

MATERIAL ISSUES IN SPACE SHUTTLE COMPOSITE OVERWRAPPED PRESSURE VESSELS

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Composite Overwrapped Pressure Vessels (COPV) store gases used in four subsystems for NASA's Space Shuttle Fleet. While there are 24 COPV on each Orbiter ranging in size from 19-40", stress rupture failure of a pressurized Orbiter COPV on the ground or in flight is a catastrophic hazard and would likely lead to significant damage/loss of vehicle and/or life and is categorized as a *Crit 1* failure. These vessels were manufactured during the late 1970's and into the early 1980's using Titanium liners, Kevlar[®] 49 fiber, epoxy matrix resin, and polyurethane coating. The COPVs are pressurized periodically to 3-5ksi and therefore experience significant strain in the composite overwrap. Similar composite vessels were developed in a variety of DOE Programs (primarily at Lawrence Livermore National Laboratories or LLNL), as well as for NASA Space Shuttle Fleet Leader COPV program.

The NASA Engineering Safety Center (NESC) formed an Independent Technical Assessment (ITA) team whose primary focus was to investigate whether or not enough composite life remained in the Shuttle COPV in order to provide a strategic rationale for continued COPV use aboard the Space Shuttle Fleet with the existing 25-year-old vessels. Several material science issues were examined and will be discussed in this presentation including morphological changes to Kevlar[®] 49 fiber under stress, manufacturing changes in Kevlar[®] 49 and their effect on morphology and tensile strength, epoxy resin strain, composite creep, degradation of polyurethane coatings, and Titanium yield characteristics.

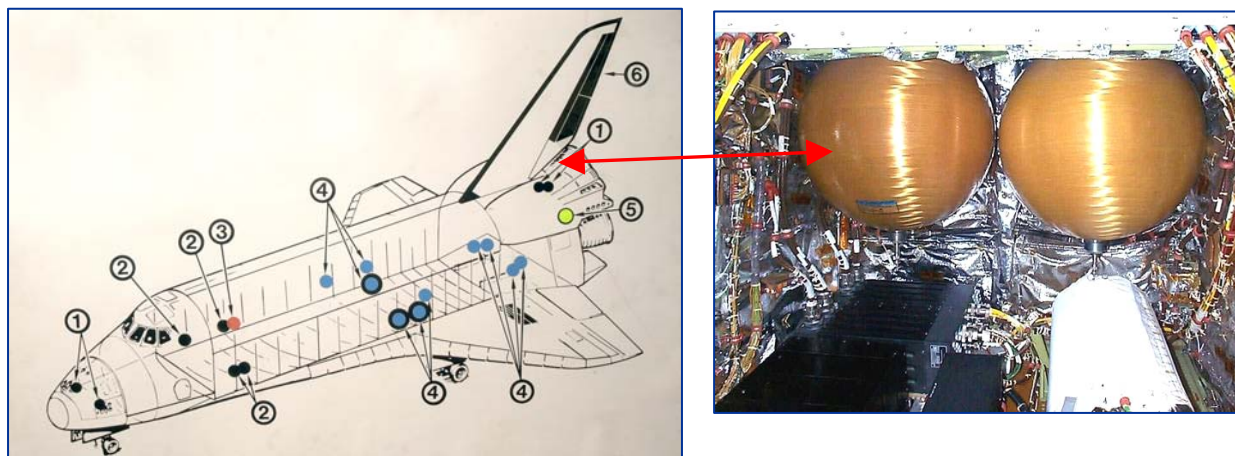


Figure 1. NASA Space Shuttle with placement of COPV

1. Background

The Shuttle program faces recertification of the many COPV distributed throughout various subsystems. The materials used in the COPV consist of Kevlar[®]49 (Figure 2) made by DuPont and an epoxy resin called LRF-092 specifically formulated by Brunswick (General Dynamics) for the filament winding of composite pressure vessels (Figure 3). The liners for the Shuttle vessels were a one-piece titanium alloy (Ti-6Al-4V). Finally, a polyurethane coating was applied to the Kevlar/epoxy shell for moisture and ultraviolet light protection.

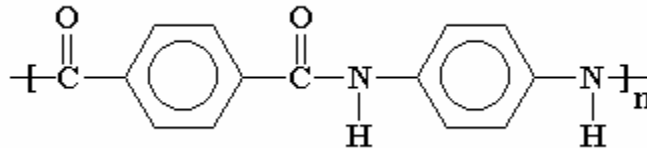


Figure 2. Chemical structure for the polyamide Kevlar[®]

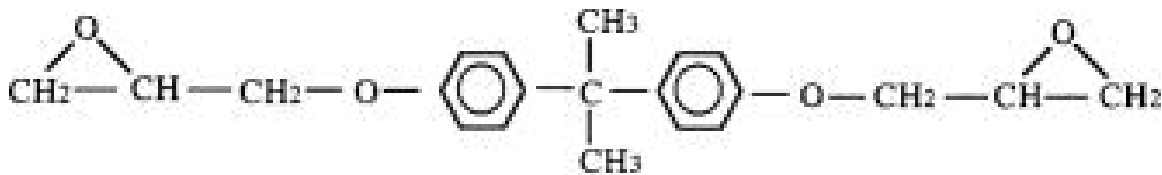


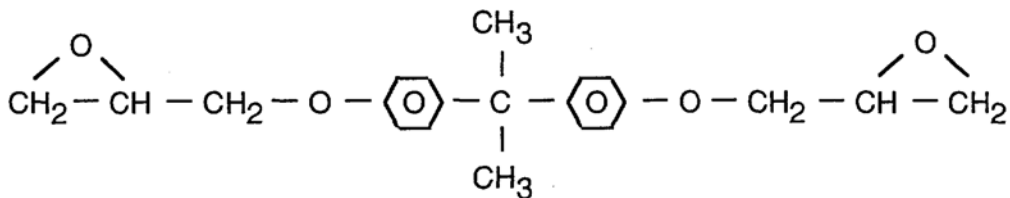
Figure 3. LRF-092: Diglycidyl Ether of Bisphenol A (Shell Epon 828)
Curing Agents: Nadic Anhydride and Benzyltrimethylamine

Originally, the Shuttle COPV were certified for 10 years. The certification extended to 20 years and is under evaluation for further extension. Rockwell performed the 10-year COPV recertification. At the time of recertification (1988), Rockwell performed three tests that provided enough evidence to grant further certification. A NESC review of these tests describes the results as insensitive. Therefore, the NESC is unable to determine if Kevlar/Epoxy overwrap has aged significantly and is more susceptible to stress rupture. The subsequent 10-year recertification was not performed in 1998.

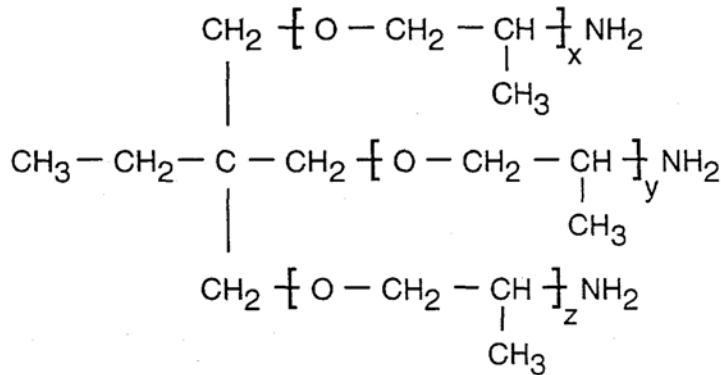
In order to validate the original findings on Kevlar[®]49 stress-rupture, NASA Johnson Space Flight Center (JSC) initiated a COPV “Fleet-Leader” program early in the Shuttle COPV program. The tanks in this fleet-leader program utilize Kevlar[®]49 fiber and construction methods representative of Shuttle COPV, but the program was limited in scope to COPV that are not directly representative of specific Shuttle Subsystem COPV. This fleet-leader program tests tanks at nominal ambient temperature and tanks tested at an elevated temperature (~175 °F). The purpose of the elevated temperature testing was to “accelerate” the degradation process. The materials in the fleet leader program consisted of aluminum liner (Al 5086), Kevlar[®]49 fiber and the same epoxy (LRF-092) used in the shuttle vessels. These COPV were pressurized using water.

Another Kevlar[®]49/epoxy COPV program performed at Lawrence Livermore National Labs provides an additional comparison for the shuttle COPV. The materials in these COPV are Kevlar[®]49, an epoxy called DGEBA T-403 with curing agents that are different from those curing agents shuttle COPV as shown below (Figure 4) and an aluminum liner (Al 1100). The NESC has tried to determine if there is sufficient life remaining in the shuttle vessels. A comparison of the COPV from these three programs was described in a subsequent paper by Grimes-Ledesma et al. This comparison is complicated by the use of different size vessels, different materials, and different liner thicknesses and in some cases (LLNL

COPV) different vintages of Kevlar[®]49 fiber. Moreover, there was/is a lack of COPV samples in the Fleet leader program and the shuttle qualification burst testing to provide a statistically significant predictive capability when determining the life of the shuttle COPV.



Diglycidyl ether of bisphenol A
(SHELL EPON 828)



$$x + y + z \cong 5.3$$

Polyether triamine curing agent
(Huntsman T403)

Figure 4. DGEBA T-403 Epoxy in LLNL COPV

A COPV Materials Team was assembled to provide support for the investigation performed by NESC Independent technical Authority (ITA) of Kevlar COPVs utilized on the Space Shuttle. Members and consultants are as follows:

Dr. James K Sutter, Lead (NASA Glenn)
Dr. Brian J. Jensen (NASA Langley)
Dr. Thomas S. Gates (NASA Langley)
Dr. John C. Thesken (Ohio Aerospace Institute)
Dr. Roger J. Morgan (Texas A&M, consultant)
Mr. Rich Moulton (Applied Poleramics, consultant)
Mr. Dennis Russell (Boeing Radiation Effects Laboratory, consultant)
Dr. Karl Chang (Dupont, consultant)

2. Results of NESC Materials Team Investigation

The NESC Materials team investigation is currently underway. Therefore, the following analyses, findings, and recommendations are preliminary. The COPV material topics include: polyurethane coatings, polymeric resin (epoxy), Kevlar[®]49, environmental effects, accelerated testing for life prediction, evaluation of NASA JSC Fleet Leader data, Kevlar[®]49 creep, differences between the Kevlar[®]49 in LLNL Vessels and Kevlar[®]49 in Shuttle Flight Hardware, significance of calendar life and possible degradation of fiber or matrix on stress rupture likelihood, tracing the heritage of Kevlar[®]49 fiber to the Shuttle Kevlar[®]49/epoxy COPV, and materials testing for long term flight rationale. The following designations F-# and R-# refer to Findings and *Recommendations*, respectively.

2.1 Polyurethane Coating

Analysis:

The polyurethane coatings on the Shuttle COPVs are old and most probably do not provide the intended protective purposes: reduce moisture adsorption and minimize the known degrading effects of ultraviolet light. Boeing and USA are aware of this materials expiration and have codified the coating yellow. This classification was published in Boeing's Use-Life Extension. The polyurethane coating is rated for 20 years minimum under static conditions. A yellow rating does not indicate the material is beyond its age limit. It simply means there is not sufficient data to allow a higher rating. In addition, several photos taken from orbiter COPVs have shown crazing that may indicate polyurethane oxidation.

- F-1 While at NASA JSC White Sands Test Facility in July 2005, the COPV ITA Team inspected the Centaur Kevlar[®]49/epoxy COPVs. These tanks were made after the Shuttle OMS, RCS, MPS, and ECLSS tanks and are 20 years old. It was evident that the polyurethane coating had degraded, as noted by small, brown congealed pools of viscous liquid that had collected in valleys of their Kevlar-49/epoxy overwrap.
- R-1 Further data from inspection of aged materials or the item itself may be warranted to assure these COPV still perform as needed beyond the current documented information.
- R-2 If the Shuttle COPVs are capable of staying in service with no additional work performed on the overwrap, then a procedure to evaluate, treat or recoat the existing COPV should be implemented by Boeing. This treatment would be appropriate if damage can be avoided to these vessels.

2.2 Epoxy Resin

Analysis 1: Potential effect of epoxy resin components on Kevlar-49 fiber

The epoxy matrix resin used to prepare shuttle COPVs was a Brunswick Corp. resin formula *LRF-092*. This formulation uses the diglycidyl ether of bisphenol A (DGEBA) as the base epoxy. Other monomers in this resin formulation are nadic methyl anhydride and benzyldimethyl amine curing agents or catalysts. Mr. Dale Tiller (General Dynamics) provided specific information on this resin. The glass transition temperature (T_g) of this resin is reported to be 265 °F. Dale Tiller reports that this T_g results from a COPV cure temperature of 264 °F. The same resin system has a similar T_g after 10 years of use in radome applications. General Dynamics cites this epoxy's stability using this long-term retention of T_g.

The Materials Team considered whether the methyl nadic anhydride would hydrolyze and form methyl nadic dicarboxylic acid during the epoxy polymerization process. Moreover, if this monomer was converted to the dicarboxylic acid, could it be a strong enough acid to hydrolyze Kevlar? This concern raised questions about one of the post-treatments for Kevlar used to wash sulfuric acid from this fiber. It is known from research performed at LLNL that sulfuric acid is responsible for premature failures of Kevlar fiber and that DuPONT carefully screens batches of Kevlar for trace acid. After discussing this with Richard Moulton [Epoxy expert at Applied Polimeramics], there is no reason to think that even if there was residual methyl nadic acid that this residue is a strong enough acid to hydrolyze Kevlar.

F-1 Degradation of the Kevlar due to components of the LRF-092 is not a concern for re-certification of Space Shuttle Program Kevlar[®]49/Epoxy COPVs.

Analysis 2: Composite Pressure Vessel Epoxy Matrix Resin Cracking

Acoustic emission (AE) plots as a function of increasing pressure showed a well-defined peak at 30% of ultimate pressure vessel burst values for the LLNL Kevlar/Epoxy vessels. An upturn in the AE plot above 90% of ultimate is associated with fiber failure. There is SEM evidence that the cracks initiate by longitudinal fiber fibrillation that subsequently transitions into the resin. At LLNL, proof testing at 70 °C was attempted where the DGEBA-T403 epoxy resin exhibits greater than 30% ultimate strain and no AE peak from resin microcracking is observed. At LLNL, the high temperature proof procedure was not adopted based a lack of apparent change in vessel life. Slow ductile resin crack propagation did not give an AE signal and the scission of the epoxy network segments decreased the ambient resin ductility from near 15% to 5%.

Based on the comments at the White Sands meeting in July 2005, plots of AE signal intensity as a function of increasing pressure were not performed on the NASA COPV'S. Resin cracking would be expected to be significant on the NASA vessels as the NASA nadic anhydride based resin, LRF-092, exhibits only 1/3 the ductility of the DGEBA-T403 (5% vs 15%) at ambient conditions. Earlier, Dale Tiller at General Dynamics noted that the LRF-092 crazes during proof. However, the LLNL COPV were not pressure proofed. Therefore, it is not known if these vessels were crazed before initiating long-term pressurization tests.

F-1 The extent to which the matrix crazing during proof that would minimize the likelihood of Kevlar[®]49 fiber failure is not known.

F-2 In Kevlar[®]49 strand tests, early resin microcracking is not of concern, as the cracks that are parallel to the longitudinal direction of neighboring fibers. But in vessels, off-axis neighboring tows will be exposed to matrix stress raising cracks which can be transverse to the fiber direction. Kevlar[®]49 fractures such that the skin tears away from the core resulting in a various fiber split lengths.¹

¹ Hamstad, M.A., and T.T. Chiao. "A Physical Mechanism for the Early Acoustic Emission in an Organic Fiber Epoxy Pressure Vessel." *SAMPE Quarterly* 5 (2) (1974): 22.

R-1 This effect contributes to decreases in apparent fiber strength would need to be addressed by fracture mechanics modeling.

2.3 Kevlar[®] 49

Analysis 1: Kevlar[®] 49 Fiber and Failure Criteria

An excellent review of Kevlar[®] 49 morphology is presented by Morgan and Allred.² Significant data that highlighted the analyses of Kevlar[®] 49 fiber after long-term aging were also provided by Prof. Roger Morgan at the TIM^{#2} @ NASA JSC on June 23-25, 2004. The review article and presentation are online at the NASA PMBA COPV website. One of the key points in Dr. Morgan's analysis concerns the effect of residual impurities³ in Kevlar[®] 49 and the potential for Kevlar[®] 49 fiber splitting because of its polyamide backbone hydrolysis. These impurities reside at ends of the Kevlar[®] 49 crystallites as shown in Figure 5.

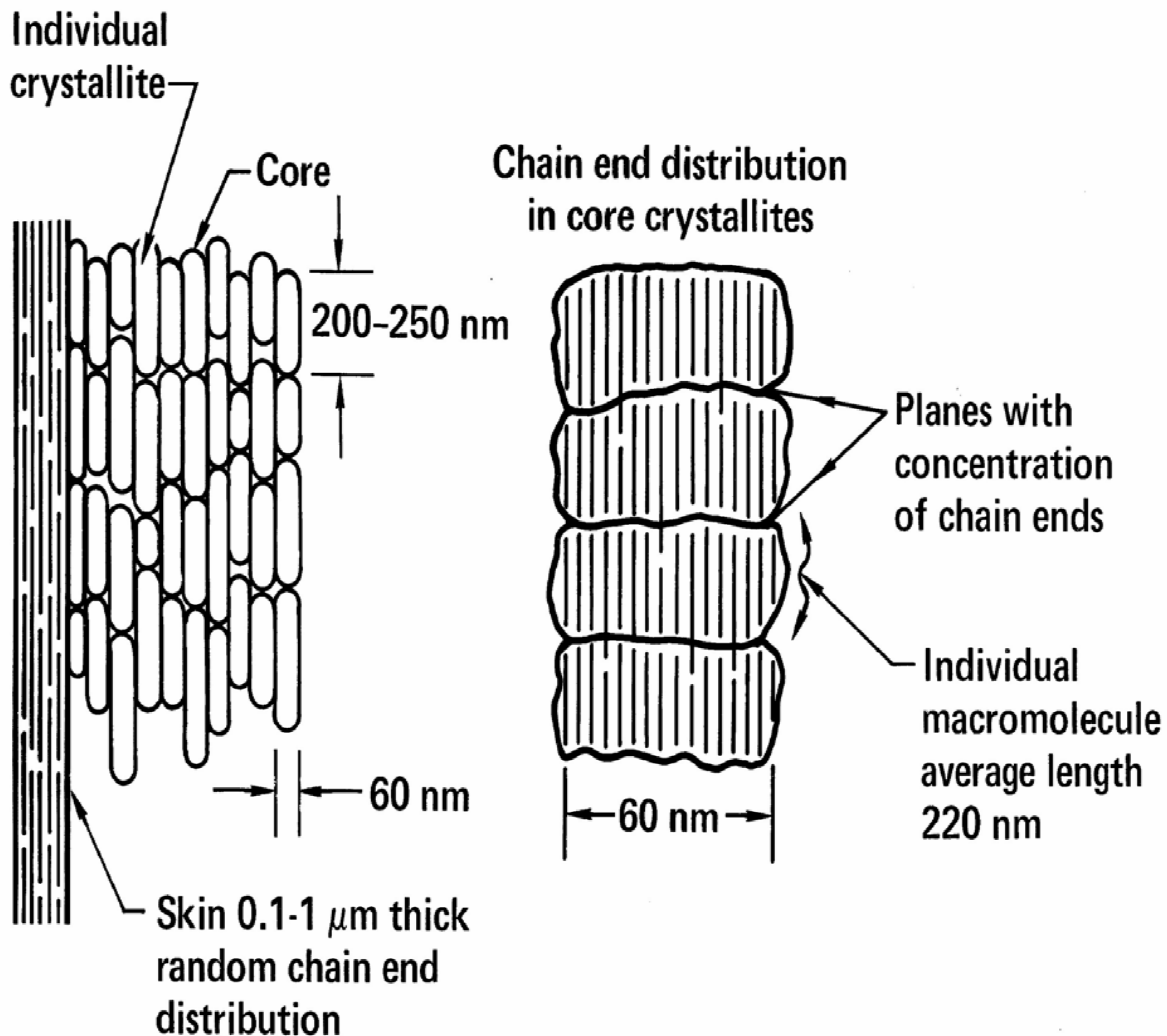


Figure 5. Morphology of Kevlar[®] 49

Hamstad, M.A., and T.T. Chiao, "Structural Integrity of Fiber/Epoxy Vessel by Acoustic Emission." *SAMPE Quarterly* 8 (1) (1976): 31.

² Morgan, Roger J. and Ronald E. Allred. "Aramid Fiber Composites." *International Encyclopedia of Composites*, Stuart M. Lee, Ed. (1990): 37-56.

Dr. Karl Chang provided another in-depth review of Kevlar fiber from DuPONT at the Technical Interchange Meeting (TIM) #1 at NASA White Sands in May 2004. A summary of this review is below in Appendix D-1 and is online at the PMBA-COPV website. It was noted that DuPONT instituted a very good quality control program for their Kevlar®49. These quality control improvements were finalized at DuPONT after the LLNL COPV program was initiated and before the Shuttle COPV production. During a telecom in June 2005, Dr. Chang summarized the quality control measures taken to improve Kevlar®49. A summary of that telecon is provided in Appendix D-1 and is on the PBMA website.

The LLNL program was put in place to monitor Kevlar®49 residual tensile strength after aging. Data on vessel life was also obtained by LLNL and is reviewed in the portion of this ITA led by Lorie Grimes-Ledesma. The Materials Team feels that data from LLNL will help determine if another long-term testing effort, similar to LLNL's, on COPVs, is needed to help predict life in the Space Shuttle Kevlar/Epoxy pressure vessels.

A contract with LLNL that requests a status for the Kevlar®49/Epoxy vessels that have undergone extension aging and testing within their program was performed. Dr. Frank Gerstle is compiling a report on the comparison of LLNL Strand testing. His report will be contained in the COPV team findings compiled by Lorie Grimes-Ledesma. However, this comment on LLNL strand testing was put forward by Dr. Roger Morgan: *“We (LLNL staff) ran the heat age strength tests on a range of the LLNL spools (240 °C, 3hours, in an air circulating air oven).The strength loss range was 0.3 to 7.1%. Any strength loss greater than 10% was considered unacceptable by DuPont. The scientific rational for a 10% strength loss or limit is qualitative.”*

By the time the shuttle COPV were manufactured DuPont had “frozen” the Kevlar®49 manufacturing process. The quality of Kevlar®49 in the Space Shuttle COPV was higher than that of the fiber used in the LLNL vessels. During the maturation of DuPont Kevlar-49 production, complex issues such as relationships between impurity levels and fiber diameter were studied and Karl Chang offers the following information.

F-1 Dr. Karl Chang from DuPONT offered the following information regarding the production of Kevlar®49: There is potential that there could be residual acid or base left in Kevlar®49 strands. These impurities could affect the life of Kevlar®49 by hydrolyzing its polyamide backbone. When the LLNL COPV program was ongoing, DuPont had not finalized the standard operating procedures for Kevlar®49 production. These trace impurities may have caused the low burst values of some of the LLNL COPV.

“There is no quantitative relationship between diameter and neutrality. The neutralization process starts with the polyamide polymer extruded (fiber precursor) in sulfuric acid through spinneret holes into a water bath. When the polymer solution enters the water bath, two things happen, thermal quenching and sulfuric acid diffusing out while water diffuse into the filament. Subsequently, the filaments go into a caustic bath in which NaOH solution is used to neutralize remaining sulfuric acid. So, there is complicated diffusion occurring of water and sulfuric acid, then sulfuric acid and NaOH. Chemical analysis of trace chemicals can detect major problems in neutrality.³ If the fiber has not been neutralized with NaOH, then the level of Na in the fiber is very low and the fiber is acidic. If the fiber is subjected to excess NaOH, then Na level would be high and the fiber would be caustic.

³ Morgan, R.J., and C.O. Pruneda, “The Impurities in Kevlar 49 fibers.” Polymer, 28 (1987): 340.

Neutrality testing and pH testing of fiber is very difficult, more so with Kevlar[®] 49 since the fiber has to go through a high temperature heat treatment process that causes large discoloration (ark yellow-brown if acidic and bright yellow if basic) if the fiber is not neutral and would cause a quality assurance (QA) flag during production. The more sensitive test of yarn neutrality is with heat age strength retention. The fiber is heated at 240 °C for 3 hrs and then tested. If the fiber is not neutral, then two things happen, 1) there would be visible color change, 2) the tensile strength would drop appreciably. So, it may be possible to use heat age strength retention to accomplish the quantitative measurement.”

R-1 If new tanks are produced for subsequent Shuttle COPV lifing programs, Kevlar[®] 49 strand tests (of the type mentioned above) should accompany the tank burst program for either carbon fiber and any other advanced fiber [Poly-p-phenylenebenzobisoxazole (PBO) and M5 fiber composite materials].

Analysis 2: Kevlar[®] 49 Quality Control

It was learned from internal Hamilton Standard and Brunswick documents (**referenced to the PMBA-COPV Website**) that in a F-16 program performed by NASA for the AF around the same time that the Shuttle vessels were made that low burst strengths were traced to impure Kevlar[®] 49. Glen Ecord at NASA JSC has stated that the problem with these F-16 tanks was a liner weld issue. However, Brunswick reported dark streaking in the F-16 qualification bottles that had low burst strengths. These documents also discuss the storage of the Kevlar[®] 49 spools in an air-circulating oven at 66 °C prior to winding in order to keep the moisture content in the Kevlar[®] 49 constant. In some cases, Brunswick reports that discoloration (brownish) of the Kevlar[®] 49 stored at 66 °C did occur in the F-16 program.

To the best of our knowledge, Brunswick did not perform the 240 °C heat aging tests on the Kevlar[®] 49 that were used in the Shuttle COPV. Additionally, there are no reports or records from Brunswick, which note the use of discolored Kevlar[®] 49 spools used to make the Shuttle COPV.

Dr. Frank Gerstle (retired DOE employee) has a small quantity of fiber left from LLNL COPV program. However, there is not enough of this Kevlar[®] 49 to do further testing that would provide a better understanding fiber impurities-tensile strengths-vessel burst strength. However, chemical analyses of these samples and an attempt to correlate the concentrations of the elemental composition with the original strand tests performed at LLNL would be a starting point but have limited statistical value.

F-1 Thorough quality control at DuPont most likely prevented impure or lower strength Kevlar[®] 49 from being shipped and used in the filament winding of the Shuttle COPV.

R-1 The NESC does recommend that when future Kevlar[®] 49 COPV are made that DuPont's procedure for heat aging of Kevlar[®] 49 be performed on filament before winding. Concomitant with this heat aging test, impurity analysis should be performed.⁴

⁴Hodson, J., C.O. Pruneda, R.P. Kershaw and R.J. Morgan. "The Deformation and Failure Processes of Kevlar 49 Single Filaments." *Composites Tech. Rev.* 5 (4), (1983): 115.

Christensen, R.M. "Interactive Mechanical and Chemical Degradation in Organic Materials." Lawrence Livermore National Laboratory Report, UCRL-88459, February(1983).

Hamstad, M.A. "Aging Results for PRD 49-3/Epoxy and Kevlar 49/Epoxy Composite Pressure Vessels." Lawrence Livermore National Laboratory Report, UCRL-9919, October(1983).

Morgan, R.J., C.O. Pruneda, N. Butler, F.M. Kong, L. Caley and R.L. Moore. "The Hydrolytic Degradation of Kevlar 49 Fibers." Proc. of 29th National SAMPE Symposium, Reno, NV, (1984): 891- 901.

2.4 Complex Environmental Effects on COPV

Analysis:

The combined effects of environmental factors (time, moisture, temperature, radiation, etc.) on COPV material systems are complex. There appears to be several databases that may have portions of the environmental conditions for Shuttle, Space Station or Fleet-leader programs but the data is not centralized. One database that appears to be missing from either the Space-based or terrestrial COPV programs is their resistance to radiation-specifically, space-based sources. There was a concern about the possible detrimental effects of space-based radiation on the Kevlar/Epoxy composite system.

The Materials team has contacted several experts in the field of materials exposure to space-based radiation. Dr. Jensen contacted Dennis Russell of the Boeing Radiation Environmental Effects laboratory. Mr. Russell indicated that they expect no degradation in these COPVs because these vessels are covered by an aluminum shelter that also provides protection from atomic oxygen.

F-1 Degradation of the Space Shuttle Kevlar COPVs due to space radiation (including atomic oxygen) exposure is not a concern for recertification of these vessels.

2.5 Accelerated Testing for Life Prediction of COPVs Analysis

Analysis:

The primary function of accelerated testing is to screen materials for specific degradation mechanisms and damage modes. This information is then used within a larger context to facilitate design and structural test. Lifetime prediction for combined mechanical, thermal, environmental effects (i.e. service) cannot be accurately performed with short-term accelerated tests. Empirical data is not sufficient and existing analysis methods do not have enough fidelity for true life-prediction. Long-term (real-time) data is the best data we can hope to have to allow an understanding of lifetime performance.

F-1 The data/studies from LLNL and the fleet-leader programs are limited and unable to substantiate the use of accelerated testing as part of the recertification of existing COPVs.

R-1 A multidisciplinary working group should be assigned to address possible future utility of accelerated testing as a method to assist design of COPVs. The NESC recommends that peer review of these tests take place before they are started.⁵

2.6 Evaluation of Fleet-Leader Data

Analysis

NASA JSC has fleet-leader test data on Kevlar[®]49 COPVs that was developed in order to assure COPV lifetime of flight articles. Any new data on Kevlar[®]49 COPVs obtained through accelerated testing would be of questionable value due to the concerns expressed in paragraph 7.3.2.4. The Materials Team believes that NASA JSC fleet-leader test data provides the best of all readily available data. However,

Brown, I.M., T.C. Sandreczki, and R.J. Morgan. "Electron Paramagnetic Resonance Studies of Kevlar 49 Fibers: Stress-Induced Free Radicals", *Polymer*, 25 (1984): 759.

Morgan, R.J., and C.O. Pruneda, "The Characterization of the Chemical Impurities in Kevlar 49Fibres." *Polymer*, 28 (1987): 340.

Chiao, T.T. "No-Stress Aging of Kevlar-49/Epoxy Composites," Internal LLNL Memo 2-9271, July 12, (1982).

⁵Salem, J. A., and M.G.Jenkins. "The effect of stress rate on slow crack growth parameter estimates", *Fracture Resistance Testing of Monolithic and Composite Brittle Materials ASTM STP 1409*, J. A. Salem et al. eds. West Conshohocken, PA: ASTM (2002): 213-227.

several environmental effects (moisture, vacuum, radiation) or damage that may affect the life of COPVs are not included in NASA JSC fleet-leader test data.

F-1 The Materials Team concludes NASA JSC fleet-leader and LLNL test data provide sufficient confidence and are the best available data to provide confidence for flight rationale. Moreover, it seems very unlikely that a “research effort” such as accelerated test methods should begin now or would change that opinion due to short time span for the remaining life of the Shuttle program. Vessel burst tests of some of the Fleet Leader and new tanks may provide enough evidence for existing shuttle COPV.

R-1 Any new test program that evaluates residual burst strength should incorporate sound statistical practices to ensure reliable Shuttle COPV life prediction. Moreover, if new tanks are manufactured for this test program then the materials used in the COPV filament winding (Kevlar[®]49, LRF-092 epoxy, polyurethane coatings, and liner alloy) should be similar to the Shuttle COPV. If there are differences in materials or their thicknesses, these differences should be accounted for by a clear engineering analysis.

2.7 Effect of Kevlar Creep in Load Sharing and COPV Fiber Stress Reductions

Analysis:

Boeing raised issues regarding the potential for Kevlar[®]49 to creep and off-load strain to the titanium liner. Creep in Kevlar[®]49/Epoxy COPV has the potential to transfer load to the titanium liner. Therefore, the stresses in the Kevlar[®]49/Epoxy overwrap are reduced, as is the COPV fiber stress ratio (Refer to Thesken et al in these proceedings). In order to qualify the extent of the reduced fiber stress ratio, Prof. Phoenix performed an analysis of the OMS tank operating stresses. Further, an explanation of the morphological changes that occur as Kevlar[®]49 and that could contribute to creep are summarized in three references.⁶

F-1 The amount of creep strain to this point in Orbiter tank life consumption beyond the proof cycles is no more than about 0.03%. This small amount of creep strain translates into an estimated reduction in OMS-Helium operating composite pressure or stress level to less than 2%.

2.8 Significant Material Differences Between the Kevlar[®]49 in LLNL Vessels and Shuttle COPV

Analysis:

After discussing the differences in Kevlar[®]49 fiber used in the LLNL and Shuttle COPVs with Dr. Karl Chang from DuPONT, it is apparent that the Kevlar[®]49 used in the LLNL vessels was an earlier production version of Kevlar[®]49 than the Kevlar[®]49 used in the Shuttle vessels. The Kevlar[®]49 used in the LLNL vessels was 380 Denier and the Shuttle vessels were 4560 denier. In short, the 380 denier was a production version of Kevlar[®]49 where the filament diameter was not as well controlled as the Kevlar[®]49 used in the Shuttle COPV. This was clearly seen in the Spool #7 of the LLNL vessels where filament diameters were >20 μm in thickness or ~2 times the accepted filament thickness. As mentioned in section 7.3.2.2, Dr. Karl Chang’s attached memo (Appendix D-1) also discussed the improvements DuPONT made in neutralizing the residual sulfuric acid in Kevlar[®]49 in the later versions or 4560 denier

⁶ Morgan, R.J., C.O. Pruneda, and W.J. Steele. “The Relationship Between the Physical Structure and Microscopic Deformation and Failure Processes of Poly (p-Phenylene Terephthalamide) Fibers”, *J.Polymer Sci.(Polymer Physics Edition)* 21 (1983):1757.

Erickson, R. “Creep of Aromatic Polyamide Fibres.” *Polymer* 26 (1985): 733.

Morgan, R.J., and R.E. Allred, "Aramid Fiber Composites," Chapter in *International Encyclopedia for Composites*, Vol. 1, S.M. Lee, Ed. VCH Publishers, (1990): 37-56.

Kevlar[®]49. This was the Kevlar[®]49 used to manufacture the Shuttle COPVs. Almost as important is the water wash of Kevlar[®]49 filaments to remove the traces of sodium hydroxide (NaOH) that is present from the neutralization of residual sulfuric acid (H₂SO₄). DuPONT has not been able to provide past records that describe any property differences for these versions of Kevlar[®]49. According to Dr. Karl Chang, they did not keep paper copies of this data.

F-1 DuPONT has not been able to supply past records from the late seventies/early 1980's for the production of Kevlar[®]49, which make comparison of different lots of Kevlar[®]49 very difficult without the original chemical analysis.

R-1 For future COPV programs the NESC recommends that examples of data sets comparing filament a tensile strength testing on all fibrous materials are needed to gain a better understanding of tensile property changes from filament to epoxy impregnated strands.

2.9 Calendar Life and Possible Degradation of Fiber/Matrix on Stress Rupture Likelihood

Analysis:

According to Dr. Roger Morgan, it takes approximately one chain scission per Kevlar-49 polymer chain to decrease strength of Kevlar[®]49 polyamide fiber by 50%. The polymer chain length for Kevlar[®]49 is ~200 repeat units in length. Currently, there are no simple analytical polymer chemistry tests that quantify this strength or stiffness reduction without extracting composite samples from the existing COPVs. Analytical polymer chemistry methods such as Dynamic Mechanical Analysis (DMA), High Pressure Liquid Chromatography (HPLC) and Fourier Transform Infrared Spectroscopy (FTIR) are *not* sensitive enough to detect such a small number of chain scissions per polymer chain. Boeing recertification (in 1988) used three tests to approximate aging of the Kevlar[®]49/Epoxy: dynamic mechanical analysis (DMA), high-pressure liquid chromatography (HPLC), and infrared spectroscopy. The NESC requested the results of these data sets. Boeing supplied only 2 of the three tests results mentioned above (DMA and HPLC). To date, the FTIR results have not been provided for the NESC to review. Appendix 2 describes the results of the DMA and HPLC tests. There was discussion from these tests that provided the Boeing conclusion that recertification was warranted (Appendix D-2). In Appendix D-3, Ed Silverman (Rockwell International M+P Supervisor), presents the extension of the Shuttle COPV recertification based three data sets: LLNL and NASA JSC burst data of non-aged and aged COPV, analytical polymer science experiments (DMA, HPLC, FTIR), and an analysis of the degradation of Shuttle COPV liner.

HPLC of Kevlar[®]49/Epoxy composites is difficult. Kevlar is not soluble in solvents other than concentrated acids such as sulfuric, phosphoric or methane sulfonic acid. The HPLC data provided by Tom Collins at Boeing-Huntington Beach, showing a 1 and 10 yr old Kevlar-49 samples comparison, had little details other than a sketched chart of the two samples. The NESC would like to know how this analysis was performed. Specifically, the solvents used in the HPLC experiment and the standards used to draw conclusions about molecular weight changes in Kevlar[®]49. Moreover, the origin of these samples was not specified as the titles of these data stated they were "Titanium Liner Sample." Tracking changes due to aging in matrix resins is difficult. Typically, oxidation is generally discovered through micrographic analyses. General Dynamics has not done this test on their Kevlar[®]49/epoxy qualification tank.

In some cases, resin aging is detected by changes in glass transition temperature or (T_g). According to Dale Tiller at General Dynamics, DMA analysis provides an accurate measure of T_g. General Dynamics recently (specific date unknown) performed Dynamic Mechanical Analysis (DMA) on a Kevlar[®]49/Epoxy (LRF-092) composite laminate sample from an Orbital Maneuvering System (OMS)

Qualification Tank. This testing revealed a Tg of 268 °F (131 °C). This specific COPV was cured at 285 °F. A DMA on sample from same laminate in October 1986 was 262 °F.

- F-1 The NESC finds that this measure of Tg (by DMA) is not sensitive enough to determine if Kevlar-49 chain scission has occurred to an appreciable extent so that a reduction in Tg would correspond to a reduction in tensile strength. While DMA data maybe worth noting, it is not the sole determinant that the Kevlar[®]49 or it epoxy matrix have aged to an extent that COPV integrity is compromised. According to Dale Tiller's (General Dynamics) analysis of the LRF-092 epoxy resin, the lack of change in the resin Tg after many years maybe an indication that the resin has not aged.
- F-2 The NESC finds that a lack of change in Tg alone should not be the only criteria to establish COPV aging. It should be noted, however, that the epoxy resin used in the Shuttle COPV, LRF-092, is widely used (rocket motor cases, radomes, pressure vessels) in a variety of aerospace and Naval structures. Currently, it is used in all of General Dynamics production pressure vessels. According to Dale Tiller at General Dynamics, radomes from A-6 aircraft were tested after 11-16 years of fleet service and were found to have the same tensile strength and flexural properties as originally delivered.
- F-3 After a NESC review of the Rockwell DMA and HPLC data, the NESC concludes that there is insufficient basis for Boeing to claim that these data are capable/sensitive enough to determine if there are aging differences between the Kevlar/epoxy in 1 yr old versus 10 yr old Shuttle COPVs.
- F-4 The NESC contends that the tensile properties are primarily fiber dominated and that resins contribute a small portion to the tensile strength of a composite. More importantly, composite aging is a result of both resin and fiber changes over time. It is not known if the Radomes mentioned are fabricated from Kevlar-49 or another fiber support.
- F-5 For Kevlar[®]49/epoxy COPV, the fiber's aging characteristics are the most important property to understand. Tg is not going to be the best characteristic for aging.
- R-1** The NESC recommends that microcopy techniques should be developed to analyze aged composite samples either from the COPV or from tests samples that are stressed for similar amounts of time as the Shuttle COPV.
- R-2** The NESC recommends that a combination of polymer science tests used to capture Shuttle COPV aging and burst tests of a representative set of Orbiter COPV (or accurate facsimile thereof) that provides a statistically significant data set would be the ideal test to determine COPV aging.
- R-3** If Boeing uses DMA in the future for testing Kevlar[®]49/Epoxy samples from the Shuttle COPVs, the NESC recommends that the calibration protocol for their the DMA instrument that measures both Tg and moduli (stiffness) changes should accompany the results in a recertification report.

2.10 Tracing the Heritage of Kevlar-49 Fiber to the Shuttle Kevlar-49/Epoxy COPV

Analysis:

Kevlar[®]49 strand testing for the fiber that was used to produce Shuttle COPV is not available from DuPONT or General Dynamics. However, Boeing at NASA-KSC has log books that came from General Dynamics and specify the lot numbers and tensile properties for the Kevlar[®]49 fiber in each COPV.

- F-1 Strand testing of Kevlar[®]49 that was used for the LLNL COPVs clearly identified by strands that contained weak fiber as a result of impurities. Elemental chemical analysis of Kevlar[®]49 fibers identifies these impurities and correlates well with reduced tensile strengths. According to John Smith (Boeing employee) at NASA KSC, there is a requirement for lot traceability for this material and the data is available on microfiche.
- R-1 NASA Orbiter Office should require that Boeing review the log books that are associated with each Shuttle COPV to determine if the strand testing results indicate if there is suspect Kevlar[®]49 used in the fabrication of the Shuttle COPV.

2.11 Materials Testing for Long Term Flight Rationale

Analysis:

Many of the existing Kevlar[®]49/epoxy COPV will be used on the Orbiter to the end of the Shuttle program.

- F-1 Based on the NESC finding #1 in “Significance of Calendar Life”, a strategy for materials tests for long- term flight rationale is needed in order to provide a long term flight rationale.
- R-1 The NESC recommends that in addition to burst testing, material tests should address three basic objectives. First to establish basic *performance characteristics* in order to guide constitutive model selection and provide an initial assessment of the sensitivity of the material response to a range of environmental and loading conditions. Next, perform tests that establish the *material property data* required by the selected constitutive model(s) and describe fundamental behavior under the complete range of environmental and loading conditions. Finally, *provide the data necessary to validate* predictive material models or failure theories. In addition, the objective of these tests is to establish empirically, the validity of the assumptions and limitations associated with the constitutive and predictive models used to predict aging and stress rupture of Orbiter COPV.
- R-2 Many of the existing Kevlar[®]49/epoxy COPV will be used on the Orbiter to the end of the Shuttle program. Therefore, a strategy for materials tests for long term flight rationale is needed. The NESC recommends that in addition to burst testing, material tests should address three basic objectives.