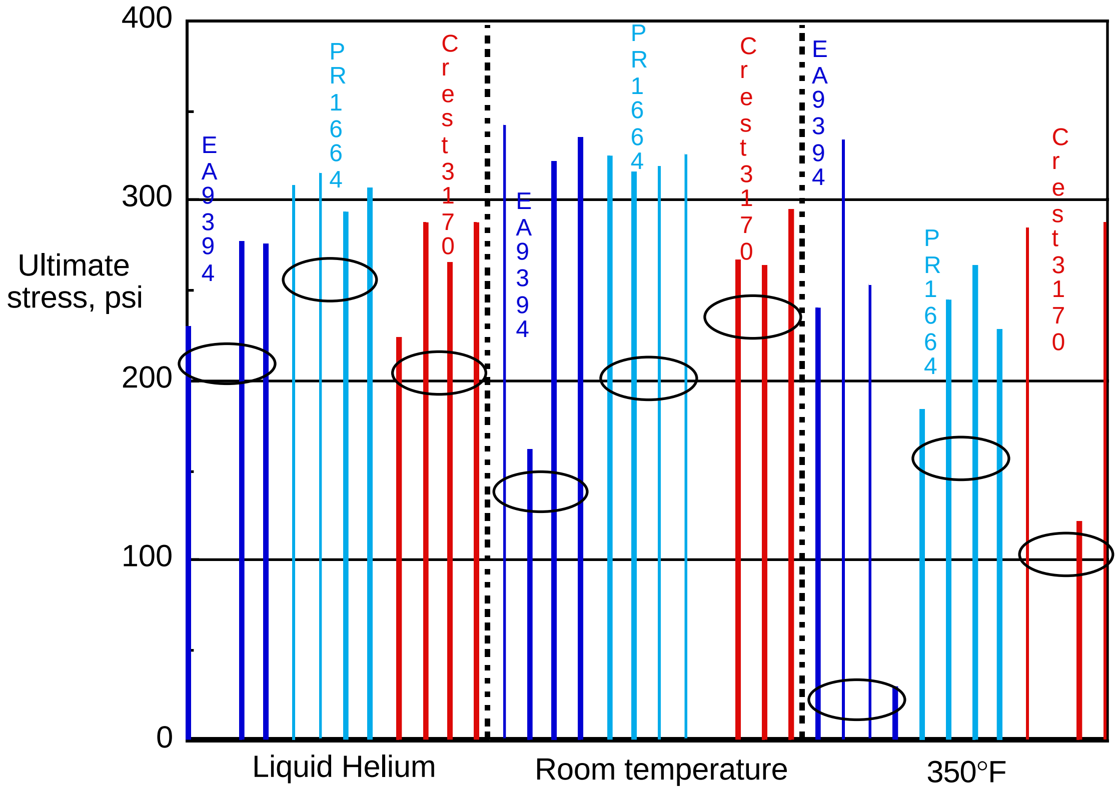

Figure 13: Ultimate stress of Rohacell WF71 foam core bonded to stainless steel with three different adhesives and three different pre-conditionings tested at room temperature.

After the specimens were thermally conditioned, they were bonded to the Al fixtures with EA 9394 adhesive and tested with a load rate of 400 lb/min. The adhesive strength after cycling to 350°F is slightly below the strength of the controls and the LHe dunked specimens, but there does not appear to be significant differences in the strength of the three room temperature cure adhesives.

Concluding Remarks

Two types of tests were performed in support of cryotank development efforts. The first involved fabricating "ravioli" shaped specimens where a foam or honeycomb core was encased in Gr/Ep. An attempt was made to pull a vacuum on the specimens when they were cycled down to liquid nitrogen temperatures. The specimens appeared to leak more as the temperatures were reduced. At liquid nitrogen temperatures, a vacuum could not be maintained and the specimen could only be evacuated to a pressure of approximately 10 torr.

Flatwise tension tests were performed on several combinations of materials being evaluated for cryotank concepts. The adhesives evaluated were PR 1664, EA 9394, Crest 3170, FM-300, and HT 435. From the tests performed, which were all at room temperature, the HT 435 was the superior adhesive. However, it is a 340°F cure adhesive. The best room temperature cure adhesive appeared to be the Crest 3170. Though these tests are incomplete, they do indicate that the HT 435 and Crest 3170 should be further evaluated for cryotank use.

Acknowledgments

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