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Aging of Weapon Seals – An Update on Butyl O-ring Issues

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Abstract

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 on several programs. All butyl o-rings molded from a proprietary formulation throughout the period circa 1999 through 2001 had less than a full cure. Engineering judgment was that under curing is detrimental and could possibly lead to sub-optimum performance or, in the worst case, premature seal failure. An aging study was undertaken to ensure that suspect o-rings installed in the stockpile will retain sufficient sealing force for a minimum ten-year service life. A new prediction model developed for this study indicates suspect o-rings do not need to be replaced before the ten-year service life. Long-term testing results are reported on a yearly basis to validate the prediction model. This report documents the aging results for the period September 2002 to January 2011.

Summary

The specification (Rubber, Butyl, For Packing, Preformed) defines the requirements for butyl rubber used in the manufacture of o-rings and seals for various programs. Butyl o-rings procured per requirements throughout the period circa 1999 through 2001 were discovered to have less than a full-cure condition even though the suspect o-rings fully conformed to every acceptance requirement, including their individual product drawing requirements. Engineering judgment was that under curing was potentially detrimental, possibly leading to less than optimum performance.

A significant finding investigation (SFI) was released in March 2002 to investigate long-term performance of o-rings installed in the stockpile. Consequently, an aging study was initiated at KCP to ensure that suspect o-rings installed in the stockpile would retain sufficient sealing force for at least ten years to allow for timely replacement. A new room-temperature aging model was also developed at KCP to predict future sealing performance based on combining existing models for physical and chemical aging mechanisms in o-rings. The closeout memo for the significant finding investigation (SFI) recommended that long-term testing results from the KCP aging study be reported on a yearly basis to either validate the prediction model developed or to indicate the need to revise the model. As a consequence of the uncertainties in the lifetime predictions, it was further recommended that the KCP aging study continue for as long as the suspect o-rings remained in the stockpile. The measuring instrument used to monitor aging degradation broke down in June 2009 and was not repairable. Replacement equipment was received in late 2010. This report documents the aging results for the period September 2002 to January 2011.

Compression stress relaxation measurements on representative o-rings indicate that the room-temperature aging data is well represented by the new KCP aging model. Current predictions indicate that replacement of suspect o-rings before the ten-year service life is unwarranted at this point. Additional long-term testing will be used to validate the prediction model.

Discussion

Scope and Purpose

Butyl o-rings procured per specification throughout the period circa 1999 through 2001 were discovered to have a less than full-cure condition. 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. Consequently, an aging study was begun at the Kansas City Plant (KCP) to ensure that the suspect o-rings installed in the stockpile would retain sufficient sealing force for at least ten years to allow for timely replacement. The aging study would also help determine if suspect o-ring performance was satisfactory so that replacement would not be necessary during the stockpile lifetime. The closeout memo for the SFI [1] recommended that long-term testing results from the KCP aging study be reported on a yearly basis to validate a proposed aging-behavior prediction model. A previous report (KCP-613-6889) documents the history of the SFI and summarizes the aging study results for the period of September 2002 to December 2003 [2]. This report updates KCP-613-6889 and summarizes the aging study results for the period of September 2002 to January 2011. Most background information has been omitted for brevity. See KCP-613-6889 for more information and a complete history of this issue.

Activity

This section describes the actions taken in response to the discovery of butyl rubber o-rings that have less than a full cure. The discovery and investigation leading to closure of the SFI are addressed in the Background section. The experimental investigation into the long-time aging of butyl rubber is described in the aging study section. The model used to interpret the experimental results and make lifetime predictions is described in the aging-model section.

Background

The specification for butyl rubber defines the property requirements and the approved suppliers for the manufacture of butyl o-rings for the various programs. Issues A, B, C, and D of the document were never released at KCP. Burke Industries and Parker Seals were both listed as the only approved suppliers on issue E, released July 1976. Bryant Rubber was added as an approved supplier on issue L, released May 1986. RD Rubber was added as an approved supplier on issue N, released August 1987. Issue V was released in early 1995 and was the controlling document at the time the under-cured o-rings were discovered. Issue V lists all four of the above butyl rubber suppliers as approved manufacturers. All of these suppliers' butyl rubber materials are different from one another and their ingredients are proprietary. Subsequent activities have identified the butyl formulation ingredients and levels for two of these suppliers: Burke Industries and Polyone Corporation, a custom rubber mixing company sub-contracted by RD Rubber.

In summer 2001, sealing-force tests at KCP detected that some war reserve (WR) butyl o-rings procured for the W76, W78, and W80 exhibited characteristics of not receiving 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. These results were subsequently confirmed at Sandia using modulus profiling and stress-strain test methods [3]. Further testing confirmed that all butyl o-rings supplied by RD Rubber Technology Corporation throughout the period circa 1999 through 2001 were approximately 50% cured versus the typical industry standard of > 90% cured. Despite this condition, all suspect o-rings fully conformed to the acceptance requirements, including their individual product drawing requirements. Engineering judgment was that under curing is detrimental and could lead to less than optimum performance or, in the worst case, premature seal failure.

A long-term aging study was initiated at KCP in September 2002 to ensure that installed suspect o-rings would retain sufficient sealing force to meet the National Nuclear Security Administration (NNSA) goal of achieving a ten-year minimum service life before replacement.

An engineering evaluation was conducted in early 2003 to assess the lifetime of the suspect o-rings [4] and close out the SFI. Aging data on butyl rubber supplied from different manufactures was used in the engineering evaluation. The lifetime estimates varied over a broad range due to uncertainties about the rate of oxidative degradation, which is likely to dominate the long-term stress relaxation behavior of the o-rings. Despite the uncertainty, model predictions based on the most likely rate constants indicated acceptable sealing forces for greater than the minimum ten-year service life. Based on the lifetime estimates along with the results of an earlier SFI [5], it was concluded that the small number of suspect o-rings installed in the stockpile will not have a detrimental impact on one project's performance (suspect o-rings were not installed in the other projects). As a consequence of the uncertainties in the lifetime predictions, it was further recommended that the KCP aging study continue for as long as the suspect o-rings remained in the stockpile and that KCP provide annual updates of the findings. The SFI closeout letter was issued in March 2003.

Butyl O-ring Aging Study

This section fulfills the SFI closeout requirement for an annual summary of the aging study results. Findings of the long-term aging study from September 2002 through January 2011 are documented in this section of the report.

Compression Stress Relaxation (CSR) testing at room temperature (22 ± 1.5°C) was chosen as the best method to represent and anticipate the aging behavior of the small number of suspect o-rings in the W78 stockpile. Stress relaxation measurements can be made in compression, shear, or tension; a variety of equipment is available for these measurements. CSR testing is commonly used to predict the service life of o-ring elastomers as compressive properties are directly relevant to their role in maintaining a seal.

CSR measurements for this study were made using a Shawbury-Wallace Compression Stress Relaxometer MK.II. This instrument (Figure 1) measures the counterforce exerted by a sample maintained at constant strain between rigid metal surfaces inside a compression jig (Figure 1) as a function of time. The samples, with or without lubrication, are first placed in the jigs and compressed to the desired strain at room temperature. The jigs are then placed individually in the stress relaxometer where a pneumatic ram with an in-line load cell is brought into contact with the jig. The ram applies an increasing load on the jig until a slight additional compression of the test sample is detected by the breaking of an electrical contact. At this point, the equipment automatically displays the force measurement and the ram motion is reversed, thus signifying that the displayed force is equal to the counterforce exerted by the test sample.

The Shawbury-Wallace Compression Stress Relaxometer began giving erratic measurements during the summer of 2009. Several repair attempts and troubleshooting efforts lasting months by the manufacturer were unsuccessful. The defect was finally traced to the display which is no longer manufactured. A new instrument was procured and installed during late 2010 (Figure 1). The procurement process also took longer than anticipated because the manufacturer is a foreign supplier located in England and the new instrument was required to be certified by a Nationally Recognized Testing Laboratory (NRTL) prior to installation.

Unfortunately, the new instrument generates measurements that are higher than the old instrument. A spring in a dedicated jig is used for detection of any instrument measurement drift. The old instrument measured 301 N and the new instrument measures 307 N. Consequently, 6 N will be subtracted from the force measurements to correct for the difference in instruments.

Figure 1. New CSR Force Measuring Instrument and 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 R&S Processing and non-suspect batch 19634 (cured July 2002) from Polyone Corporation. Suspect o-rings made from 17996 are currently installed within the W78 stockpile. Since small o-rings were readily available for testing, multiple samples made from a single batch were needed per jig to produce sufficiently high sealing-force measurements for the long-term aging study. Consequently, 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 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 sealing force for each jig is periodically measured at room temperature and reported as normalized sealing force, which is arrived at by dividing the total force measured by the total circumferential length of the five o-rings.

Aging data from September 2002 through January 2011 (3020 days) are shown in Figure 2. The data indicate a slightly higher rate of sealing-force decline for the suspect batches from R&S Processing. 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 [2].

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 Polyone slabs that showed only minor differences between post cure and no post cure.

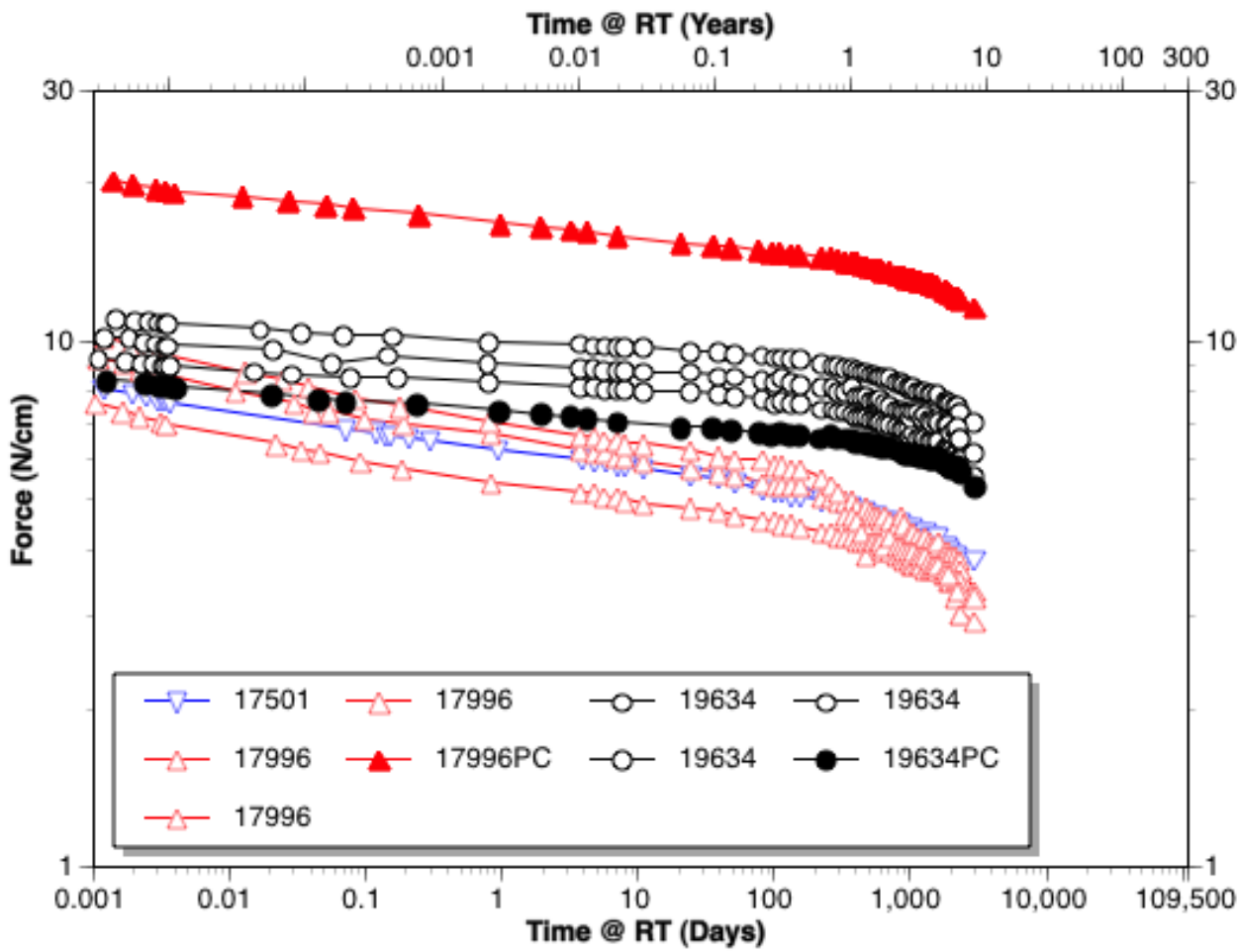

Figure 2. CSR Testing Results at Room Temperature. (Symbols denote a single CSR jig loaded with o-rings from the designated lot number. A PC suffix indicates only these samples were post cured.)

Aging Model

An aging model has been developed to fit the room temperature CSR data being measured and to predict future aging behavior based on benchmark aging behavior of butyl rubber from Burke Industries. The model combines physical relaxation processes that dominate early on with chemical degradation processes that dominate at longer times [2].

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 [6].

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

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 cross-link density and temperature dependence [7].

An example of how the physical stress relaxation behavior was modeled in this study is shown in Figure 3 where the Chasset-Thirion equation was used to fit the aging behavior for batch 17501 during approximately the first 100 days. Values for F_e ranged from 2.9 to 7.6 N/cm for all the samples in this study.

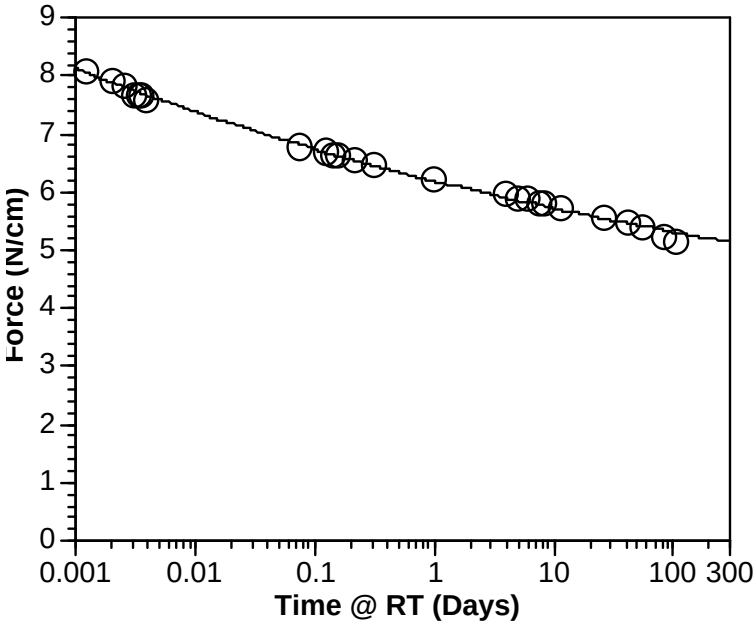

Figure 3. CSR Testing at Room Temperature for Batch 17501 in Jig 13V. (Symbols denote measured values and the solid line denotes the fit to the Chasset-Thirion physical stress-relaxation equation where F_e is 2.89 N/cm, τ is 7.132 days, m is 0.06696 days, and the R^2 value is 0.997.)

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 [8, 9]. They have determined that the CSR behavior for these compounds is dominated by bond scission due to oxidation. Unfortunately, activation energies for R&S Processing's suspect butyl formulation have not, as yet, been determined. Therefore, the activation energy for chemical stress relaxation of Burke Industries' butyl formulation, determined to be 75 kJ/mol at 23°C by Gillen *et al*. [8], is used here as an estimate for chemical stress relaxation in R&S Processing's butyl formulation.

Burke Industries' 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 Burke-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 [8]. Thus, any aging behavior of the suspect o-rings that outperforms the predicted aging behavior of Burke Industries' o-rings would be considered acceptable during the planned ten-year test period.

Gillen *et al*. [8] describe the Arrhenius, or time-temperature superposition technique, used to predict normalized CSR at 23°C dominated by chemical stress relaxation for Burke Industries' butyl rubber. Consequently, the percentage drop in sealing force with time due to chemical relaxation effects alone can be obtained from Figure 4.

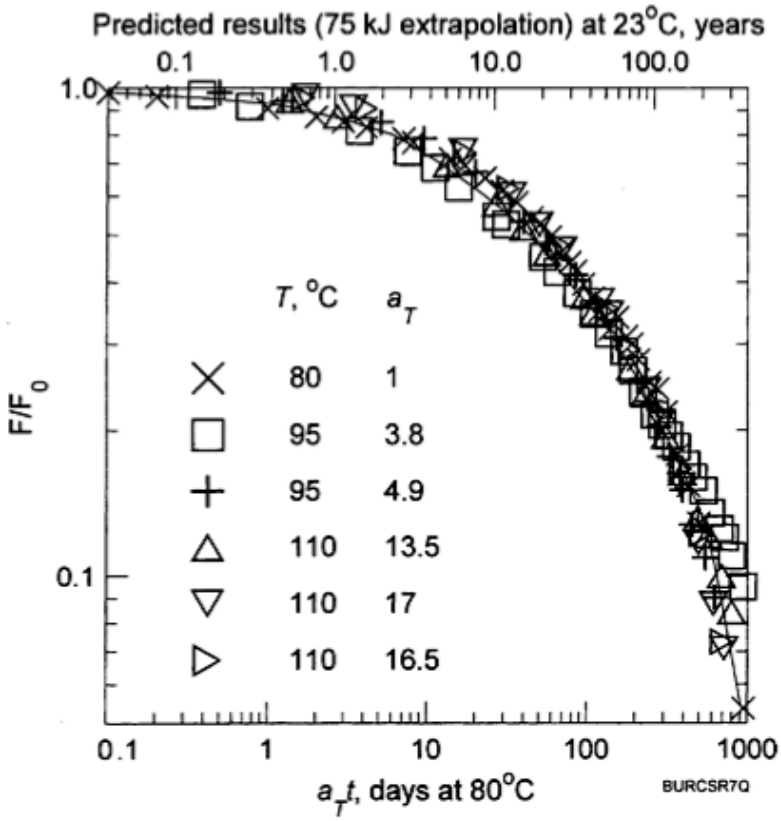

Figure 4. Chemical Stress-Relaxation Prediction for Burke Industries' Butyl Rubber Using the Time-Temperature Superposition Technique [8]. (Upper x-axis represents the predicted time scale at 23°C assuming a 75 kJ/mol activation energy obtained from the oxygen consumption results is valid from 80° to 23°C.)

Combined Physical and Chemical Stress Relaxation Model

The Chasset-Thirion equation and Figure 4 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:

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

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

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

Where $F_p(t = 100 days)$ is calculated from Equation 1 and $F(t)/F_0$ is obtained from Figure 4. An example of plotting Equations 2 and 3 for Batch 17501 is shown in Figure 5.

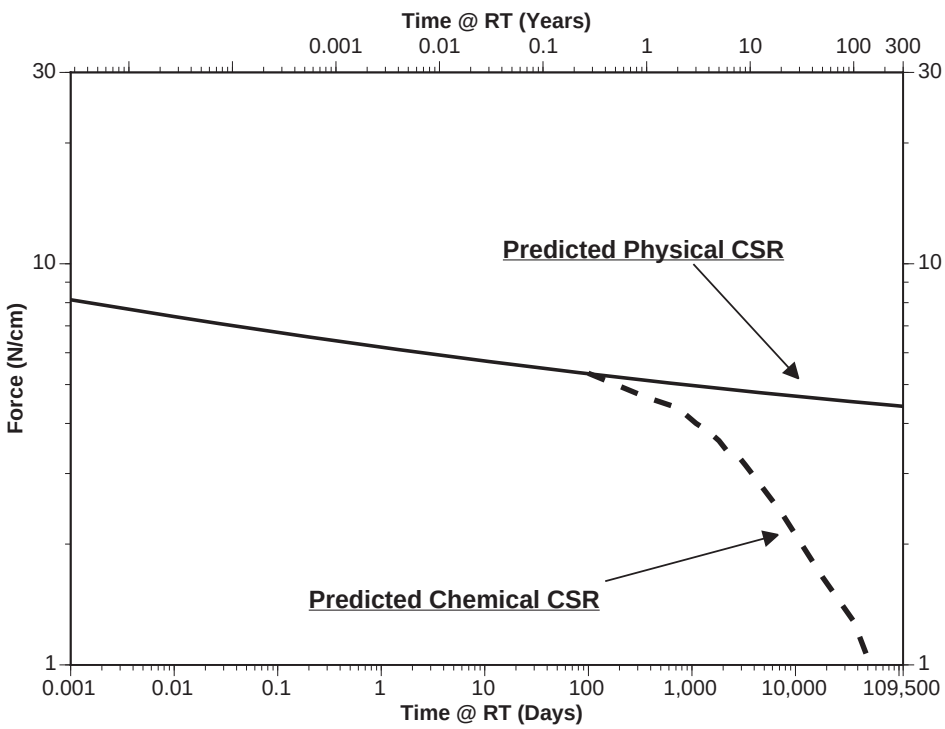

Figure 5. Physical and Chemical Stress-Relaxation Predictions for Batch 17501, Jig 13V, at Room Temperature. (The solid line depicts stress-relaxation predictions dominated by physical effects from the Chasset-Thirion equation. The dashed line depicts stress-relaxation predictions dominated by chemical effects from Figure 4 that represents worst-case performance of Burke Industries' butyl rubber.)

The graph from Figure 2 is reproduced in Figure 6 and Figure 7 showing the sealing-force measurements plotted with worst-case, benchmark predictions from Equations 2 and 3.

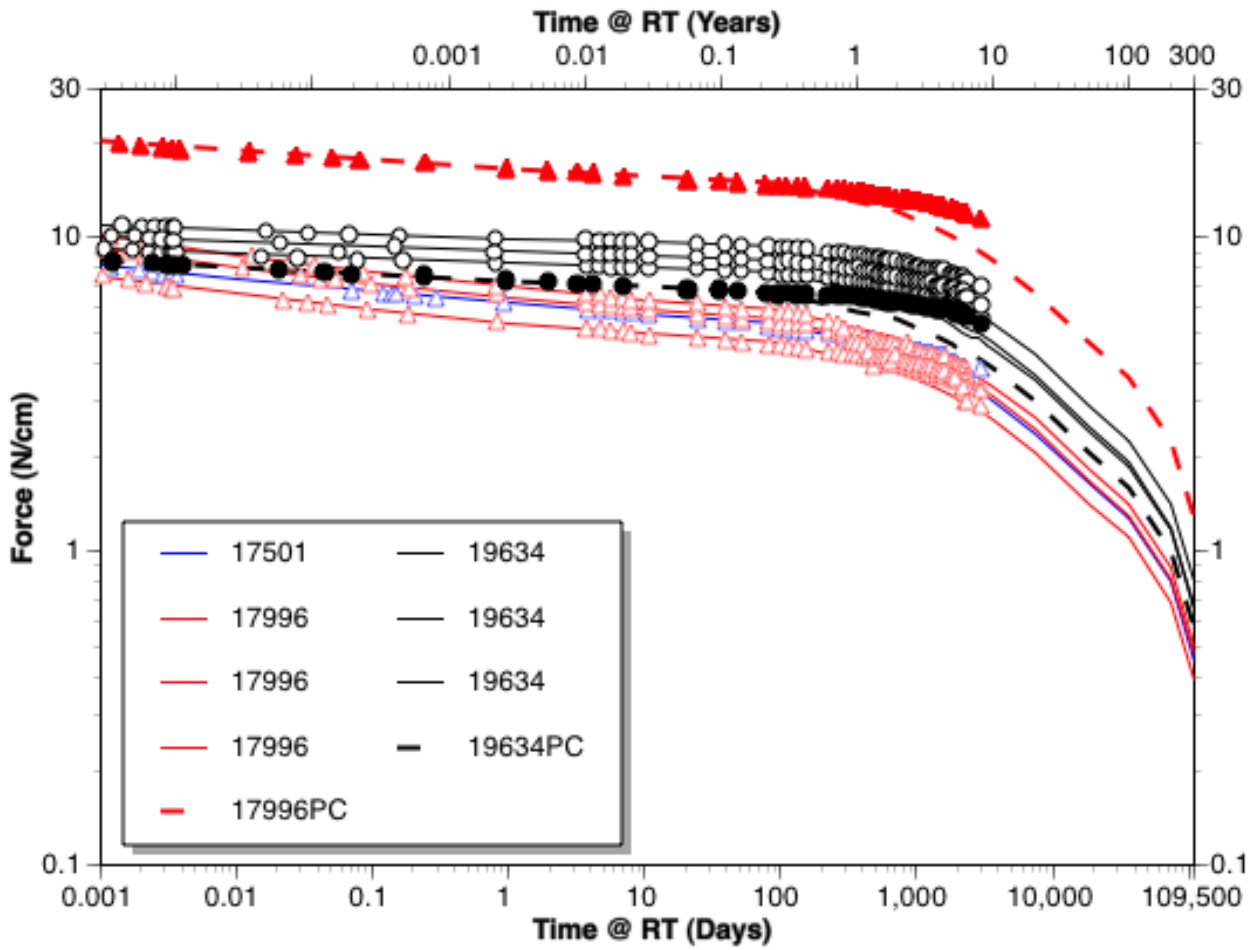

Figure 6. CSR Testing Results and Predictions at Room Temperature. (Plot from Figure 2 is reproduced with each line depicting predicted, worst-case Burke material aging behavior for a single jig. Symbols denote a single CSR jig loaded with o-rings from the designated lot number. A PC suffix indicates only these samples were post cured.)

Model Prediction and Lifetime Estimate

The room-temperature aging data is well represented by the model predictions based on the Chasset-Thirion equation and an assumed, worst-case chemical aging behavior based on Burke Industries' butyl rubber compound. However, this is not surprising since the first 100 days of data is specifically fit to the Chasset-Thirion equation. Future force measurements are important to ensure that they do not abruptly fall below the "worst-case" Burke predictions. Such behavior could indicate adverse sealing performance due to the less-than full-cure condition. On the other hand, it could also indicate inherently inferior aging resistance for the R&S Rubber's butyl formulation that has nothing to do with the level of cure.

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 [9, 10]. Predicted aging behavior for the suspect o-rings combining Chasset-Thirion with E_a (activation energy) for Burke'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 6).

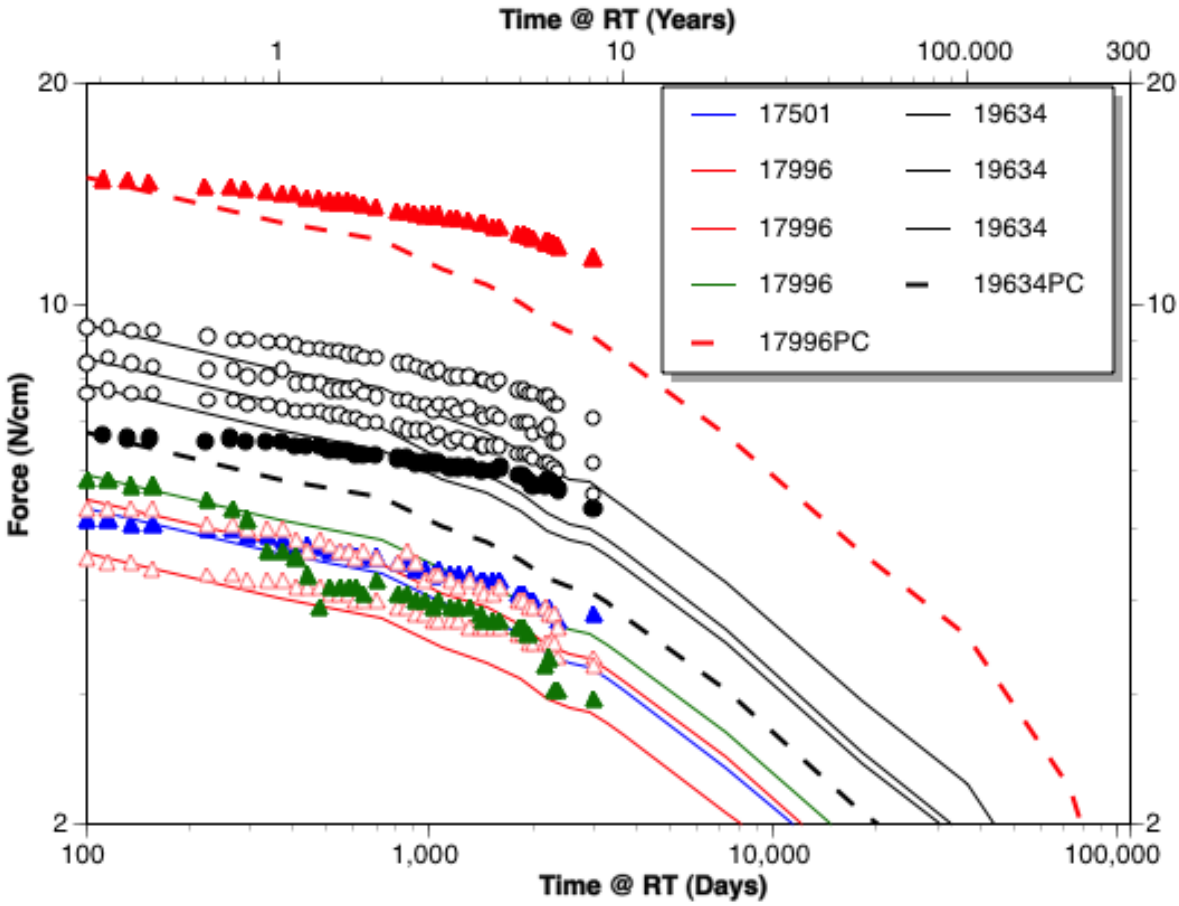

Figure 7. Expanded Scale Plot of CSR Testing Results and Predictions at Room Temperature. (Plot from Figure 6 is reproduced with zoomed scale to indicate experimental data symbol position relative to line prediction. Note: Non-smooth solid lines are graphing software spline-fitting artifacts and do not represent real prediction fluctuations.)

The 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 based on Burke Industries' butyl. Any significant downward deviation from the predicted chemical stress relaxation values would cause concern and initiate discussions 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.

Lastly, measured CSR values for one of the jigs (W27 batch 17996) shows an anomalous deviation from the model's prediction after approximately one year of aging (Figure 8). The shape of this curve initially depicted the unwanted behavior expected for premature failure; nevertheless, it is unknown if the behavior is caused by a jig malfunction or if the o-ring is truly behaving differently than the other two jigs containing o-rings made from the same batch. However, it is unlikely that the five o-rings randomly chosen for this jig would behave in a significantly different manner from the ten o-rings in the other two replicate jigs.

In addition, there were various difficulties taking consistent measurements with this jig early in the aging program. Therefore, a defective jig is being assumed at this point.

Defective jigs have occurred in the past where an adhesive layer bonding to a nonconductive ceramic wafer has failed, which caused inconsistent measurements. Recent data indicate a leveling off of degradation results that still support a defective jig as the root cause. This jig will continue to be monitored and results specifically discussed in future annual reports.

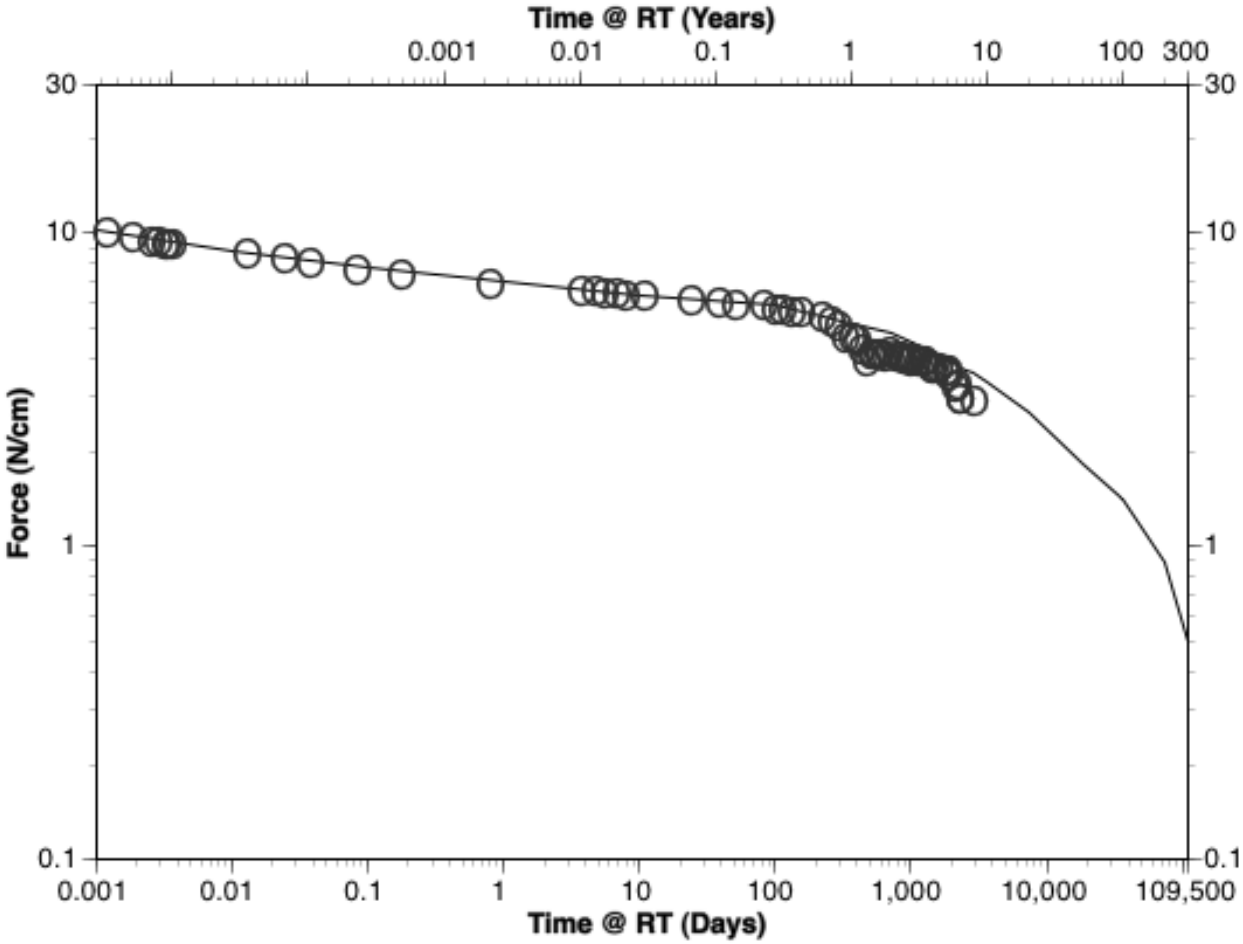

Figure 8. CSR Testing at Room Temperature for Jig W27, lot 17966. (Symbols denote measured values and the line denotes combined physical and chemical aging model predictions.)

Accomplishments

Representative samples of “suspect” o-rings were obtained and a long-term compression stress relaxation study has accumulated aging data over an 3020-day period at room temperature. An aging model was developed that reasonably predicts the decay in sealing force with time at room temperature arising from both physical and chemical aging mechanisms.

Future Work

Additional long-term testing will be performed to validate the prediction model.

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