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Bioassay Vessel Failure Analysis

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Abstract

Two high-pressure bioassay vessels failed at the Savannah River Site during a microwave heating process for biosample testing. Improper installation of the thermal shield in the first failure caused the vessel to burst during microwave heating. The second vessel failure is attributed to overpressurization during a test run. Vessel failure appeared to initiate in the mold parting line, the thinnest cross-section of the octagonal vessel. No material flaws were found in the vessel that would impair its structural performance.

Content weight should be minimized to reduce operating temperature and pressure. Outer vessel life is dependent on actual temperature exposure. Since thermal aging of the vessels can be detrimental to their performance, it was recommended that the vessels be used for a limited number of cycles to be determined by additional testing.

Background

The Savannah River Site, operated by the Washington Savannah River Company, a Department of Energy contractor, performs routine bioassay sample digestion for personnel testing. Two polymeric vessels failed at recirded temperatures from 220-230°C and pressures ranging from 325 to 550 psig. The door of a microwave oven door glass blew out during an earlier failure. (Figure 1).

During normal test procedures, a small bioassay sample, a gel-type cation resin, and concentrated nitric acid are placed into a PTFE (polytetraflurorethene) inner vessel and a thermoplastic polyetherimide (PEI) outer vessel. The vessel is then heated to a maximum of 220°C for a minimum of 35 minutes. The maximum pressure is pre-set at 550 psig before system shutdown during the test cycle. The sample vessels are hot after the test and are allowed to cool down prior to safe handling. Gel-type resin is used for selective separation of metals, specifically plutonium and americium, from the bioassay sample.

The inner vessel is designed for temperatures up to 250 °C (PTFE softening temperature) and for pressures up to 625 psig. Tests by the manufacturer revealed vessel failure at 1500-1700 psig at 23°C and approximately 1200 psig at 220°C. These tests did not include a pressure relief device which is normally used in bioassay testing. A pressure relief disk and pressure relief device is normally mounted on the top of the vessel that releases pressure at 720 psig per manufacturer's testing. The pressure relief disk did not release during the two vessel failures described in this paper.

During normal testing, ten vessels are inserted in the microwave carousel and one of these vessels is connected to a pressure sensor which controls microwave wattage. Power is increased incrementally until reaching the maximum pressure per test procedure. The electronic pressure protection system shuts off power at a controlled 625 psig vessel pressure. The control system also monitors temperature in the same vessel.

The vessel design, Figure 2, includes an inner vessel with a slip on cap that holds the pressure relief device. The pressure relief device includes a threaded nozzle with an internal hole and a pressure relief disk. The threaded nozzle is made of PTFE (polytetrafluoroethylene) polymer while the relief disk is made of PFA (perfluoroalkoxy, a variation of PTFE). The inner vessel, containing the biomaterial, is machined from a modified PTFE polymer (Dyneon TFM™ PTFE 1700). This vessel is inserted into the outer vessel, made of injection-molded polyetherimide GE Ultem™ 2300. PTFE, Ultem™ and PFA polymers are transparent to microwave energy due to their low dissipation factors (ratio of the material's power loss to the power transmitted through it) [3-6]. Thus, heating of the inner and outer vessels is due to boiling of the contents. The inner vessel heats to approximately 220°C, with the outer vessel at a lower temperature because of the limited thermal conductivity of polymers.

Results and Discussion

A) First Failure

Figure 3 shows that the bottom of the outer vessel fractured with no visible cracking in the upper part of the vessel. The cap did not fail. In Figure 4, the thermal shield is inserted into the bottom piece of the vessel in the upright position. The top surface of the shield is above the fractured surface. However, where the shield is shown upside down (Figure 5), the position of the fractured surface is near the bottom edge of the shield. This substantiates the manufacturer position that the vessels will fail with an inverted thermal shield. When the thermal shield is installed correctly, the installed inner vessel and cap will look like Figure 4. When installed incorrectly, there is a slight gap, approximately 1/16 inch, as shown in Figure 5. The upside down position of the thermal shield would therefore impose additional compressive stresses on the inner vessel.

Using a thermal expansion coefficient of 1.1x 10-05 in/in-°F for PEI [3], the thermal shield expands to a diameter of 1.895 inches. This is still less than the minimum ID (1.901 inches) of the outer vessel. Thermal shield expansion is close but not sufficient to cause failure. Of course, this assumes that the outer vessel stays at room temperature. Using similar thermal expansion calculations and a thermal expansion coefficient of 9.4 x 10-05 in/in-°F for PTFE, the bottom OD of the inner vessel (1.888 inches max.) would expand to 1.954 inches. Since the minimum ID at the bottom of the outer vessel is 1.901 inches, pressure is applied to the outer vessel by the inner vessel. Allowing for 3% elongation (ambient temperatures), the maximum elongated ID is 1.958 inches, still slightly larger than the expanded OD of the inner vessel. However, with an elongation of 1.55% (elevated temperature), the maximum elongated ID is 1.930 inches. Thus, the expanding inner vessel may be able to burst the outer vessel if pressures are excessive. This is a worst case situation due to the assumption that the outer vessel does not grow at higher temperatures. One factor against this situation is that the 1.55% elongation value of PEI is at 150°C. It is unlikely that circumferential pressure from thermal expansion of the thermal shield is sufficient by itself to cause failure. However, the combination of thermal shield and inner vessel pressure may be sufficient to cause failure at the bottom of the outer vessel.

B) Second Failure

Initial observation of this failure revealed that the outer vessel (PEI) cracked into multiple pieces while the inner vessel was relatively intact (Figure 6). Sides of the inner vessel (PTFE) appeared to have blown out with failure occurring near the bottom (Figures 7-8). Half of a bulge is visible on the side of the PTFE vessel, above the notch in Figure 8. The notch also appears in the outer vessel, just below the notch in the inner vessel (Figure 8). The bulge is further magnified in Figure 8B. No defect in the PTFE is visible at this location but this could be the initial failure site of the PTFE. It appears that pressure in the PTFE vessel caused expansion and ballooning, specifically at the bulge, with both circumferential cracking at the bottom and linear cracking through the bulge and other locations.

In order for the PTFE vessel to expand and blow out, the outer vessel has to expand and fail first. However outer vessel expansion is limited to only 3% at room temperature and less at higher temperatures. As expansion increases, failure can occur due to overpressure and material flaws. When the failed outer vessel is taped together (Figure 9), cracking appears to be non-linear although the cap has one straight edge. In Figure 10, one crack is linear and is at the mold parting line. An injection molded part usually displays two lines, 180° apart where the mold separates, similar to a clamshell. When the components of Figures 9 and 10 lay side by side, the fracture at the mold parting line is visible (Figure 11). The vessel appears to open at the mold parting line. Further evidence of crack propagation in the mold parting line is visible in Figure 11. In the thread area, the crack appears to propagate diagonally from the mold parting line.

Based upon the above discussion, the outer vessel appeared to fail first due to overpressurization from expansion of the inner vessel. Pressurization of the outer vessel and subsequent failure could also occur due to moisture in the annular space between the two vessels. The addition of pressures from moisture in the annular space and inner vessel pressure may cause failure at lower than expected test pressures. The failures appear to have initiated near the same area due to the dual fracture peaks shown in Figure 8.

SEM analysis of the fracture surfaces showed two different types of fractures. One, Figure 12, shows a tearing type fracture (ductile) with visible fibers in the light color area (C) of Figure 11. The other type fracture observed below the light color area, Figure 13, shows a flat, brittle surface with holes that are probably prior fiber locations. When compared to the fracture surface of a deliberately failed vessel, the induced fracture surface (Figure 14), the surface of Figure 13appears very similar. Fibers are visible along with a few holes left behind from pulled out fibers. Some fiber pullout is expected on fracture but additional pullout probably occurred at higher temperatures.

C) Pressure Relief Device Testing

A common element in these failures is that the relief device did not release. Pressure testing was performed to determine release pressures. The pressure relief device includes a threaded nozzle (Figure 15) allowing it to be hand threaded into the cap on the inner vessel and a rupture disk. The rupture disk, a solid, circular disk (Figure 16) made of Teflon PFA (polyperfluoroalkoxyethylene), is inserted in the cap prior to threading the nozzle. The disk is approximately 0.020 inch thick with a 0.315 inch diameter and deforms around the circumference to allow pressure release. The manufacturer has tested the pressure relief device for pressure release at 720 psig. An inner vessel cap was drilled and threaded to allow for hose attachment to a high pressure fitting (Figure 17). Early testing with a used nozzle and new rupture disk resulted in pressures of 1025-1267 psig (pressure rise of 120 psig/min). Pressure release data is summarized in Table 3. Heater tape was wrapped around the cap for testing at higher temperatures, 98-104°C. Pressure release was then measured at 785-968 psig using a new nozzle of the old design and low pressure rise. Pressure release was very audible and gage pressure dropped significantly. It was also observed that the used nozzle was easy to hand thread whereas the new nozzle was more difficult. After testing with the new nozzle, threading was similar to the used nozzle. Pressurization of the new threads probably caused thread deformation to allow easier fit-up during the next use. Doubling the pressure rise to 240 psig/min. resulted in pressures of 1398-1428 psig with a used and new nozzle (old design). Since these pressures were very high, a pressure rise of 120 psig/min. was used for remaining tests. A new nozzle design (Figure 18) with a flat face was also tested. At room temperature, the release pressures were 832-848 psig with gage pressures dropping very slowly. These pressure values were a little higher than with the old design nozzle. This is expected since the nozzle design has a flat head versus the bevel design on the old nozzle. In all tests, the rupture disk did not fail. The disk is designed to deform and allow air to escape through the threads.

D) Calculations

Pressure vessel calculations were performed on the outer vessel according to hoop stresses per Roark and Young [9] and ASME Section VIII [10]. The maximum circumferential stress is 2731 psi while the longitudinal stress is only 1091 psi using an internal pressure of 550 psi. With internal pressures of 600 psig and 800 psig, the circumferential stress is 2980 psi and 3973 psi, respectively [9]. The allowable stress level at 177°C per Table 1 is below the calculated stress values. Thus, the actual pressure at failure of the December 13 vessel could be approximately 600 psig per the Roark and Young calculation. The ASME calculation results in an allowable stress of 2340 psi at a pressure of 550 psig. At 600 psig pressure, the ASME allowable stress is 2550 psi. However, at 700 psig, the result is 2976 psi. This is further evidence that pressures were within the range of 600-800 psig at vessel failure.

Material Properties

Polytetrafluoroethylene (PTFE) is used for the inner vessel (Figure 5) primarily for its superior chemical inertness. The actual material is Dyneon TFM™ PTFE 1700, a modification of Dupont PTFE. The mechanical properties of the Dyneon TFM™ PTFE 1700 (Table 1) show that tensile strength is approximately 5800 psi and the elongation is 650% at room temperature [3]. At 204°C and 260°C, the tensile strength drops significantly to 1250 psi and 870 psi, respectively. The 870 psi value is based on Dupont PTFE data [4] and may be slightly higher than that for the Dyneon PTFE. Elongation values above room temperature are not available but are assumed to be higher than those at room temperatures. While there is no definitive glass transition temperature for PTFE, the softening temperature is 260°C and also the continuous use temperature for this version of PTFE. This is above the standard bioassay test temperature of 220°C.

The outer vessel and the thermal shield are injection molded with a polyetherimide (PEI) thermoplastic filled with 30% glass fiber [5]. The tensile strength of this polymer is approximately 4 times higher than the PTFE strength (Table 1) and about 8 times the strength at 150°C. PEI strength above 150°C shows an approximate 50% reduction at 220°C. Although strength is much higher than PTFE, the PEI resin is limited in ductility and toughness. At ambient temperature, the elongation value is only 3% [5] and is estimated at 1.55% at 150°C. The manufacturer's product guide states that the PEI resin is suitable for continuous service at temperatures up to 180°C [5]. A potential fatigue problem may exist with long term use of this PEI polymer at high temperatures. The glass transition temperature, T_g, for the PEI material is 215°C (419°F) which means that increased molecular mobility above this temperature may cause significant changes in material properties [6].

Data for the PEI resin show a significant reduction in impact strength after 40 hours of steam sterilization cycles (30 minutes/cycle) at 132°C per ASTM D1822 [7]. The effect of dry sterilization at 160°C (time not specified) shows no effects on this particular PEI polymer [8]. Therefore, the presence of moisture appears to have significant impact upon temperature stability. In addition, multiple temperature cycles above these temperatures may increase degradation and therefore the number of test cycles should be limited. Testing should be performed to identify this cycle limit.

Conclusion and Recommendations

Three bioassay vessels failed in the SRS bioassay laboratory facilities during October-December, 1999, The first vessel failure is attributed to incorrect placement of the thermal shield disk. A bright color stripe is suggested for use at the top of the inner vessel to allow quick identification of improper placement of the thermal shield. The second vessel failure is attributed to overpressurization based on calculations and failure of the pressure sensor. No flaws were found in this vessel that would impair structural integrity. Overpressurization could be due to high inner vessel pressure and/or moisture in the annular space. Although the failed vessel from October 2 was not available, it is similar in appearance to the December 13 failure and high pressures are suspect. A digital display of the temperature and pressure may be necessary to allow the operator to respond to faulty sensors. The use of thicker, cylindrical vessels or poly-reinforcement type webbing wrapped around the outer vessel would provide additional pressure protection. If possible, content weight should be reduced to allow a lower operating pressure. Since moisture can cause pressure in the annular space, the vessels need to be as dry as possible to minimize pressure buildup. Because thermal aging of the vessels may be detrimental to their performance, it is recommended that additional tests be performed in order to determine the cycle life. Testing is also needed to verify uniform heating and pressure generation at maximum temperatures for all vessel locations.

References

1. Questron Technologies Corporation Website (www.qtechcorp.com), January-February 2000.
2. Phone conversation with Robert Brenna, ATS America Inc (609-586-4986), December 17, 1999.
3. Materials Reference Web Site (www.matweb.com), January-February 2000.
4. Phone conversation with Phyllis Flynn, Dupont Co. (302-479-7731), January 4, 2000.
5. GE Engineering Thermoplastics Product Guide, Ultem PEI Resin, October 1997.
6. Engineered Materials Handbook, *Engineering Plastics*, Volume 2, ASM International (1988), p. 16-21.
7. Plastics Design Library, *The Effect of Sterilization Methods on Plastics and Elastomers*, William Andrew (1994), p. 171
8. Ibid., p. 161.
9. R. J. Roark and W. C. Young, *Formulas for Stress and Strain*, 5th Edition, McGraw-Hill (New York, 1975), p. 504.
10. ASME Boiler and Pressure Vessel Code, Section VIII-Division I, Pressure Vessels, Section UG-27, (1992), p. 24.

Acknowledgements

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Figure 1. One failure occurred in this microwave. Parts of the failed vessel remained in the microwave after failure (shown by arrows) and the vessel carousel was also damaged.

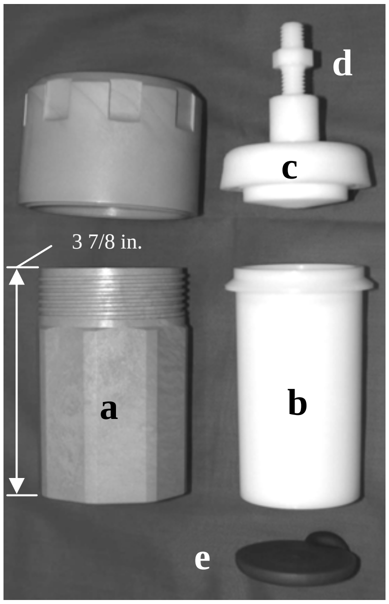

Figure 2. Components of outer (a) and inner (b) vessels and caps. The inner vessel cap (c) includes a threaded pressure relief nozzle (d). Thermal shield (e) is inserted in bottom of outer vessel.

Figure 3. The first vessel failure reveals full bottom head separation. This failure mode is unique compared with the other failures in Figure 6.

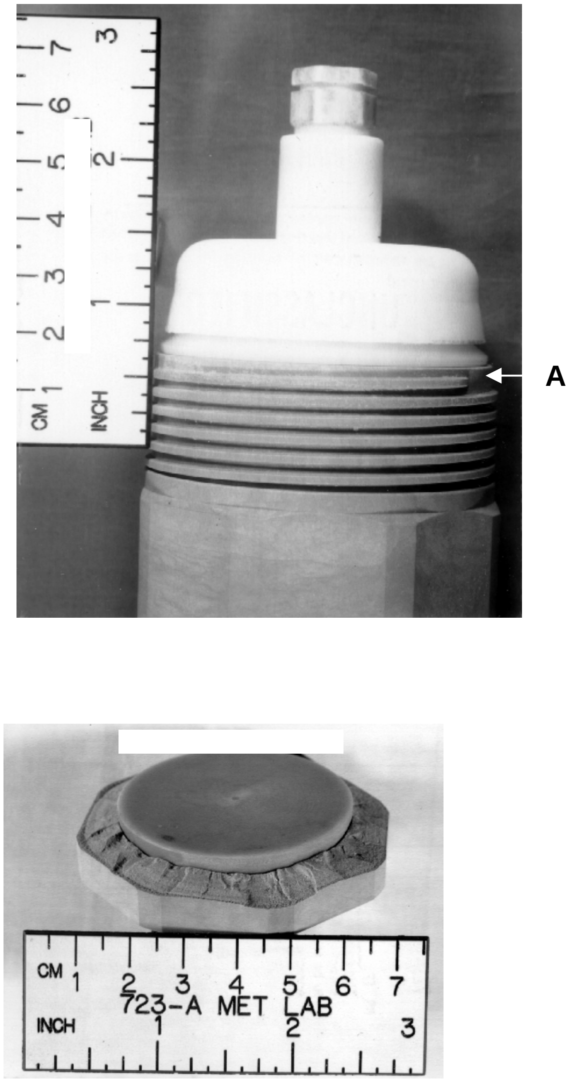

Figure 4. **Inner vessel shown inserted into outer** vessel with correctly placed thermal shield (lower photo). No gap is visible at A.

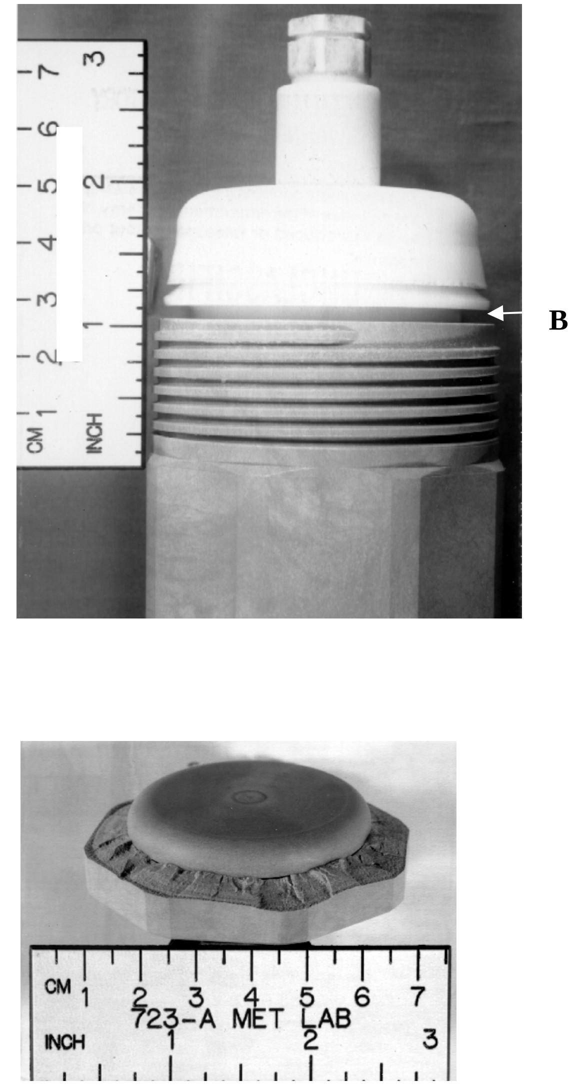

Figure 5 Inner vessel shown inserted into outer vessel with inverted thermal shield as shown in lower photo. Note ~1/16 inch gap at B between inner vessel and top of outer vessel.

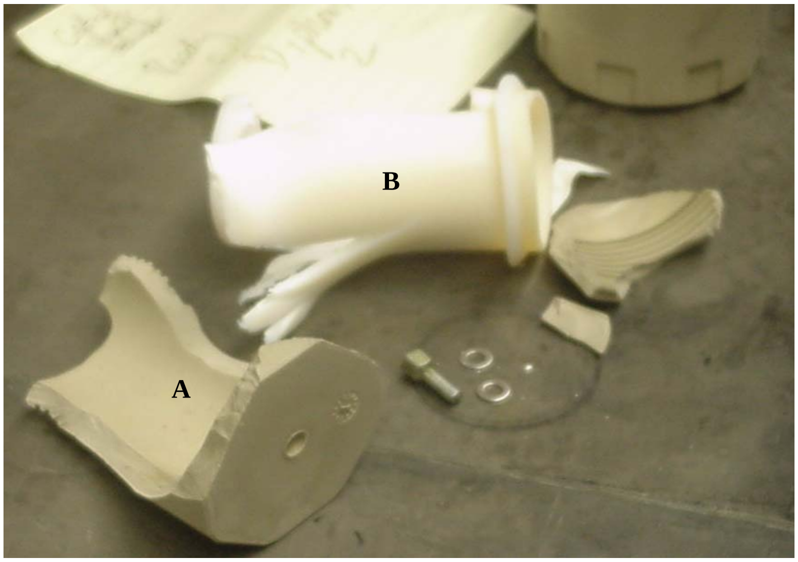

Figure 6. Parts of the second failed vessel that were ejected from the microwave oven. The outer vessel is identified by A with the inner vessel by B. The single screw and washers are not part of this vessel. The round component beneath the washers is the thermal shield.

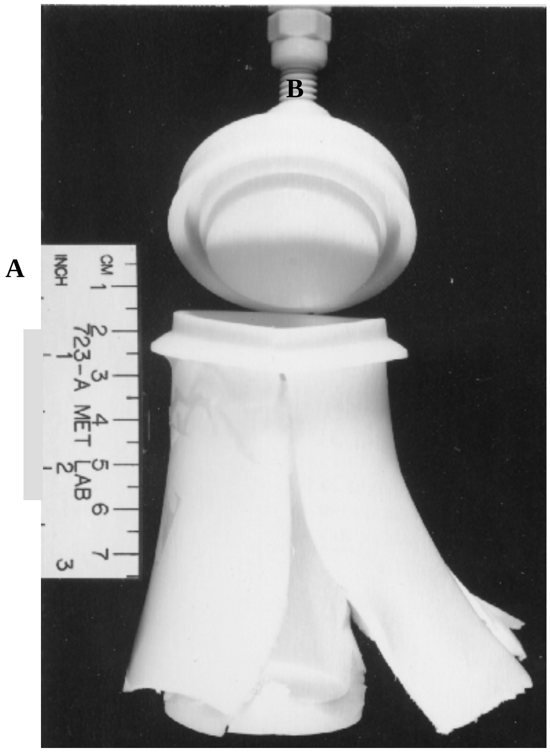

Figure 7. The initiation of failure in the inner PTFE vessel (second vessel failure) appears to occur either circumferentially at the bottom, in a vertical direction or both.

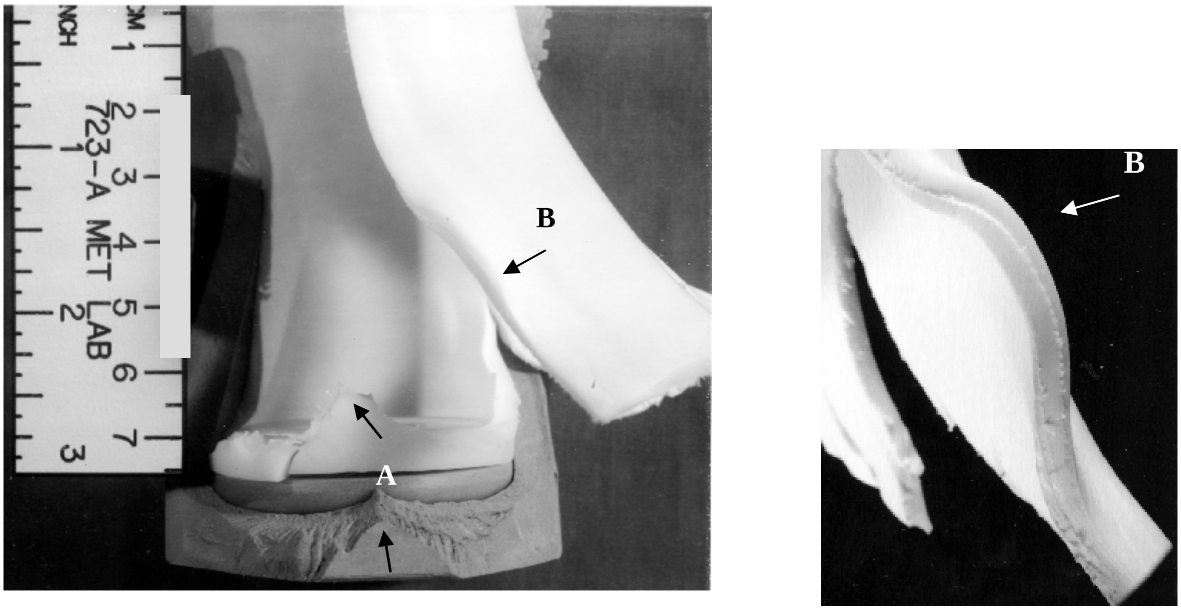

Figure 8. Inner PTFE vessel of Figure 7 is shown positioned within outer vessel. Note matching fracture peaks in inner and outer vessels (A). A bulge in the PTFE is visible at B with an enlarged view on right which is most likely the initial site of the PTFE vessel failure after failure of the outer vessel.

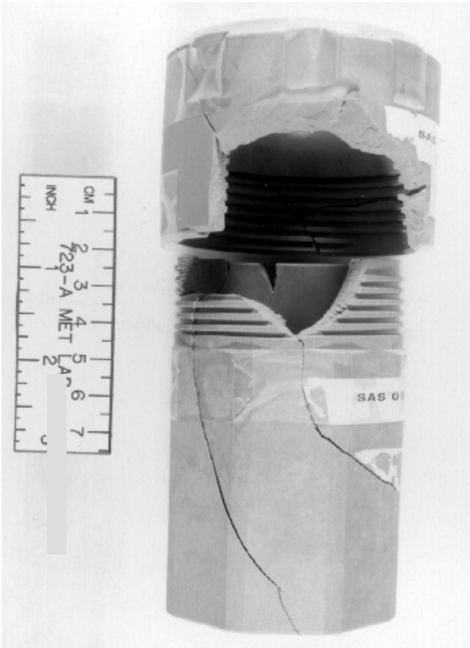

Figure 9. The outer vessel from the second vessel failure showing components taped together. Note that all cracks propagated along a curved path on the bottom part of the shell in this photo.

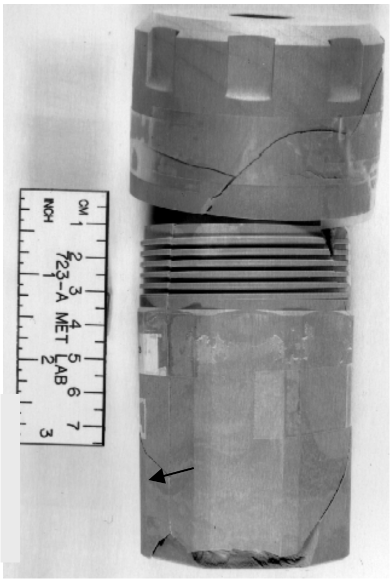

Figure 10. Opposite side of the failed outer vessel from Figure 9 with components taped together. In this case, a crack is barely visible along the mold parting line at arrows.

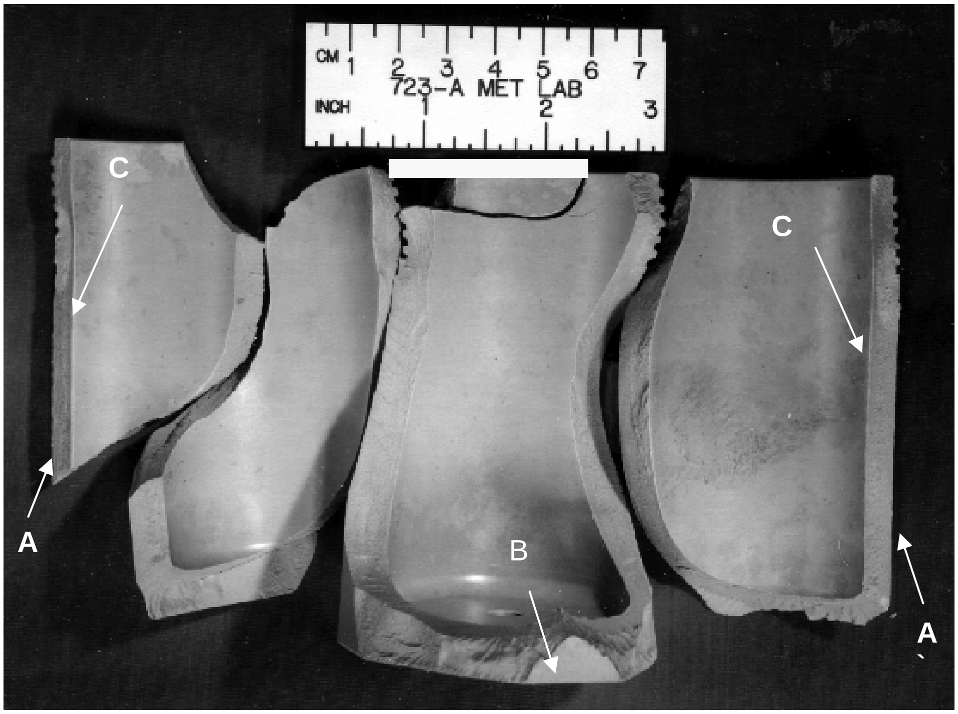

Figure 11. Second vessel failure. Failed outer shell components lined up side by side to show vessel fracture surfaces. The mold parting line is located at arrows marked A. The crack appears to initiate either near B or slightly above it where the bulge in the PTFE vessel occurred. At C the fracture surface appears lighter, possibly due to fiber orientation, stress whitening, flow characteristics, etc.

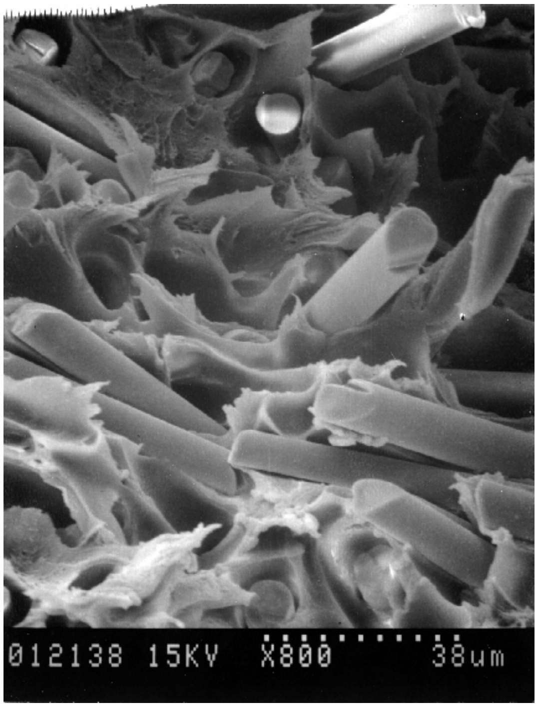

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Figure 13. Fracture surface at C location (light color) in Figure 11 showing glass fibers sticking out of a torn surface.

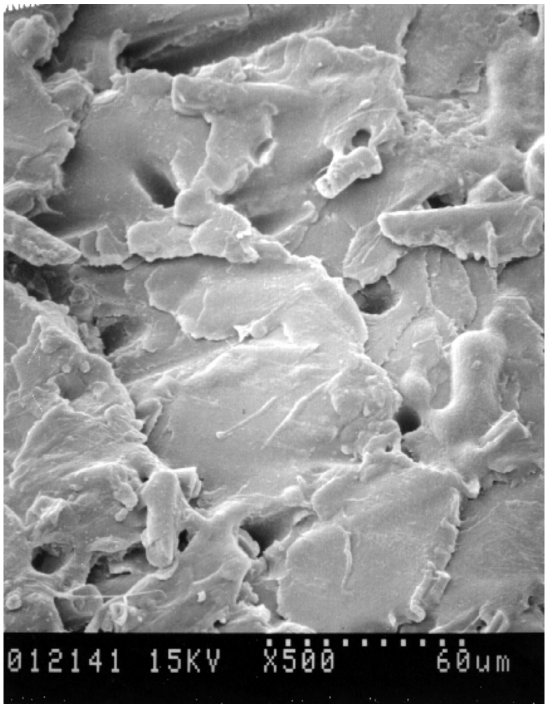

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Figure 12 . Fracture surface below light color C location in Figure 13 showing completely different appearance. The surface appears very brittle. Round holes are prior fiber locations. Note that the magnification is only 500X compared with 800X in Figure 12.

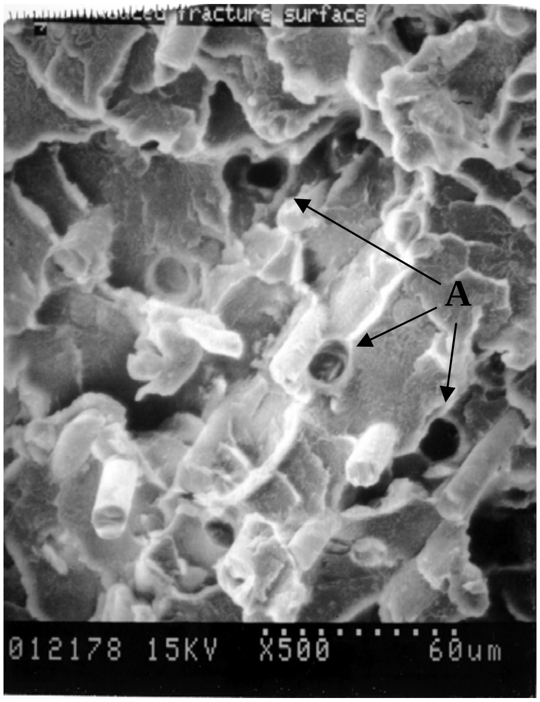

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Figure 14. (left). Fracture surface of induced failure of new vessel showing relatively flat surface with fibers and a few holes (A) where fibers were pulled out. This fracture surface is similar to Figure 12 above.

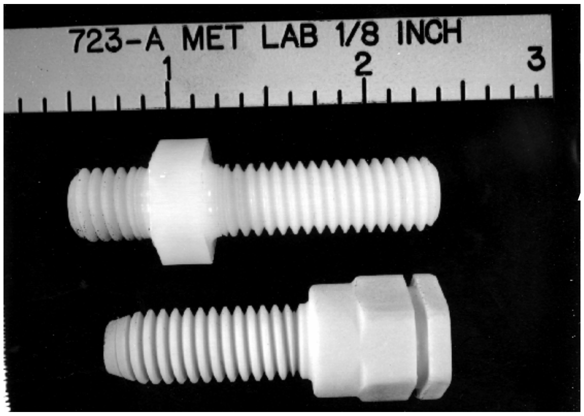

Figure 15. Pressure relief nozzle types. Type A (new design) was used in the October 2 failure. Type B (old design) was used in both December failures. Note the longer taper on Type B versus Type A.

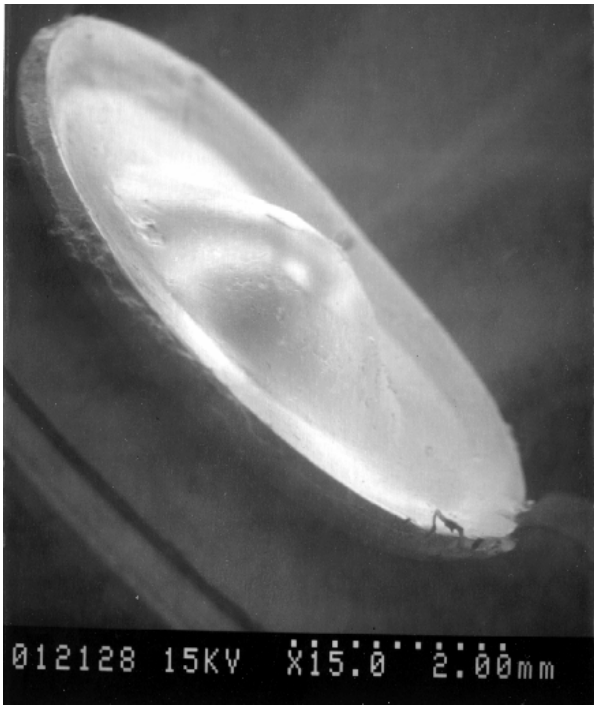

Figure 16. Pressure relief disk from testing. The taper on the nozzle allowed disk deformation as pressure increased. Note the rolled-up edges. This disk does not rupture at normal operating pressures but distorts to allow air to escape around the nozzle threads.

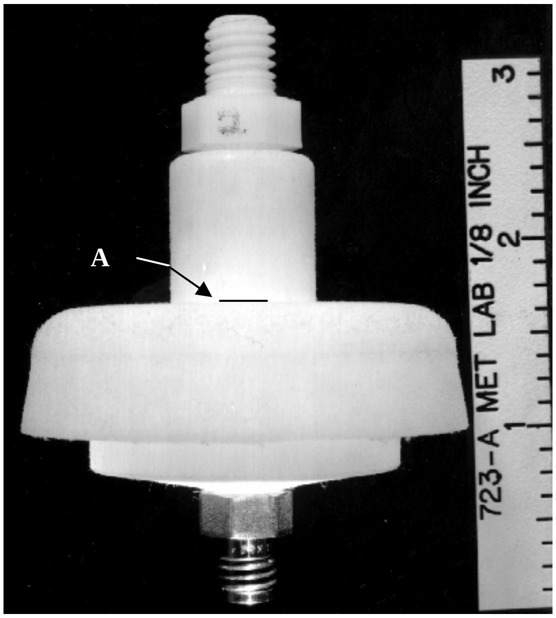

Figure 17. PTFE inner vessel cap with pressure fitting attached for testing rupture disk failure. Heating tape was wrapped around the outer diameter to increase temperature. The pressure relief disk is inserted at position A, beneath nozzle.

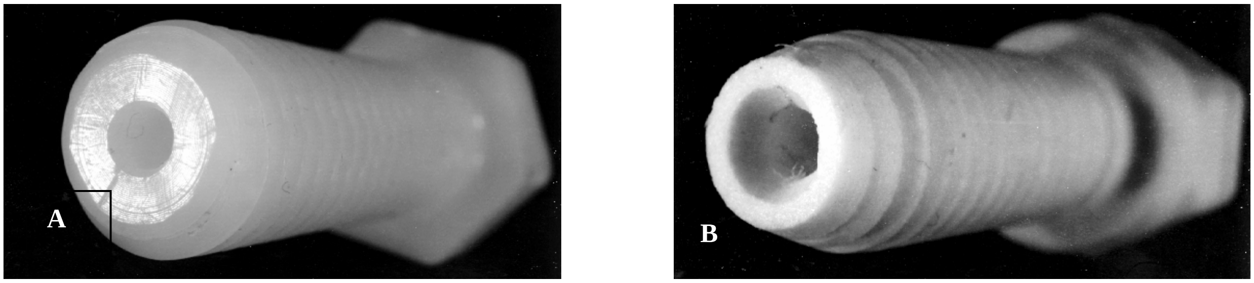

Figure 18. Face of Type A pressure relief nozzle is flat with no ID taper. Face diameter is approximately 5/16 inch. Hole diameter is approximately 0.075 inch. Face of Type B pressure relief nozzle has a taper. Face diameter is approximately 5/16 inch. Hole diameter (B) is approximately 0.080-0.084 inch.

Table 1. Mechanical Properties of Vessel Materials

	PEI Outer Vessel (30% glass reinforced)	PTFE Inner Vessel
Ultimate Tensile Strength, psi		
23°C (73°F)	23,300	5,800
150°C (302°F)	14,225	
177°C (351°F)	12,000	
204°C (400°F)		1,247
190°C (374°F)	8,000	
220°C (446°F)	8,190*	1,000*
Allowable Strength, psi (manufacturer's Data)		
-20°C (-4°F)	8,000	
0°C (32°F)	7,100	
23°C (73°F)	6,200	
93°C (199°F)	4,600	
177°C (351°F)	2,900	
Elongation, %		
23°C (73°F)	3	650
150°C (302 °F)	1.55	NA
Continuous Use Temperature		
°C (°F)	210** (410)	260 (500)

* linear regression values from tensile stress vs. temperature data

** ASTM A-648 test of deflection under 1.8 Mpa load