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Aging Performance of Model 9975 Package Fluoroelastomer O-Rings

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Abstract
The influence of temperature and radiation on Viton® GLT and GLT-S fluoroelastomer O-rings is an ongoing research focus at the Savannah River National Laboratory. The O-rings are credited for leaktight containment in the Model 9975 shipping package used for transportation of plutonium-bearing materials. At the Savannah River Site, the Model 9975 packages are being used for interim storage. Primary research efforts have focused on surveillance of O-rings from actual packages, leak testing of seals at bounding aging conditions and the effect of aging temperature on compression stress relaxation behavior, with the goal of service life prediction for long-term storage conditions.

Recently, an additional effort to evaluate the effect of aging temperature on the oxidation of the materials has begun. Degradation in the mechanical properties of elastomers is directly related to the oxidation of the polymer. Sensitive measurements of the oxidation rate can be performed in a more timely manner than waiting for a measurable change in mechanical properties, especially at service temperatures. Measuring the oxidation rate therefore provides a means to validate the assumption that the degradation mechanisms(s) do not change from the elevated temperatures used for accelerated aging and the lower service temperatures. Monitoring the amount of oxygen uptake by the material over time at various temperatures can provide increased confidence in lifetime predictions.

Introduction

The Savannah River Site (SRS) stores packages containing plutonium (Pu) materials in the K-Area Materials Storage (KAMS) facility. The Pu materials are packaged per DOE-3013 standard and stored within 9975 shipping packages in KAMS.

The KAMS facility DSA (Documented Safety Analysis) credits the 9975 package to perform several safety functions, including criticality, impact resistance, containment, and fire resistance to ensure the plutonium materials remain in a safe configuration during normal and accident conditions. In KAMS, the 9975 package is assumed to perform its safety function for at least 12 years from initial packaging. The DSA recognizes the degradation potential for the materials of package construction over time in the KAMS storage environment and requires an assessment of materials performance to validate the assumptions of the analysis and ultimately predict service life and the need for repackaging.

The Model 9975 double configuration primary and secondary containment vessels (PCV, SCV) are each sealed with dual O-rings (Parker Seals V0835-75) based on Viton® GLT fluoroelastomer. This formulation was specifically developed in the 1970s to allow peroxide curing and improve low-temperature performance. Due to its wide range of properties, the V0835-75 compound is used in many applications, including aerospace, military, chemical, and automotive. The compound is specified in several radioactive material package designs and is not exclusive to 9975.

The Model 9975 is a robust design for shipping, but it was not specifically designed for long term material storage. A program was initiated in 1998 to approve the use for the 9975 shipping package for interim storage in the KAMS facility. Based on available literature and limited test data in combination with a surveillance program, the Model 9975 shipping packages were approved for storage in KAMS for a 12-year period (2-year shipping + 10 year storage). The need for longer storage periods dictated that a surveillance program be developed to predict Model 9975 lifetime in KAMS. Receipt of actual shipments began in 2003.

The aging performance of the O-rings and other package components is therefore being studied to develop lifetime prediction models for each material. The O-ring lifetime prediction model will be used to project O-ring lifetime and provide the storage facility with advanced notice for O-ring replacement, if needed.

Previous testing of O-rings in the SRS Pu surveillance program has three main components 1) field O-ring surveillance and follow-up laboratory verification, including a more thorough analysis of the O-rings removed from one 9975 package that is selected for destructive examination each year, 2) leak testing of mock-up PCV fixtures aged at bounding conditions, and 3) accelerated aging studies using compression stress relaxation (CSR) as a metric for O-ring performance. Information from all three of these efforts has been used to develop a lifetime prediction model.

While the laboratory based accelerated aging testing uses CSR behavior as a primary metric for O-ring performance in defining an end-of-service life condition, it also includes confirmatory elements of high temperature leak testing, and oxygen consumption evaluation. Details of CSR and high temperature leak testing and interim results have been previously reported **[1]**. This paper describes efforts to date to evaluate oxygen consumption rates of the Viton® GLT O-ring material.

Leak-tightness of the O-rings, the primary functional requirement, is related to the retention of mechanical properties. As long as the polymer retains a certain degree of counterforce against the sealing surfaces when compressed, a leak-tight seal is maintained. The minimum counterforce required to maintain leak-tightness in the 9975 seal design has not been established, but is believed to be quite low. Other investigators have suggested threshold force values of 1 N/cm, though not as an absolute value for all designs [2]. In order to predict O-ring service life for this application, compression stress relaxation and leak testing are performed at elevated temperatures to accelerate the degradation mechanisms. Results from these tests can then be extrapolated to actual service temperatures based on appropriate mathematical models, which typically follow the form of an Arrhenius relationship. A limitation of this approach is the possibility that degradation rates observed at elevated temperatures do not extrapolate reliably to lower temperatures due to changes in the degradation mechanism(s). This might be addressed by aging at lower temperatures, but increasingly longer test durations are likely needed in order to reach a failure point.

One way to address this limitation is through the use of oxygen consumption (uptake) analysis [2, 3, 4, and 5].. For most polymers, oxidation is the dominant factor in aging when exposed to oxygen–containing environments, and oxidation rates are generally proportional to the rate of degradation in mechanical properties. More importantly, oxidation rates can be measured with precision in a relatively short period of time, even at relatively low aging temperatures. Therefore, by monitoring the oxygen consumption rate over a temperature range including both service temperatures and elevated mechanical aging temperatures, confidence is gained in the extrapolation of mechanical test results to service conditions.

Experimental

The methodology for oxygen consumption analysis using a fuel cell respirometer has been described by other researchers [2, 3, 4, 5]. Slabs of Parker Seals compound V0835-75 (0.3 cm thick) were cut into 0.6 x 5.0 cm pieces. Each piece was individually weighed. Groups of four were placed in mini Conflat (trademark of Varian, Inc.) (CF) flanged vessels sealed with gold-coated copper gaskets and connected to a valve on each end. The assembly was helium leak tested to ensure leak tight seals. A free volume measurement was also performed. The vessel was connected to a Sable Systems Oxzilla II dual fuel cell respirometer and cylinder air was passed at 20 cc/min through the vessel to flush out any remaining helium and establish a known oxygen content consistent with pure air. The valves were then closed. Vessels with enclosed samples were thermally aged at 40, 60, 80, 100, or 120 ºC for periods up to 1000 hrs.

Upon completion of thermal aging, the vessel with enclosed samples was reconnected to the Oxzilla II and an oxygen depletion measurement was determined relative to an empty reference vessel. In this process, the same cylinder air used to fill the sample vessel flows through the reference vessel and a bypass line. Once the instrument comes to equilibrium in reading the correct oxygen concentration in both the reference vessel and the bypass line, the sample vessel is valved into the bypass line and the measurement begins. The oxygen concentrations of the gas flushed from the reference vessel and from the sample vessel are tracked separately. The difference in measured oxygen concentration between the sample vessel curve and the reference vessel curve was calculated and converted to percent oxygen depletion.

Results and Discussion

There was no significant change in weight for the samples during aging. Oxygen consumption is measured by comparing a composition of oxygen in the surrounding gas in a vessel containing samples versus an empty vessel, see Figure 1.

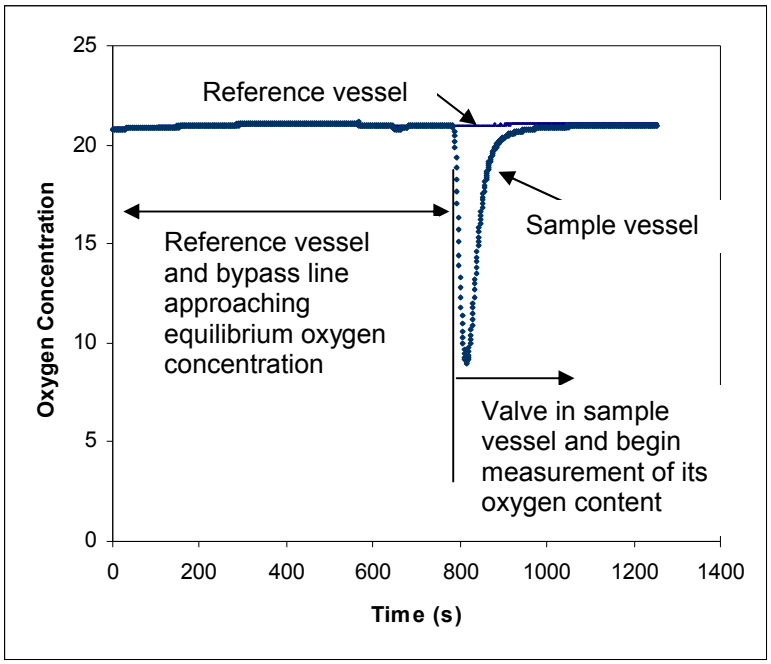

Figure 1 Example of oxygen consumption analysis curve comparing the vessel with sample to the empty reference.

As the cylinder air flows through the sample vessel, it dilutes the vessel air as this mixture flows to the respirometer. In the case illustrated in Figure 1, the oxygen concentration of the diluted gas from the sample vessel drops from 20.95% to 9%, indicating that actual oxygen concentration in that vessel had dropped to significantly less than 9%. The oxygen deficiency of the sample vessel can be calculated by multiplying the gas flow rate by the integral of the oxygen concentration versus flow time (i.e. the area between the two curves). The volume of oxygen was then converted to moles of oxygen and divided by the sample weight and aging time to provide a normalized oxidation rate. The area between the two curves in Figure 1 is proportional to the oxygen depleted from the sample vessel due to uptake by the polymer. A control vessel with no polymer present was aged and tested to verify that the vessel itself did not absorb a significant amount of oxygen.

There are several considerations in the interpretation of this data. For example, if a significant fraction of the oxygen present is consumed during the aging period, the driving force for additional oxidation of the polymer will decrease over time. The magnitude of this effect can be

calculated if measurements are made following increasing aging intervals to track the rate at which the oxygen concentration decreases. However, oxygen consumption is also controlled at some point by the rate at which additional oxygen can diffuse into the polymer. This latter diffusion-limited oxidation effect will control oxidation processes in actual O-rings in service, while the former effect of oxygen depletion will be less important. While there is a limited oxygen source available to the O-rings within the sealed containment vessels, this gas volume is significantly larger relative to the polymer volume than was present in the test vessels. Therefore, it is desirable to minimize the degree of oxygen depletion within the sample vessel during a test. This might be accomplished through a smaller sample volume, a larger vessel volume, or a shorter aging time.

It is also noted that the O-rings are lightly lubricated with silicone vacuum grease in service, potentially reducing oxygen availability to the O-rings. This aspect is not yet accounted for nor credited for oxidation protection.

Another consideration comes from the aging duration. Each measurement provides an indication of the oxygen that was consumed over the period of aging. This yields an average oxidation rate. However, if the oxidation rate varies over time, due either to diffusion limited oxidation effects, depletion of the oxygen in the vessel or other mechanisms, then this average oxidation rate may mask details of how the degradation rate changes over time. Better information regarding this effect can be obtained from limiting the time prior to measurement that the vessel is sealed. In other words, the sample can be aged in a vessel with one valve open to provide a consistent source of oxygen. At periodic intervals, the valve will be closed for a set period followed by a measurement of the oxygen consumed during that period. The valve is then left open for additional aging prior to the next test interval. This approach should provide a closer approximation to the instantaneous oxygen consumption rate throughout an extended aging period.

Several trends are seen in the data collected to date. The oxygen consumption varied with the aging temperature and duration. Longer thermal aging times resulted in greater oxygen consumption at the higher aging temperatures, but not at 40 ºC, see Figure 2.

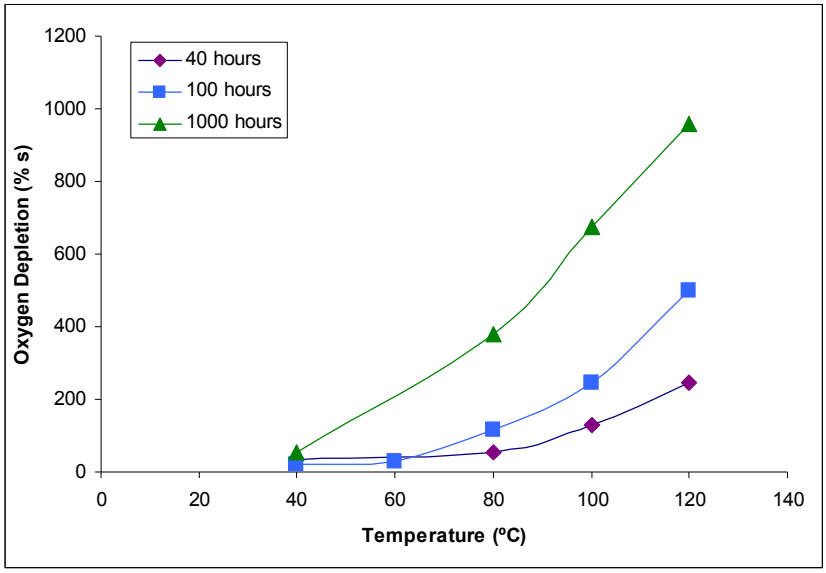

Figure 2 Oxygen consumption as a function of thermal aging temperature for aging durations of 40, 100, and 1000 hours.

Oxygen consumption versus aging time suggests that a rapid consumption rate occurs within 100 hours of thermal aging. The rate of consumption is larger for higher thermal aging temperatures, see Figure 3.

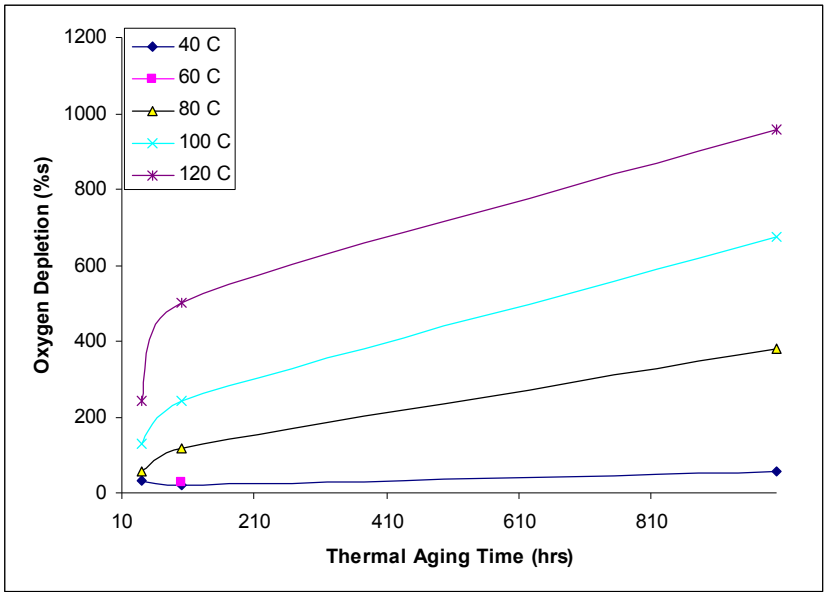

Figure 3 Oxygen consumption versus thermal aging time.

The total amount of oxygen consumed per gram of sample was calculated taking into account the gas flow rate,and the amount of oxygen consumed by the sample. An Arrhenius relation between oxidation and aging time is found, see Figure 4, with elastomer aged at higher temperatures having increased amounts of oxidation per gram of elastomer.

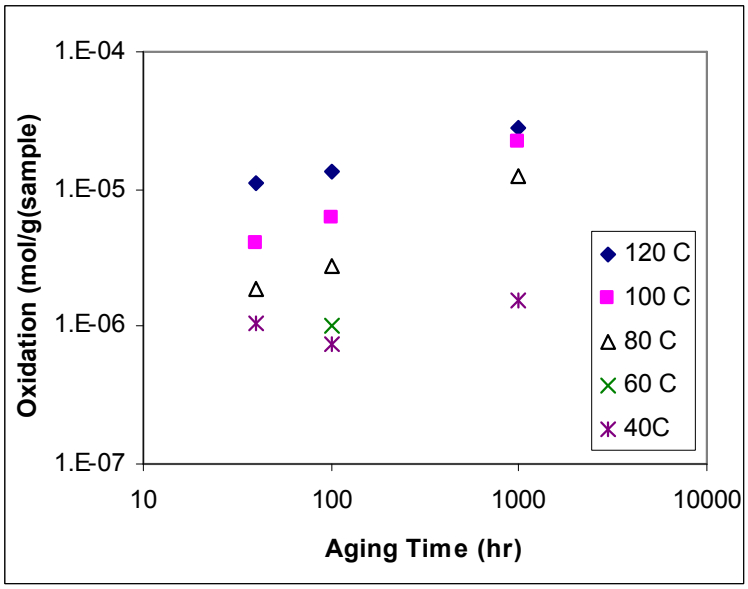

Figure 4 Normalized oxidation amount versus aging time. Amount of oxidation generally increases with increasing time and aging temperature.

By applying the William-Landel Ferry (WLF) method of time-temperature superposition [6], Figure 5, long term oxidation can be predicted for other temperatures. From the data, a continuous rise in amount of oxidation appears to occur, with a tapering of the curve at 100,000 hours (or about 11.4 years).

Table 1 summarizes the shift factors used for the time-temperature superposition. These shift factors are plotted as a function of inverse temperature in Figure 6. The linear relationship seen in the semi-logarithmic plot in Figure 6 shows that there is a consistent trend over the temperatures tested to date. This provides a preliminary indication that no significant change in the degradation mechanism occurs within the temperature range tested.

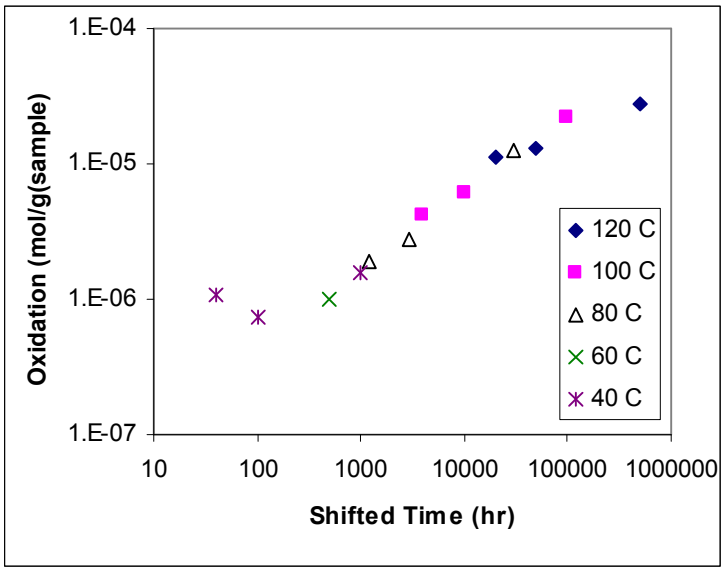

Figure 5 Time temperature superposition principle applied to the elastomer oxidation amounts with data shifted relative to 40 ºC (reference temperature).

Temperature (ºC)	Shift Factor
40	1
60	5
80	30
100	100
120	500

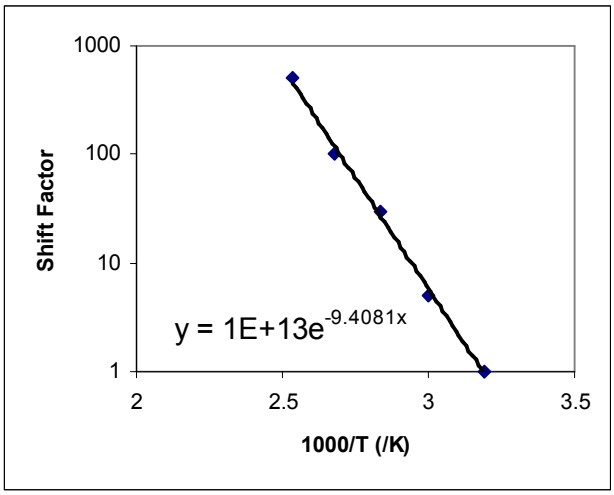

Figure 6 Time temperature superposition shift factor versus inverse temperature. The correlation between the two factors is exponential.

Additional work is in progress to explore the impact of limiting the amount of available oxygen that is consumed during a given aging cycle, and to optimize the sample size and aging duration.

Conclusion

Preliminary oxygen consumption analysis of a Viton GLT-based fluoroelastomer compound (Parker V0835-75) using an Oxzilla II differential oxygen analyzer in the temperature range of 40-120 ºC was performed. Early data suggests oxygen consumption rates may level off within the first 100,000 hours (10-12 years) at 40 ºC and that sharp changes in the degradation mechanism (stress-relaxation) are not expected over the temperature range examined. This is consistent with the known long-term heat aging resistance of fluoroelastomers relative to hydrocarbon-based elastomers, and in absence of antioxidants that may be consumed over time. Additional experimental effort will be undertaken in the short term range within the first 100 hours of thermal aging to capture further details of the oxygen consumption rate.

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