

# Use of Raman Spectroscopy and Delta Volume Growth from Void Collapse to Assess Overwrap Stress Gradients Compromising the Reliability of Large Kevlar/Epoxy COPVs

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**ABSTRACT.** Composite Overwrapped Pressure Vessels (COPVs) are frequently used for storing pressurized gases aboard spacecraft and aircraft when weight saving is desirable compared to all-metal versions. Failure mechanisms in fibrous COPVs and variability in lifetime can be very different from their metallic counterparts; in the former, catastrophic stress-rupture can occur with virtually no warning, whereas in latter, a ‘leak before burst’ design philosophy can be implemented. Qualification and certification typically requires only one burst test on a production sample (possibly after several pressure cycles) and the vessel need only meet a ‘design burst strength’ (the maximum operating pressure divided by a ‘knockdown’ factor). Typically there is no requirement to assess variability in burst strength or lifetime, much less determine production and materials processing parameters important to control of such variability. Characterizing such variability and its source is crucial to models for calculating required reliability over a given lifetime (e.g.  $R = 0.9999$  for 15 years). In this paper we present a case study of how lack of control of certain process parameters in COPV manufacturing can result in variations among vessels and between production runs that can greatly increase uncertainty and reduce reliability. The vessels considered are 40-inch ( $29,500 \text{ in}^3$ ) spherical COPVs with a 0.74 in. thick Kevlar49/epoxy overwrap and with a titanium liner of which 34 were originally produced. Two burst tests were eventually performed that unexpectedly differed by almost 5%, and were 10% lower than anticipated from burst tests on 26-inch sister vessels similar in every detail. A major observation from measurements made during proof testing (autofrettage) of the 40-inch vessels was that permanent volume growth from liner yielding varied by a factor of more than two ( $150 \text{ in}^3$  to  $360 \text{ in}^3$ ), which suggests large differences in the residual stress gradient through their overwraps. This resulted in large uncertainty in true fiber stress ratio (fiber stress at operating pressure divided by fiber stress at burst) which governs lifetime. The vessels were originally designed with tight safety margins, so it became crucial to develop a non-destructive evaluation (NDE) technique to directly measure the overwrap residual stress state of each vessel, and to identify those vessels at highest risk of having poor reliability. This paper describes a Raman Spectroscopy technique for measuring certain patterns of fluctuation in fiber elastic strains over the outside vessel surface (where all but one wrap is exposed at certain locations) that are shown to directly correlate to increased fiber stress ratios and reduced reliability.

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## Nomenclature

$\Delta V_{pf}$	= ‘delta volume’, permanent volume change of vessel due to proof-testing (autofrettage)
$R$	= Reliability expressed in number of nines (e.g., 0.99999 probability of survival)

## I. Introduction

Composite Overwrapped Pressure Vessels (COPVs) are frequently used for storing pressurized gases aboard spacecraft and aircraft when weight saving is desirable compared to all metallic pressure vessels. Unfortunately, when compared to their metallic counterparts, failure mechanisms in fibrous COPVs and variability in burst strength and lifetime can be very different; in the former, catastrophic stress-rupture can occur with virtually no warning, whereas in latter, a ‘leak before burst’ design philosophy can be implemented similar to what is used in gun barrels. After finalizing a COPV design for flight application, qualification and certification typically requires only one burst test on a production sample (possibly after a fixed number of pressure cycles) and the acceptance criterion is that the vessel burst strength meet or exceed a specified ‘design burst’ value. This value is the maximum operating pressure in service divided by a knockdown factor. There is no requirement to assess variability, in burst strength or lifetime, much less determine production and manufacturing parameters important to controlling such variability. This is especially true when the winding process involves ‘pre-pregs’ (epoxy resin pre-impregnated and partially cured fiber tows), which have a limited shelf life before the state of epoxy cross-linking causes unacceptable stiffness increase and reduction in the ability of tows to bond to each other during final cure. In winding large vessels, such pre-pregs can differ in state of cure resulting from differences in time spent in refrigeration and in subsequent warming to ambient conditions before winding occurs. Differing states of cure, winding tension and thermal conditioning, as the tow winds onto the vessel, can affect degree of tow packing and extent of entrainment of air voids (as can also occur during pre-preg processing itself).

Variability in lifetime is crucially important since models to forecast a required reliability over a specified lifetime, such as  $R = 0.9999$  for 15 years, require an accurate variability measure, such as the Weibull lifetime shape parameter. In the absence of suitable data on the actual vessel and material system, designers typically predict reliability based on a data that may not involve the same fiber/epoxy material system, overwrap design and vessel size. At best large uncertainty in the reliability may result and at worst the actual reliability may be much worse than initially calculated during the design and qualification phase.

In this paper we present a case study of how the lack of control of certain process parameters in COPV manufacturing can result in variability that greatly reduces reliability, especially lower confidence bounds. The vessels considered are 40-inch ( $29,500 \text{ in}^3$ ), Kevlar49/epoxy spherical COPVs with titanium liners. Thirty-four such vessels were originally produced, and two burst tests were eventually performed, on SN002 and SN011. The burst strengths of these two vessels unexpectedly differed by almost 5%, and were also about 12% lower than anticipated from the burst performance of 26-inch sister vessels that were similar in virtually every design detail. At the very least, this led to large uncertainty in the true fiber stress ratio (the fiber stress at maximum operating pressure divided by the fiber strength at burst), which is necessary to make accurate lifetime predictions using a Kevlar49/epoxy data base of laboratory-scale vessels and epoxy impregnated strands. Since these vessels were originally designed with tight safety margins, it became crucial to determine the root causes of the variability in terms of variation in overwrap fabrication parameters, and to develop a Non-Destructive Evaluation (NDE) technique to identify those particular vessels still in service at high risk of having unacceptably poor reliability. This paper describes a Raman Spectroscopy technique for measuring elastic strains and fiber stresses in the outside wrap that are shown to directly correlate to high fiber stress ratios and reduced reliability.

## II. Causes of Vessel-to-Vessel Variability and Implications on Fiber Stress Ratio

An investigation of the possible causes of burst strength variability led to the discovery that the permanent volume growths,  $\Delta V_{pf}$ , called ‘delta volumes’ from plastic yielding of the titanium liner during the proof test (autofrettage), varied among production vessels by a factor of 2.3. This fact emerged from study of the manufacturer-supplied, Acceptance Data Packs (ADPs) for each vessel, and revealed  $\Delta V_{pf}$  values ranging from  $150 \text{ in}^3$  to as high as  $360 \text{ in}^3$ . The latter represents a permanent volumetric strain of 1.2% rather than the 0.44% value corresponding to  $\Delta V_{pf} = 130 \text{ in}^3$  based on the design parameters, as calculated from the original finite element analysis (FEA). (This FEA was repeated by the manufacturer in 2005 and study of the results indicated  $\Delta V_{pf} \approx 160 \text{ in}^3$ .) Thus it has

become very important to determine why some vessels, particularly those early in production, had delta volumes more than double those predicted from the design.

Mechanics calculations have shown that for two vessels at the same service pressure, a delta volume difference of 150 in<sup>3</sup> results in a 20% difference in fiber stress on the inner wraps against the titanium liner. This, in turn, results in a large increase in the fiber stress ratio and reduction of lifetime since  $lifetime \approx (fiber\ stress\ ratio)^{-24}$ . For instance a 10% increase in fiber stress ratio reduces lifetime by a factor of 10, and a stress ratio increase of 20%, corresponds to a mean lifetime decrease by a factor of 250. This is obviously unacceptable for vessels that originally had tight design margins on stress-rupture lifetime.

Based on evidence from dissected vessels, and other experimental observations, the root cause of high  $\Delta V_{pf}$  growth was determined to be entrained air pockets and voids in the composite overwrap, most likely occurring during winding on the overwrap but possibly also during the epoxy pre-preg process of the Kevlar tows (typically performed days to weeks before actually winding on the overwrap). Over three production runs spanning several years, there appeared to be large differences among vessels and production runs, especially the first two runs. Mechanics models have shown that a void content of just 5% in the 0.74-inch thick Kevlar/epoxy overwrap results in large delta volume growth when the voids collapse under a proof pressure of 6520 psi held for several minutes. Since the titanium liner plastically deforms during proof, it accommodates any excess growth in  $\Delta V_{pf}$ . Thus upon depressurizing to 0 psi afterwards, the final compression load on the liner differs little from what would occur for a design delta volume of  $\Delta V_{pf} = 130\text{ in}^3$ . Consequently the *average* hoop stress through the thickness of the overwrap remains about the same irrespective of delta volume both at zero pressure and maximum operating pressure. However, since the fiber stress on the inner-most wraps must be much higher for vessels with unusually high  $\Delta V_{pf}$ , the fiber stress on the outer-most wraps must necessarily be much lower (since these wraps draw inward as voids collapse) so as to maintain the fixed liner compressive load irrespective of  $\Delta V_{pf}$ . Further analysis also shows that during failure, enhanced stresses on the inner wraps cannot not be compensated by reduced stresses in the outer wraps, since once tows from inner wraps begin to fail they shed load to outer wraps rapidly increasing their failure rates and ultimately forming a catastrophic cascade.

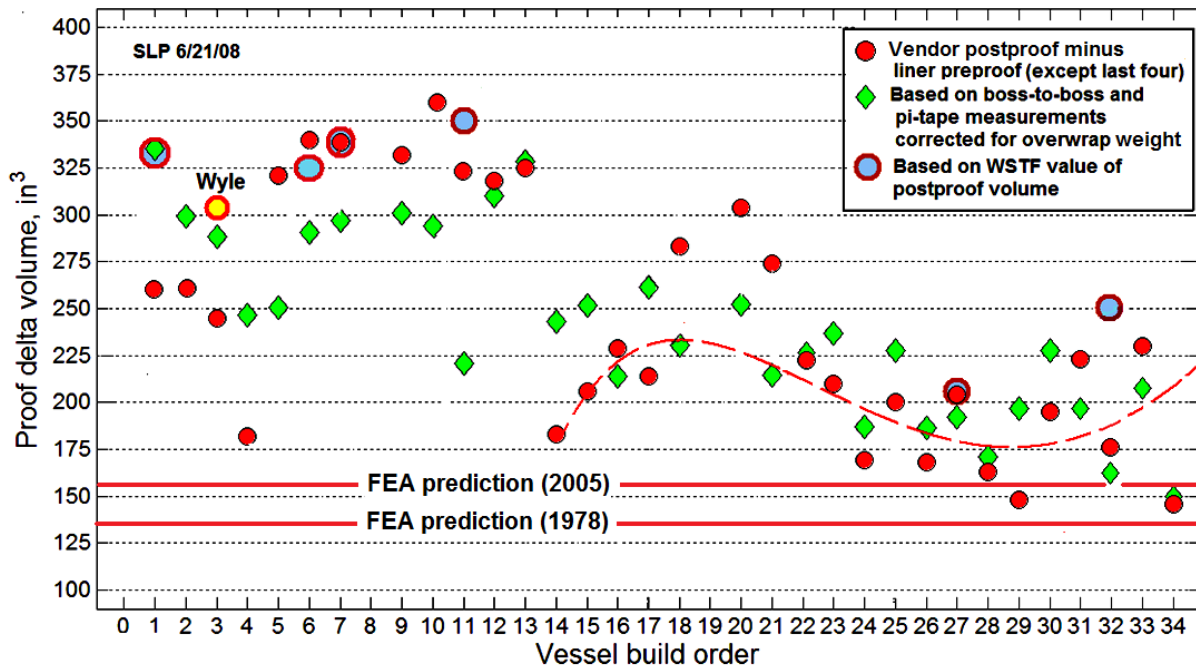


Figure 1. Measurements of vessel delta volumes using three different approaches. The first 13 vessels constituted one production run, the next 17 a second run, and the last four (with a different liner manufacturer) a third run.

The key to identifying vessels currently at risk of low reliability was to develop an NDE technique to accurately measure elastic fiber strains, and thus residual fiber stresses in all the wraps at the locations where they rise to the

surface. This became particularly important once it was discovered that the delta volume measurements,  $\Delta V_{pf}$ , in the ADPs of the manufacturer were unreliable. Figure 1 shows the results of one effort by the first author to calculate the delta volumes for the thirty-four 40-inch vessels that were fabricated in the late 1970's and early 1980's. Repeat volume measurements recently made on a few accessible vessels by NASA-JSC White Sands Test Facility (WSTF) showed that some post-proof delta volume measurements made by the manufacturer in the late 1970's and early 1980's have considerable error (in one case more than 70 cubic inches) as shown in Figure 1. Furthermore, the pre-proof vessel volumes by the vessel manufacturer failed to agree with the original liner volume measurements by the liner manufacturer. Since the individual liner volumes by the liner manufacturer are in close statistical agreement with volumes calculated by the authors from the multiple liner circumference measurements in the ADPs made prior to winding, and *not* with the vessel manufacturer pre-proof volumes, the liner manufacturer volumes were judged to be much more trustworthy (except for the final four vessels when the liner manufacturer was changed). Thus to circumvent these  $\Delta V_{pf}$  uncertainties and noting that it is the overwrap fiber stress gradient that drives high fiber stress ratios, a reliable technique, based on Raman Spectroscopy, was developed to directly measure the fiber elastic strains in the wraps of the vessel exposed at the outside surface. This allows an independent calculation of the fiber stress gradient, without having to rely on the original ADP delta volume measurements, several of which seem to be in error and are of concern. In Figure 1, the vessels still in service of most concern are SN018, SN020 and SN021 since the manufacturer  $\Delta V_{pf}$  seem "out of family". This paper describes the Raman spectroscopy measurements of overwrap residual strains, their analytical interpretation and key findings.

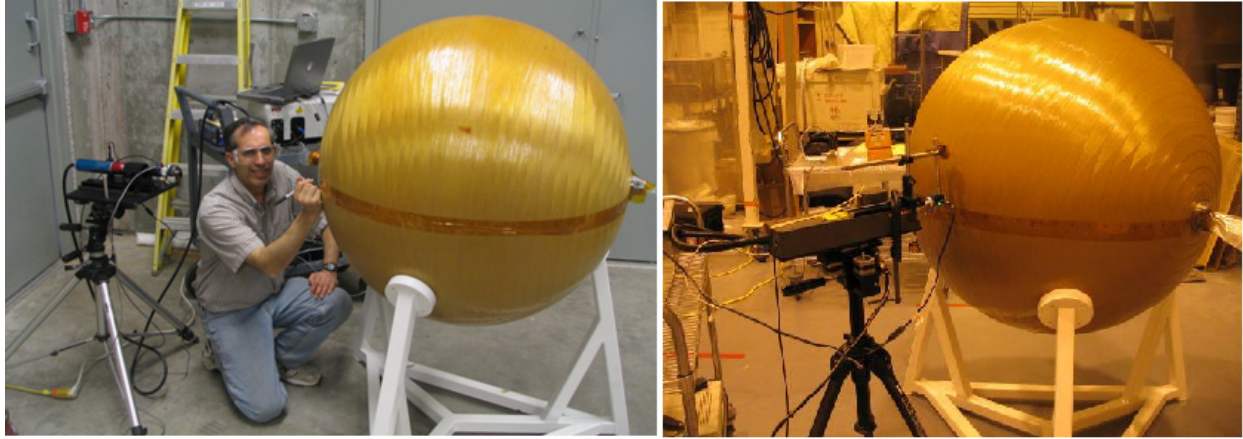
### III. Raman Elastic Strain Measurements

Raman spectroscopy based strain measurements were collected from the surfaces of Kevlar/epoxy overwraps from several vessels located at the NASA-JSC White Sands Test Facility (WSTF). Raman spectra were collected using two systems. The first was a Renishaw Series 100 Spectrometer connected to a RP20V remote probe mounted on a computer-controlled 3-axis motorized stage supported by a tripod. By moving the tripod for coarse movement and utilizing the motorized stage for fine movement (including focusing), the probe could be positioned to focus on the desired spots on the surface of the COPV for analysis. A 20X magnification long-working-distance objective was mounted onto the compact probe. The incident laser excitation was focused onto the COPV surface through this objective, and the same objective was simultaneously used to collect the Raman signal light. The excitation source was a 514 nm wavelength argon ion laser with the emitted laser beam coupled into the compact probe by fiber optics.

The laser power at the exit of the objective (which is what the vessel is subjected to) was set at 3.75 mW. This laser beam power is substantially lower than the 50 mW that the laser is capable of providing. The lower 3.75 mW was selected based on previous experience at NASA Glenn Research Center (GRC) that showed that this power would not produce any measurable heating of the vessel surface that might alter the data (since the Raman peak shifts are sensitive to both strain & temperature). In addition, the power density was also far below that which might damage the vessel surface, as verified by 24 hour laser exposures at GRC on a overwrap sample.

Because the strain measurements were extracted by analyzing the small shifts of the Kevlar Raman peak at 1610  $\text{cm}^{-1}$ , it was important to maintain spectrometer calibration. Initial spectrometer calibration was performed using spectral lines from an internal neon lamp in the spectrometer. To enable monitoring of possible drifting out of calibration, a krypton lamp was used so that the krypton spectral lines would be present in every COPV spectrum and could be used to adjust for any shifts in calibration. A krypton lamp was selected because it has two spectral lines (at 1456 and 1483  $\text{cm}^{-1}$ ) that are close to the 1610  $\text{cm}^{-1}$  Kevlar peak, but do not overlap. The separation of the two krypton peaks remained steady, indicating that the scale remained in calibration; however, there was occasional drifting in the peak positions, indicating a slight change in calibrated offset. Therefore, the Kevlar peak position was always measured with respect to the 1483  $\text{cm}^{-1}$  krypton peak so that any offset drift was always accounted for. Using the krypton lines thus allowed accurate determination of small shifts of the 1610  $\text{cm}^{-1}$  Kevlar peak. A separate issue was to identify the peak position that corresponded to zero strain. Once the peak position for zero strain is identified, any peak shift can then be converted to absolute elastic strain. While in the past we have used small removed sections of overwrap from sister COPVs as a zero-strain reference, we found that the Kevlar in these overwrap pieces still had small residual strains frozen in depending on their surface location. Thus we now use bare Kevlar tows as a zero strain standard. Therefore, before every set of COPV measurements, a number of spectra are first collected from the Kevlar fiber tow, and the average value for the Kevlar peak position from these measurements is used as the zero-stress peak position.

For the first two vessels studied, SN002(2) and SN027, Raman spectra were collected along the length of three meridians, identified as the 0, 120, and 240 degree meridians, from boss to boss. Both band number and distance from the AN4 boss were recorded for each measurement. The COPV was rotated in its stand to position the desired meridian for the Raman probe. The Raman probe, mounted on its tripod, was then moved horizontally along the length of the meridian (from the AN4 to the AN11 boss) to collect spectra at a spot on each band. Figure 2 (right frame) shows the Raman probe positioned for analysis of a spot on the COPV surface. Analysis time at each spot was about 1 minute for the COPV spectrum and another minute for a krypton line spectrum. Including repositioning and refocusing, each analysis spot required about 10 minutes.



**Figure 2. Left, COPV on a frame being marked for Raman measurements using the Kaiser system. Right frame shows the Renishaw system set up to gather data near the equator.**

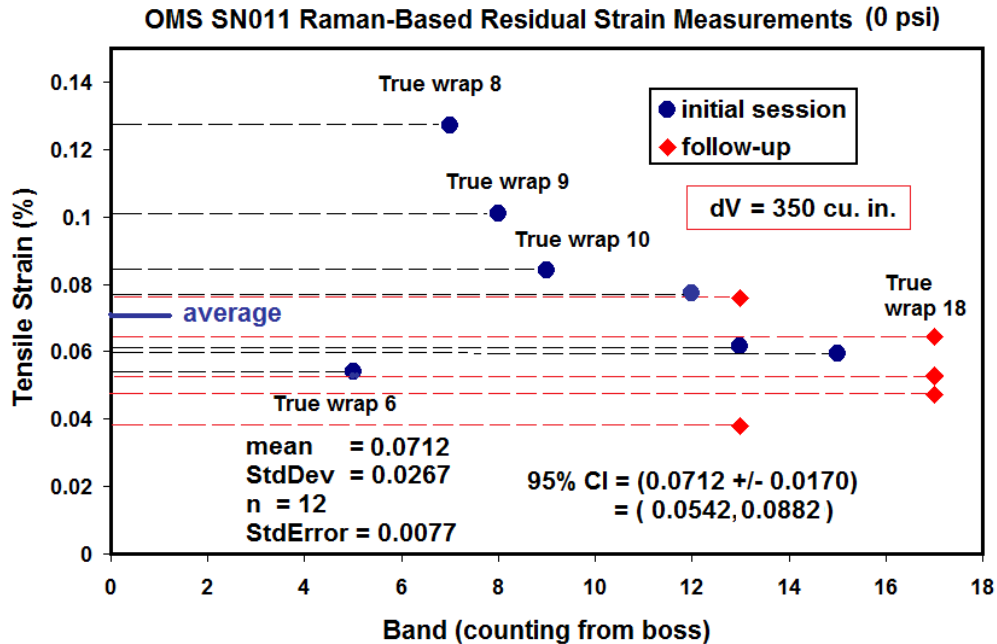
Table 1 shows residual elastic strains measured on the two COPVs, SN002 and SN027, using the Renishaw system. These vessels were found to have relatively low  $\Delta V_{pf}$  values of around 210 in<sup>3</sup> to 240 in<sup>3</sup>, and the Raman measured strains were around 0.20% or 2000 $\mu\epsilon$  as shown in Table 1. For both sets of data, summarized in Table 1, there were issues with optimization of data collection or stabilization of room environment that make our confidence in the 0 degree data (first collected) lower than for the other meridians. Even so, the zero degree meridian data fell in line with the rest. There were no significant trends in strain along the meridians or between the meridians. The large scatter would have prevented us from detecting small (less than 0.1%) longitudinally-dependent changes in strain. It was not initially clear if the larger scatter in strain values observed for SN002 and SN027, compared to much less scatter in the earlier OMS11 strain measurements (discussed shortly) is real or an artifact due to the less controlled environment (temperature). However as is discussed later a second Raman system with wider beam resulted in much less scatter on subsequent vessels.

**Table 1. Residual elastic strain measurements on two 40-inch vessels known to have low  $\Delta V_{pf}$  s.**

COPV#	Meridian	Average strain (%)	Standard deviation (%)	Number of measurements	Mean strain 95% confidence interval (%)
2	0	0.258	0.109	15	0.258 ± 0.060
2	120	0.209	0.130	35	0.209 ± 0.045
2	240	0.191	0.114	35	0.191 ± 0.039
27	0	0.142	0.098	19	0.142 ± 0.047
27	120	0.200	0.128	23	0.200 ± 0.055
27	240	0.232	0.084	23	0.232 ± 0.036

The same Renishaw system was used earlier on vessel SN011 during cycling and prior to burst testing and from WSTF volume measurements and original liner vendor measured volume was found to have a large delta volume  $\Delta V_{pf} \approx 350$  in<sup>3</sup>. The results appear in Figure 3. At that time the Raman procedure and sequence of bands to

consider was less developed (in fact the burst testing of SN011 brought this issue of residual stresses to light) and fewer locations on the vessel surface were measured for residual elastic strain. Nevertheless, during pressurization of SN011, the Raman system proved to act as an extremely accurate strain gage, with strain changes matching extremely closely those of nearby strain gages attached to the surface. The results in Figure 3 indicate an average residual strain of about  $700\mu\epsilon$  as compared to the  $2000 - 2400\mu\epsilon$  expected for a vessel with a  $\Delta V_{pf}$  close to that originally calculated during vessel design (around  $\Delta V_{pf} \approx 160 \text{ in}^3$ ) and seen in SN00(2) (third last vessel manufactured) and SN021 as shown in Table 1. These results supported the premise that Raman measured strains could be used to assess the state of residual strain and stress through the overwrap.



**Figure 3. Raman measured residual elastic strains taken on the surface of SN011, which was found to have a delta volume of about  $350 \text{ in}^3$  and an unexpectedly low burst strength.**

The residual elastic strains were measured on the surface of a second group of three 40-inch COPVs, SN006 and SN007 (recently removed from service and replaced) and SN001 (first manufactured vessel), known to have much larger delta volumes than SN002(2) and SN027 above. For these vessels a Kaiser system was used with a PhAT probe that had a 785 nm wavelength laser light source. The incident power on the vessel surface was 100 mW focused on a 6 mm spot size at a 20 cm working distance. Each measurement took about 5 seconds. Otherwise the procedure was very similar as used on the previous two vessels. The left frame in Figure 2 shows the Kaiser system and third author. Three equally spaced meridians were measured at 35-37 wrap locations, and three repeats were performed per wrap. Measurements were made at 0 psi and at 1000 psi.

Figure 4 shows residual elastic strain profiles taken from SN001, known to have a  $\Delta V_{pf}$  of  $330 \text{ in}^3$ . Immediately apparent is the fact that in the membrane region and equatorial region the elastic strains at 0 psi average to about 0.1% or  $1000\mu\epsilon$ , which is about half the values in Table 1 for the first two vessels with much lower  $\Delta V_{pf}$ . Furthermore the strain ‘humps’ of 0.15% or  $1500\mu\epsilon$  near the bosses were measured on the wrap patterns that, while emerging at the surface at that location, lie closest to the liner in the membrane region surrounding the equator.

Figure 5 shows a meridional cross-section of the overwrap, liner and boss in the boss region. It should be noted that wrap 1, a nearest the boss is covered over by wrap 2, so the band numbering in Figure 4 (and later in Figure 6) is one less than the wrap number in Figure 5. A key point is that, at 0 psi vessel pressure, the high strains measured in wraps 3 4, and 5 (bands 2, 3 and 4) in Figure 4 occur where the titanium liner is thickened in the boss region and carries more load than elsewhere when the vessel is at operating pressure (about 4800 psi). This reversal, relative to expectations of low elastic strain, is strong indication that the cause of the increased elastic strain is high tension in these wraps in the membrane region closer to the equator. On the other hand the low tension in wraps 6 onward towards the equator (wrap 19) is the result of the collapse of voids in the overwrap pulling them inward towards the

liner, thus lowering the fiber path length in the equatorial direction. Once the pressure is increased to 1000 psi, the reinforcing effect of the thickened boss region becomes apparent relatively reducing the strains in wraps 3, 4 and 5 compared to wraps 6 through 18. As seen in Figure 4, this strain reduction effect also occurs at the equator since the titanium liner is somewhat thicker in a region spanning a few inches on each side of the equator.

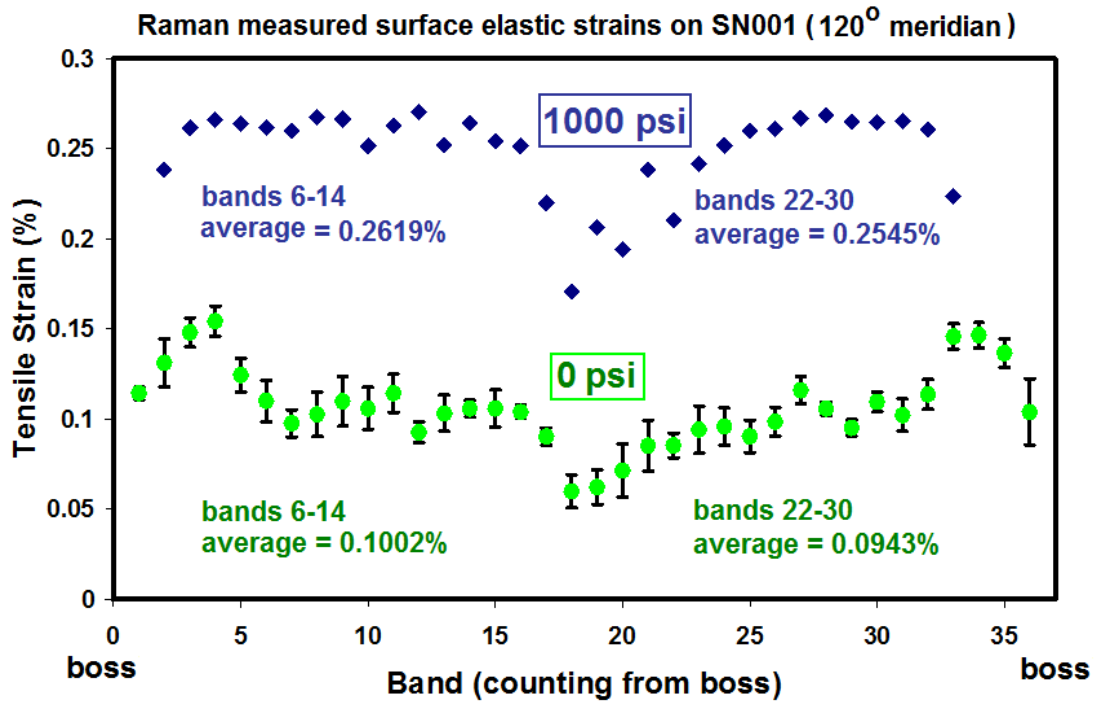


Figure 4. Residual elastic fiber strains at 0 psi and 1000 psi measured in a SN001 known to have a high  $\Delta V_{pf}$ .

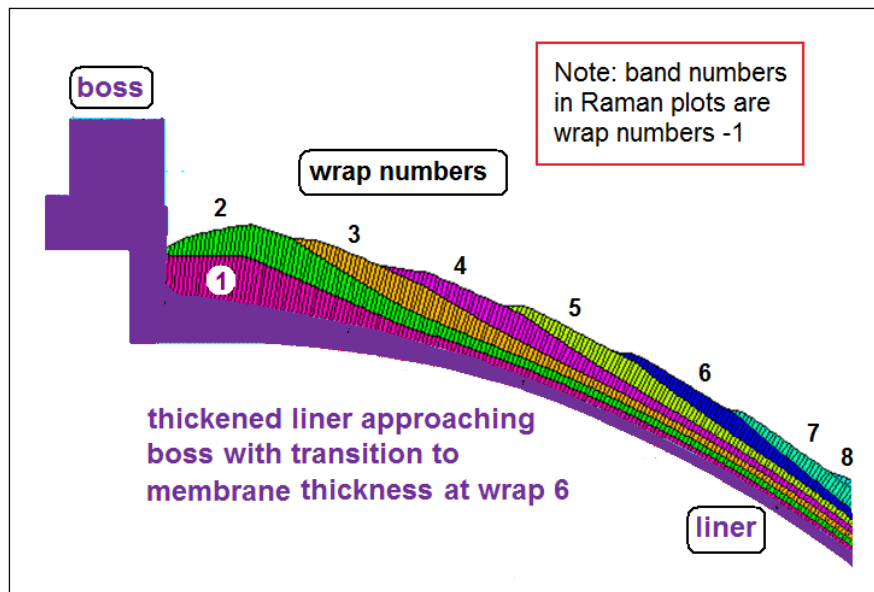


Figure 5. Meridional cross-section of overwrap, titanium liner and boss showing the location of wraps 1 through 8 as they reach the vessel surface and thickened liner out to about wrap 6. At the exposed locations, the fiber path is actually tangent to the boss (and perpendicular to the plane of the figure).

Figure 6 shows residual elastic strain profiles taken from the fourth 40-inch COPV, SN006, known also to have a  $\Delta V_{pf}$  of about 330 in<sup>3</sup>. Again the membrane region and equatorial region strains average to about 0.098% or

980 $\mu\epsilon$ , which is again about half the values in Table 1 for low  $\Delta V_{pf}$  but slightly above those measures in SN011 with a  $\Delta V_{pf}$  of about 350 in<sup>3</sup>. Strain ‘humps’ of 0.15% or 1500 $\mu\epsilon$  again appear near the bosses.

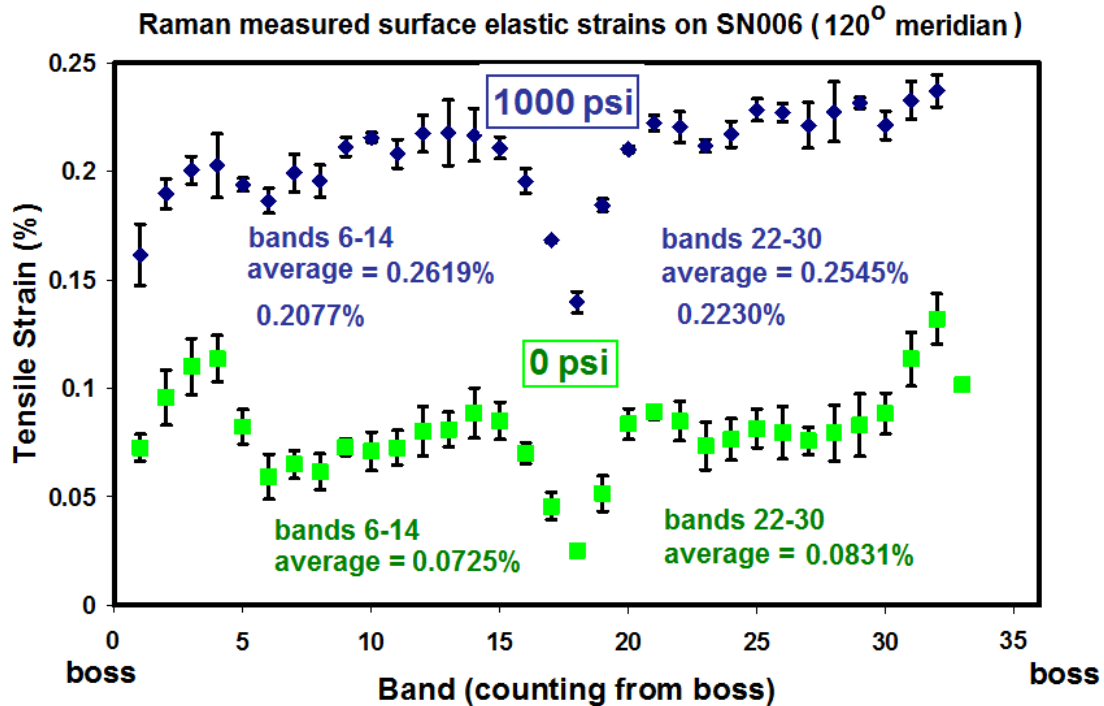


Figure 6. Residual elastic fiber strains at 0 and 1000 psi measured in SN006 also known to have high  $\Delta V_{pf}$ .

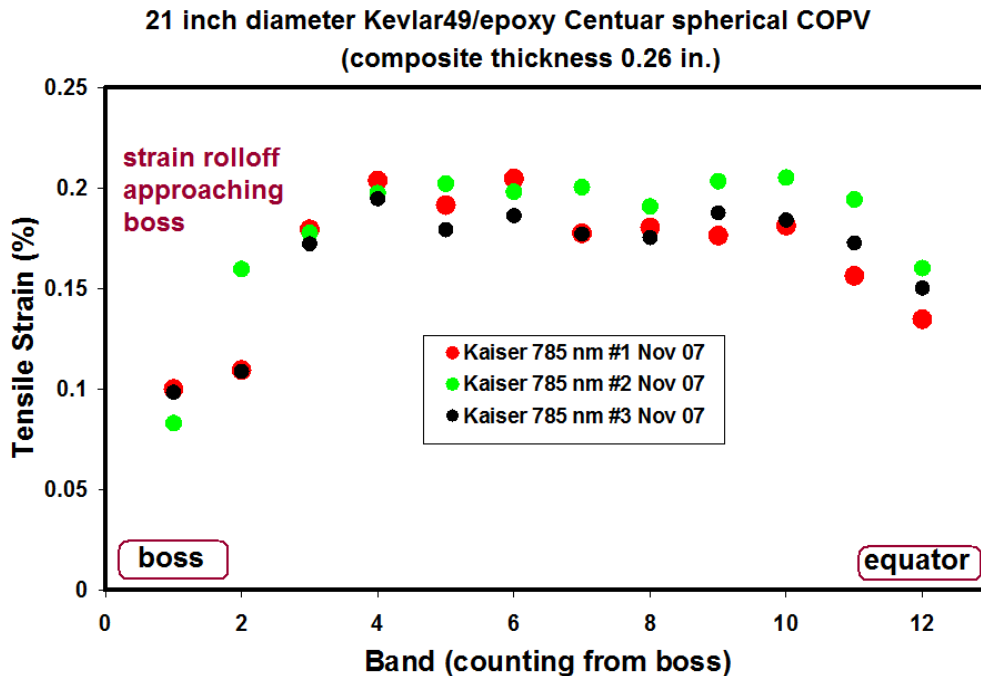


Figure 7. Raman elastic strains measured on a Centaur Kevlar49/epoxy, spherical pressure vessel.

By comparison, Figure 7 shows Raman residual elastic strains measured at WSTF on the surface of a 21 inch Centaur Kevlar49/epoxy overwrapped vessel with a stainless steel liner, again measure using the Kaiser Raman system. This Centaur vessel, with a 0.26 inch thick overwrap, had a low  $\Delta V_{pf}$  in line with its design, and is seen



found to have much higher membrane residual strains. Furthermore residual strains rolled off approaching the boss, rather than locally peaking as shown in Figures 4 and 6.

#### IV. Correlation of Raman Strain Measurements to Delta Volume Growth and Reliability

Using the data from previous figures, Figure 8 shows the strong correlation between Raman measured elastic strains in the outer overwrap bands in the membrane region and delta volume measured during proof. Note that the delta volume measurements of S/N002(2) are of questionable accuracy due to inaccuracies in the pre-proof volume (the liner manufacturer had just been changed and the initial liner volume measurement was inaccurate). Liner circumference measurements prior to winding suggest the delta volume is 25 to 30 cubic inches smaller than plotted.

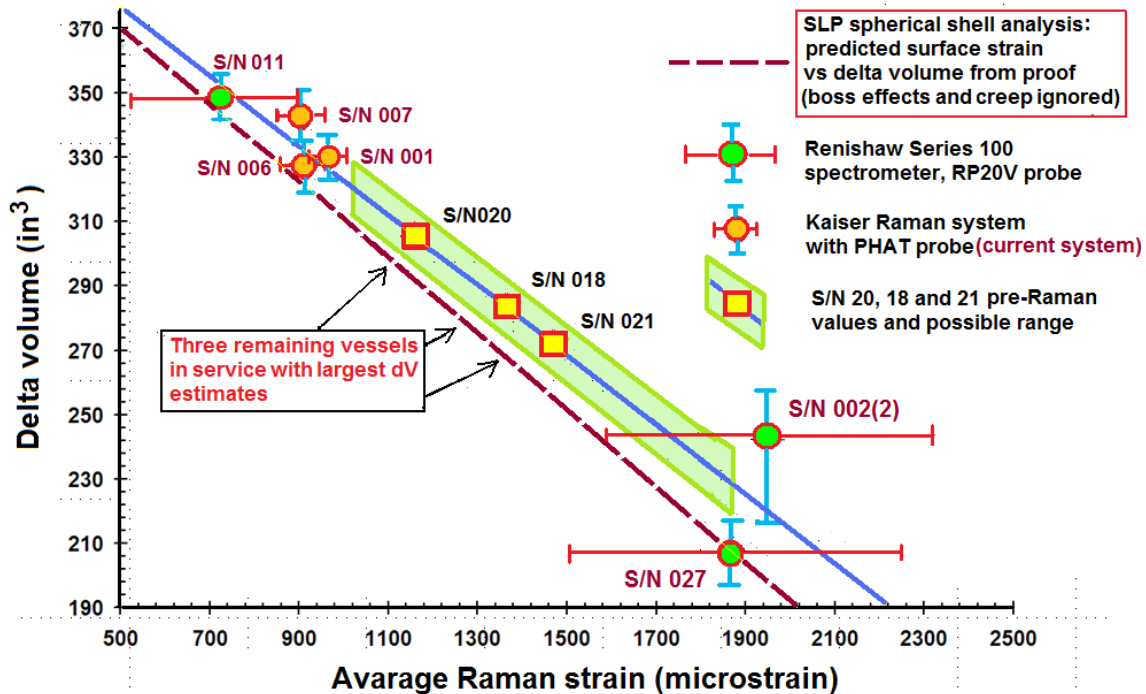


Figure 7. Correlation of Raman measured strain and delta volume on six 40-inch COPVs. Also shown are three COPVs in service whose true delta volumes (and thus fiber stress ratios) are of concern.

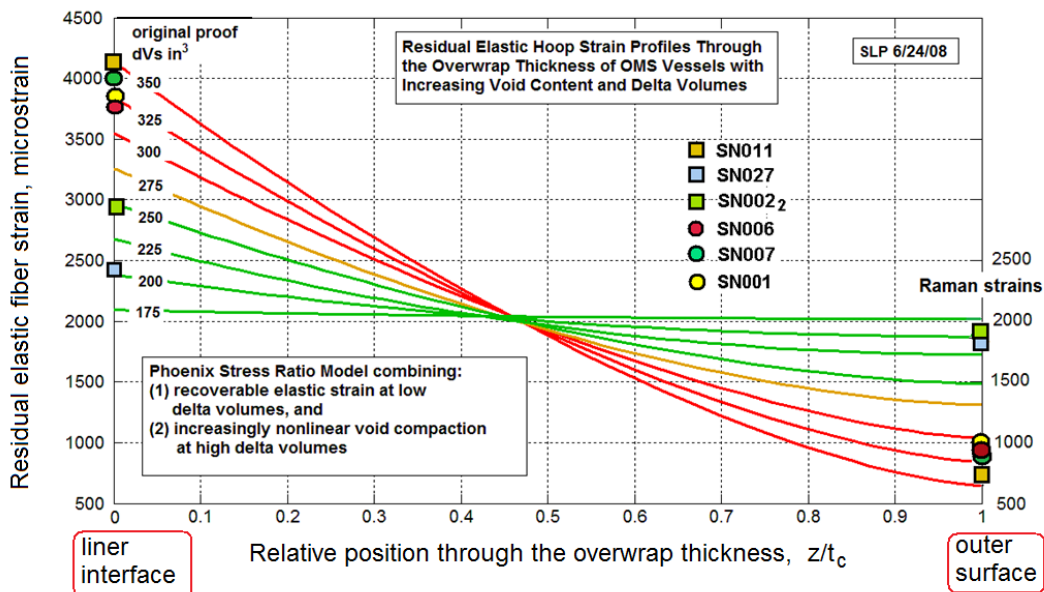


Figure 8. Strain gradient through the overwrap at zero vessel pressure and for various delta volume values.

Shown on the plot in Figure 7 are three vessels, SN018, SN020 and SN021, mentioned earlier in connection with Figure 1. These are vessels for which Raman data would be important to obtain. Based on manufacturer's delta volume data, their  $\Delta V_{pf}$  values are the highest of those remaining in service and there is a possibility that these are lower than indicated, but they could also be higher still, especially SN020 with  $\Delta V_{pf} = 305 \text{ in}^3$ , since some measurement patterns were similar to SN011, which had a much lower than expected burst strength.

Regarding the residual stress pattern in the fibers of the overwrap, Figure 8 shows the strain variation (the slope is the gradient) through the overwrap thickness for several possible delta volume values during proof. The six vessels that have been tested using Raman are shown. These plots were generated from a comprehensive model of the proof process validated by many measurements on many vessels during various pressure cycles. The increasing slope approaching the liner is a standard feature of vessels that cannot be viewed as thin walled structures. Also the inside fiber elastic strains can simply be understood by taking the excess delta volume over and above the value  $\Delta V_{pf} = 175 \text{ in}^3$  and determining how much fiber strain will be generated due to the extra volume since the fibers are adjacent to the liner and by necessity must absorb the extra volume as elastic strain. It is easy to calculate that at  $\Delta V_{pf} = 350 \text{ in}^3$  for a total volume of about  $29,800 \text{ in}^3$  compared to  $\Delta V_{pf} = 175 \text{ in}^3$ , the hoop strain difference will be about 2000 microstrain as shown, and thus greatly reduced on the outside surface to maintain the same compressive force in the liner.

Figure 9 shows the effect of delta volume on the predicted reliability of the 40-inch COPVS for one mission cycle of several hundred hours of service. The main influencing factor is that the mean lifetime depends on fiber stress raised to the power 24. Thus the indicated increases in stress ratio, coupled to a Weibull lifetime shape parameter of about 1.6, lead to reliability reductions spanning more than 'three nines'. Clearly vessels with high delta volume will have unacceptable reliabilities. It is essential to establish the true delta volumes of the remaining vessels in service in order to establish their reliability as they continue service.

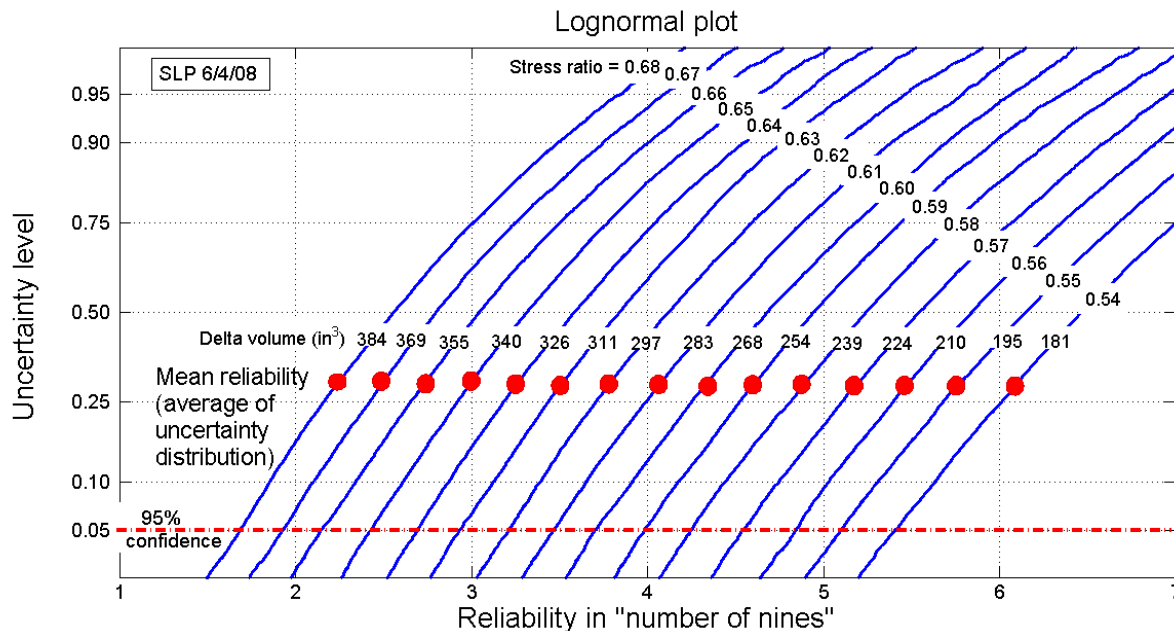


Figure 9. Predicted mean reliability in number of nines for one mission cycle of the 40-inch vessels in remaining service as a function of delta volume.

### V. Summary and Conclusions

The effects of compaction of overwrap voids on inducing high stress gradients through the overwrap and consequently increased fiber stress ratio, are not unique to Kevlar/epoxy COPVs. In fact, for a given void content the severity of the gradient is directly proportional to the fiber modulus, so carbon/fiber epoxy pressure vessels will

also be susceptible. Fortunately carbon fibers are also Raman active, so the same technique may be developed to apply to carbon/epoxy COPVs.

### **Acknowledgments**

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<sup>1</sup>Phoenix, S.L. *New Stress Ratio Formulas Based on Study of the Mechanical Response of OMS SN011 in WSTF Tests*, **White Paper**, November 2, 2007.