Room Temperature Aging Study of Butyl O-rings

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Introduction

During testing under the Enhanced Surveillance Campaign in 2001, preliminary data detected a previously unknown and potentially serious concern with recently procured butyl o-rings. All butyl o-rings molded from a proprietary formulation throughout the period circa 1999 through 2001 had less than a full cure. Tests showed that sealing force values for these suspect o-rings were much lower than expected and their physical properties were very sensitive to further post curing at elevated temperatures. Further testing confirmed that these o-rings were approximately 50% cured versus the typical industry standard of > 90% cured. Despite this condition, all suspect o-rings fully conformed to their QC acceptance requirements, including their individual product drawing requirements.

These o-rings were considered suspect because the long-term performance for o-rings with less than a full cure was not known. However, engineering judgment was that under-curing is potentially detrimental and could lead to less than optimum performance or, in the worst case, premature seal failure.

An action plan was developed wherein the Kansas City Plant (KCP) would perform further testing to determine the consequences of under-curing on the functionality of the suspect o-rings installed in the stockpile:

- Long-term compression stress relaxation testing (CSR) would be performed at room temperature to represent and anticipate the aging behavior of the small number of suspect o-rings in the stockpile
- The test duration goal would be 10 years minimum at room temperature because:
    - Accelerated aging at elevated temperatures is problematic due to the less than full cure condition of the o-rings; i.e., addition curing vs. aging effects
    - To mitigate replacement consequences, removal of the suspect o-rings, if necessary, will be most feasible after at least 10 years in the stockpile

A new room temperature aging model was developed to predict future sealing performance based on combining existing models for physical and chemical aging mechanisms to meet the following criteria.

- Prediction must ensure there will be no failures before the minimum 10 year replacement goal
- Prediction must detect adverse behavior early enough to allow for timely field return and replacement of o-rings

*Operated for United States Department of Energy under Contract No. DE-ACO4-01AL66850.

Experimental

CSR measurements for this study were made using a Shawbury-Wallace Compression Stress Relaxometer MK.II. This instrument measures the counterforce exerted by a sample maintained at constant strain between rigid metal surfaces inside a compression jig.

O-rings made from three different butyl batches from two suppliers are being tested: suspect batches 17501 (cured 3Q99) and 17996 (cured 2Q00) from Vendor A and non-suspect batch 19634 (cured July 2002) from Vendor B. Suspect o-rings made from 17996 are currently installed within the stockpile. Multiple samples made from a single batch were needed per jig to produce sufficiently high sealing-force measurements for the long-term aging study. Five o-rings with an internal diameter of 6.07 mm and a cross-sectional diameter of 1.60 mm were lubricated with Krytox 240 AD fluorocarbon grease and were nominally compressed 25% in each CSR jig. In addition, o-rings placed in two jigs from batches 17996 and 19634 were post cured 30 minutes in air at 149°C to compare under-cured samples with more fully-cured samples. Sufficient o-rings were available to allow replicate sample testing only for non-post cured batches 17996 and 19634. The counterforce for each jig is periodically measured at room temperature and reported as a normalized sealing force by dividing by the total force measured by the total circumferential length of the five o-rings.

Results and Discussion

Aging data from September 2002 through November 2008 (2385 days) are shown in Figure 1. The data indicate a slightly higher rate of sealing force decline for the suspect batches from Vendor A. Post curing causes the initial and subsequent sealing force to be significantly greater for the suspect batch 17996. The increase in sealing force with post cure is expected and mirrors the change in physical properties (e.g., higher hardness) measured on post-cured test slabs.

The variability in data makes it questionable to conclude any significant effect post curing may have on sealing force for the non-suspect batch 19634. This behavior correlates with the physical property measurements on Vendor B slabs that showed only minor differences between post cure and no post cure.

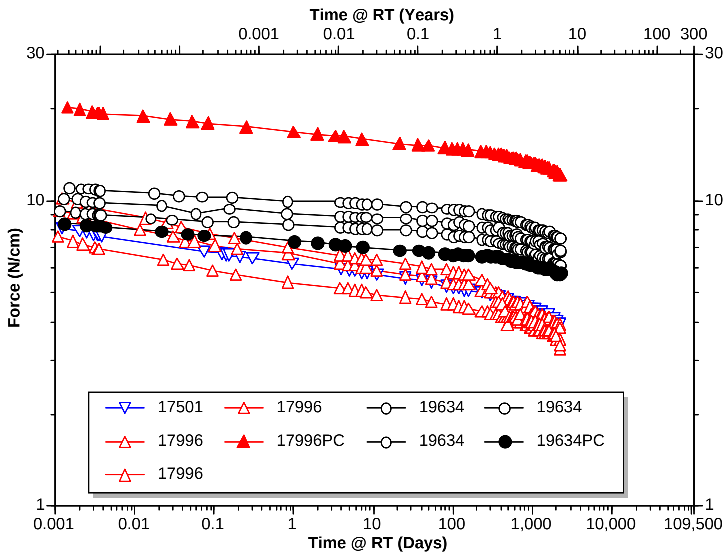

Figure 1. CSR Test Results at Room Temperature. (PC suffix: samples were post cured.)

An aging model was developed to fit the room temperature CSR data being measured and to predict future aging performance based on benchmark aging behavior of butyl rubber from Vendor C. The model combines physical relaxation processes that dominate early on with chemical degradation processes that dominate at longer times [1].

Physical Stress Relaxation

The decrease in sealing force per unit o-ring length (F divided by L) from physical effects is modeled using the Chasset-Thirion equation [2].

$$F_p(t) = F_e[1 + (t/\tau)^{-m}] \tag{1}$$

The Chasset-Thirion equation is an empirical model that predicts viscoelastic relaxation dynamics where F_e represents the purely elastic equilibrium stress and m and τ are material parameters that have been linked to a crosslink density and temperature dependence [3].

Chemical Stress Relaxation

Gillen and coworkers at SNL/NM have determined CSR parameters for chemical stress relaxation (i.e., activation energy) for many of the butyl o-ring formulations used in the stockpile [4, 5]. They have determined that the CSR behavior for these compounds is dominated by bond scission due to oxidation. Unfortunately, activation energies for Vendor A's suspect butyl formulation have not, as yet, been determined. Therefore, the activation energy for chemical stress relaxation of Vendor C's butyl formulation, determined to be 75 kJ/mol at 23°C by Gillen et al. [4], is used here an estimate for chemical stress relaxation in Vendor A's butyl formulation.

Vendor C's butyl formulation was selected due to its relatively low activation energy for oxidative degradation, thereby providing a lower boundary, worst-case condition for o-ring sealing performance. In addition, o-rings returned for surveillance testing showed the Vendor C manufactured product had the highest compression set measurements of all the approved manufacturers. It is also noted that actual aging of suspect o-rings in the stockpile will be ~50% slower than in this study because the nitrogen gas backfill in the weapon decreases the concentration of oxygen and the rate of oxidative degradation [4]. Thus, any aging behavior of the suspect o-rings that outperforms the predicted aging behavior of Vendor C's o-rings would be considered acceptable during the planned ten-year minimum test period.

Gillen et al. [4] describe the Arrhenius or time-temperature superposition technique used to predict normalized CSR at 23°C dominated by chemical stress relaxation for Vendor C's butyl rubber. Consequently, the percentage drop in sealing force with time due to chemical relaxation effects alone can be obtained from Figure 2.

Combined Physical and Chemical Stress-Relaxation Model

The Chasset-Thirion equation and Figure 2 can be combined to predict the sealing force with time at room temperature. For the proposed model it is assumed that the stress relaxation within the first 100 days is predominately caused by physical effects and any chemical effects represent a small (<10%) contribution. Parameters for the Chasset-Thirion equation can be modified in the future by fitting to a smaller time scale if significant chemical effects are suspected during 100 days of aging. Thus, Equation 1 is used to represent the early stress relaxation.

$$F(t) = F_e[1 + (t/\tau)^{-m}] \qquad \text{for } t \le 100 \text{ days} \tag{2}$$

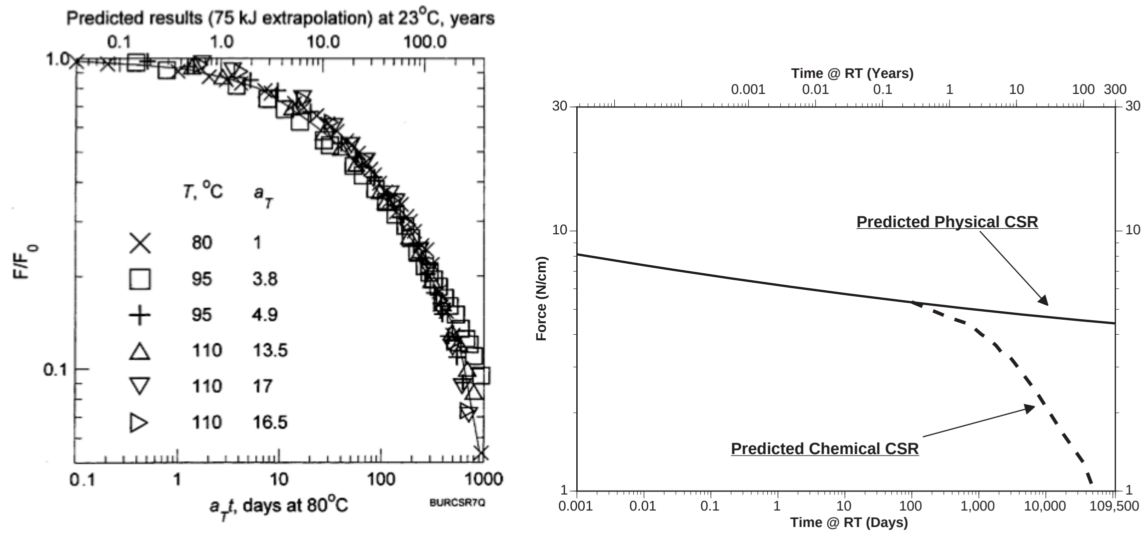

Figure 2. Left plot depicts chemical stress-relaxation prediction for Vendor C's butyl rubber using the time-temperature superposition technique [4]. (Upper x-axis represents the predicted time scale at 23°C assuming a 75 kJ/mol activation energy obtained from the oxygen consumption results is valid from 80° to 23°C). Right plot depicts physical and chemical stress-relaxation predictions for Batch 17501, Jig 13V, at room temperature. (The solid line depicts stress-relaxation predictions dominated by physical effects from the Chasset-Thirion equation. The dashed line depicts stress-relaxation predictions dominated by chemical effects that represents worst-case performance of Vendor C's butyl rubber.)

After 100 days, chemical effects dominate and the stress relaxation can be represented by:

$$F(t) = F_p(t = 100 days) * (F(t)/F_0) \quad \text{for } t > 100 \text{ days} \tag{3}$$

Where $F_p(t = 100 days)$ is calculated from Equation 1 and $F(t)/F_0$ is obtained from Figure 2. An example of plotting Equations 2 and 3 for Batch 17501 is shown in Figure 2.

The graph from Figure 1 is reproduced in Figure 3 showing the sealing-force measurements plotted with worst-case, benchmark predictions from Equations 2 and 3.

Previous work has determined that a sealing force of 1 N/cm is a conservative lower limit to prevent leakage for this type of sealing application [5, 6]. Predicted aging behavior for the suspect o-rings combining Chasset-Thirion with E_a for Vendor C's butyl shows force-per-unit o-ring length values remain above the 1 N/cm definition of potential seal failure in excess of 100 years (Figure 3).

Conclusions

The new predictive model provides a comparator to gauge the actual aging of the suspect o-rings with the predicted aging for a worst-case chemical stress relaxation mechanism based on Vendor C's butyl. Any significant downward deviation from the predicted chemical stress-relaxation values would cause concern and initiate discussions on whether to return and replace suspect o-rings before the 1 N/cm failure limit would be reached.

Results to date show good agreement with the model and CSR values measured at room temperature. Initial predictions indicate replacement of suspect o-rings before the ten-year goal is unwarranted at this point.

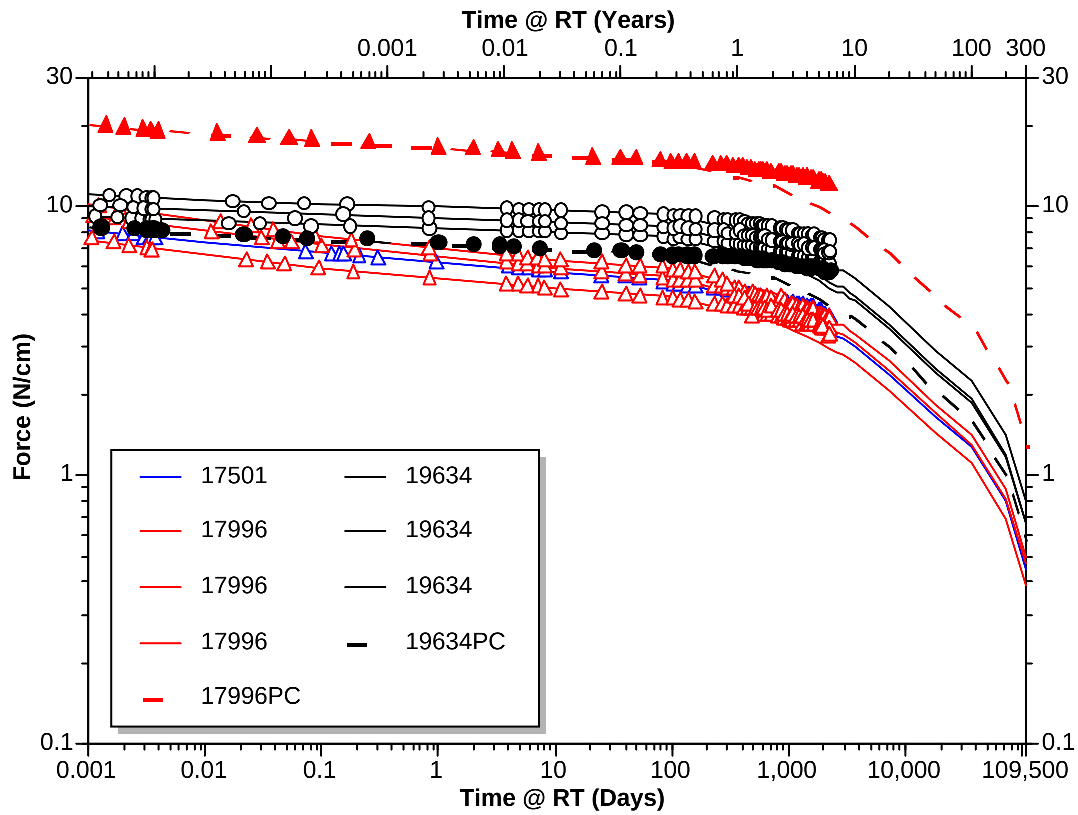

Figure 3. CSR test results and predictions at room temperature. (Plot from Figure 1 is reproduced with each line depicting predicted, worst-case Vendor C material aging behavior for a single jig. Symbols denote a single CSR jig loaded with o-rings from the designated lot number. A PC suffix indicates that these samples only were post cured.)

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