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Fluorosilicone and Silicone O-ring Aging Study

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Abstract

Fluorosilicone o-ring aging studies were performed. These studies examined the compressive force loss of fluorosilicone o-rings at accelerated (elevated) temperatures and were then used to make predictions about force loss at room temperature. The results were non-Arrhenius with evidence for a lowering in Arrhenius activation energies as the aging temperature was reduced. The compression set of these fluorosilicone o-rings was found to have a reasonably linear correlation with the force loss. The aging predictions based on using the observed curvature of the Arrhenius aging plots were validated by field aged o-rings that yielded degradation values reasonably close to the predictions. Compression set studies of silicone o-rings from a previous study resulted in good correlation to the force loss predictions for the fluorosilicone o-rings from this study. This resulted in a preliminary conclusion that an approximately linear correlation exists between compression set and force decay values for typical fluorosilicone and silicone materials, and that the two materials age at similar rates at low temperatures. Interestingly, because of the observed curvature of the Arrhenius plots available from longer-term, lower temperature accelerated exposures, both materials had faster force decay curves (and correspondingly faster buildup of compression set) at room temperature than anticipated from typical high-temperature exposures. A brief study on heavily filled conducting silicone o-rings resulted in data that deviated from the linear relationship, implying that a degree of caution must be exercised about any general statement relating force decay and compression set.

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Introduction

Polymers are widely used in weapon components. They are known for their aging and degradation problems, and have been an ongoing source of stockpile reliability problems even when service life is relatively short. Lifetime extension to the 40-60 year range puts us in the position of answering questions on a time scale not normally known or even considered for commercial applications of polymers. Past lifetime prediction estimates for stockpile materials and components involved qualitative methods (mostly based on the Arrhenius approach), which are now known to be dangerous in many instances. As such, lifetime prediction techniques for polymeric materials need substantial refinement. In addition, for both predictive and confirmatory purposes, new and improved approaches for monitoring materials in stockpile must be developed to assist on-going surveillance efforts. A significant general challenge for aging studies of polymers as well as other weapon materials involves the difficulty in obtaining new materials equivalent to the materials originally installed in weapons several decades ago. This means that predictive methods must be developed which do not depend upon access to such often-unavailable samples. This project focused on addressing the above issues concentrating on o-ring materials which are of critical importance for several stockpile systems.

Aging issues associated with o-rings have been the focus of an extensive amount of work in our group over a multi-year period. O-rings that must maintain a seal under static conditions are used in a number of applications. Often these o-rings need to maintain a seal for extended times, ranging from years to decades. Previous work has focused on o-ring materials made of butyl or ethylene propylene diene monomer (EPDM) materials and has led to a better understanding of o-ring aging as well as a change in the way the weapon complex deals with certain types of o-rings.[1-3] This work directly extends from the previous knowledge gained in the weapon complex.[3] The focus of this work involves applying the lessons learned from the previous studies to new work involving the loss in sealing force associated with o-rings made from fluorosilicone material. While fluorosilicone is known to have significantly higher oxygen and water permeation rates compared to that of butyl or EPDM material, it is nonetheless used quite frequently as an o-ring material (Table 1).

Table 1: Water permeability of different o-ring materials; direct reproduction of table from previous publication [4]

Material	Water permeability ccSTP/cm/s/cmHg
Butyl	$\sim 1.9 \times 10^{-9}$
EPDM	$\sim 3.5 \times 10^{-8}$
Silicone	$\sim 1.8 \times 10^{-6}$
Fluorosilicone (LS-53)	$\sim 1.5 \times 10^{-6}$

Sealing force is arguably the most important o-ring property. The simple measurement of the sealing force is a difficult task due to the fact that the elastomer will physically relax when placed under stress, such that the force will decay with time until it achieves an equilibrium sealing force. Reaching equilibrium typically takes an extensive period of time. A previous publication has discussed the possibility of over-compression as a means around this problem.[5] Previous work by our group has described the development of an empirical over-compression approach that led to estimates of the equilibrium sealing force of butyl o-ring materials in a reasonable timeframe.[2] In essence this involves removing the physical component of the elastomer relaxation ‘quickly’ so that the equilibrium sealing force can be estimated. It was discovered that this can be accomplished by over-compressing for a few days and then releasing to the desired level of compression. Testing the validity of this methodology for a fluorosilicone material was one of the goals of the current study.

Over the past several years, we have derived improved approaches for predicting lifetimes of o-rings based on developing compression stress-relaxation (CSR) methods. These methods eliminate diffusion-limited oxidation artifacts and allow more effective extrapolation to ambient aging temperatures. We then showed that the predicted results for the sealing force decay (the degradation parameter of fundamental interest) are in reasonable accord with compression set measurements taken on field-aged o-rings. We also derived a method for obtaining estimates of the sealing force on surveillance-removed o-rings. Finally a method was developed for quantitatively connecting sealing force decay with the more easily measured compression set results, leading to the on-going development of a viable surveillance approach. These studies were completed and publications written.[1,2,6,7] The goal of this publication is to highlight analogous studies on fluorosilicone o-ring material that utilized the knowledge and techniques developed previously with the goal of predicting fluorosilicone lifetimes. The predictions are then compared to surveillance results for fluorosilicone o-rings aged for periods up to 25 years in the field.

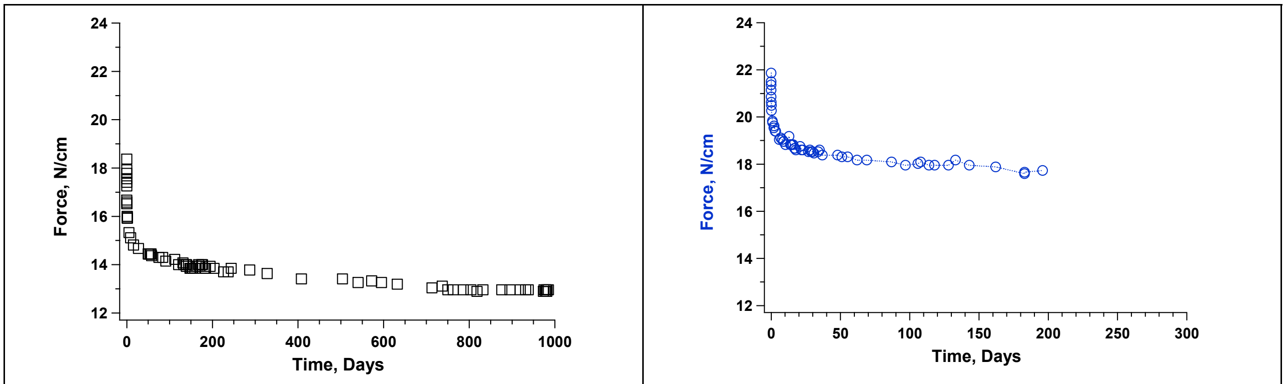
Experimental

The material used in this study was a fluorosilicone rubber, LS-53 from Dow Corning Corporation. The o-rings were 3.5 mm (139 mils) cross section by 32.5 cm (12.8 inches) diameter (ID). Part # 267970 lot 266919, Mfg. code BFV, cure date early 1990. They were received in mid 1990 and stored in a benign environment, uncompressed in the original packaging. Force measurements were obtained on a Shawbury-Wallace Compression Stress Relaxometer (CSR) MK II (Wallace Test Equipment, Cryodon, England). Typical experimental procedure involved a commercial CSR jig which allowed the measurement of the sealing force for o-rings at various gap sizes. In each jig a circumferential section of the o-ring portion was cut into five pieces and the pieces placed in the jig such that there was a reasonable air gap remaining between each piece after the pieces were squeezed.

Results and Discussion

Equilibrium Sealing Force Studies

A long-term, room-temperature CSR experiment was initiated with fluorosilicone o-rings to demonstrate the lengthy time period required to reach physical relaxation. This was achieved by setting the gap size of the CSR jig to ~2.64 mm (~104 mils) which yielded ~25% compression of the o-ring. The subsequent force drop (physical relaxation) was measured as a function of time at room temperature (Figure 1A). Based on the nature of the jigs it was very difficult to achieve an average value of exactly the desired distance. As expected, even small differences in gap size resulted in rather substantial changes in the force (Figure 1B). Care was taken to achieve an average value as close to the desired value as possible, and often this involved multiple iterative attempts to achieve the desired gap size.

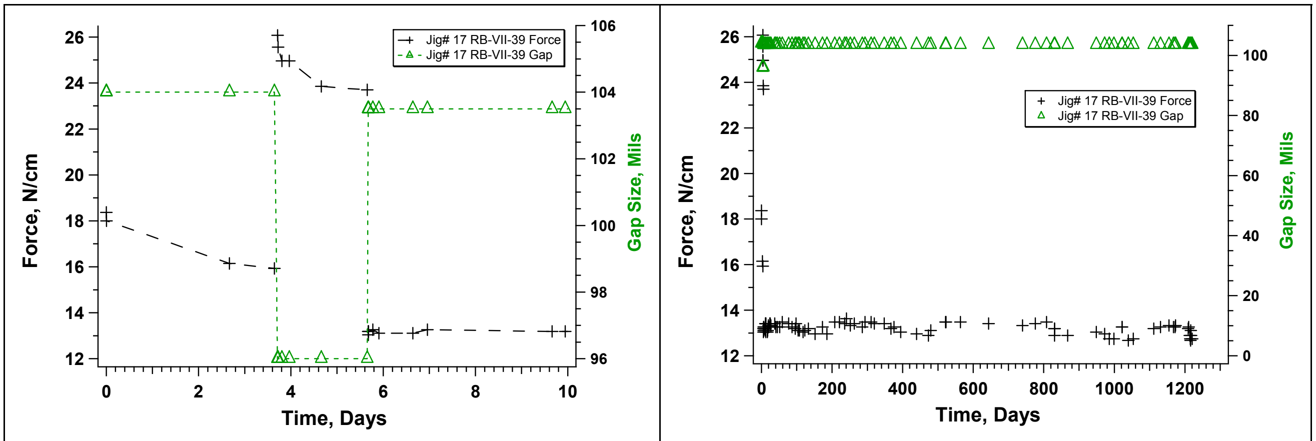


A) 2.65 mm (104.25 mils)-25% compression	B) 2.5 mm (98.5 mils)-29% compression

Figure 1: Long term physical relaxation of a fluorosilicone o-ring; sealing force as a function of aging time for a constant gap size.

Once the correct gap size was obtained, the force values were monitored as a function of time, and resulted in continuously dropping sealing force values. Even after 2 years the force was still dropping; only after ~2.5 years does the value appear to have reached a fairly stable value. This demonstrates the need for a technique for achieving the equilibrium sealing force value in a reasonable timeframe.

The over-compression technique developed for rapidly achieving the equilibrium sealing force for butyl materials[2] was applied to this fluorosilicone material.[8] The gap size for all the jigs was initially set at ca. 25% compression which is ca. 2.64 mm (104 mils). The force was measured for each jig as a function of time. A rapid decrease in the force was observed followed by a slower longer-term force decrease. After a number of days the o-rings were 'over compressed' to ca. 30%, e.g., to approximately 2.44 mm (96 mils). The samples were allowed to sit for two days, and then released back to the desired value of ~2.64 mm (~104 mils ±1 mil). Examination of the force curve as a function of time demonstrates the usefulness of the technique to rapidly achieve the equilibrium force (Figure 2A). The force value is relatively stable when examined over an extended time period of years (Figure 2B).



A B

Figure 2: Over compression technique A) Short time period B) Complete time period

Direct comparison of the simple compression and over-compression samples (for similar gap sizes) makes apparent the difference in timescales to achieve estimates of the equilibrium values (Figure 3). It also validates the usefulness of the over-compression technique to rapidly achieve the equilibrium sealing force. The comparisons demonstrate that the equilibrium sealing force is the value obtained by this over-compression technique, and is the same value that would be obtained by simple compression if a long time period is allowed.

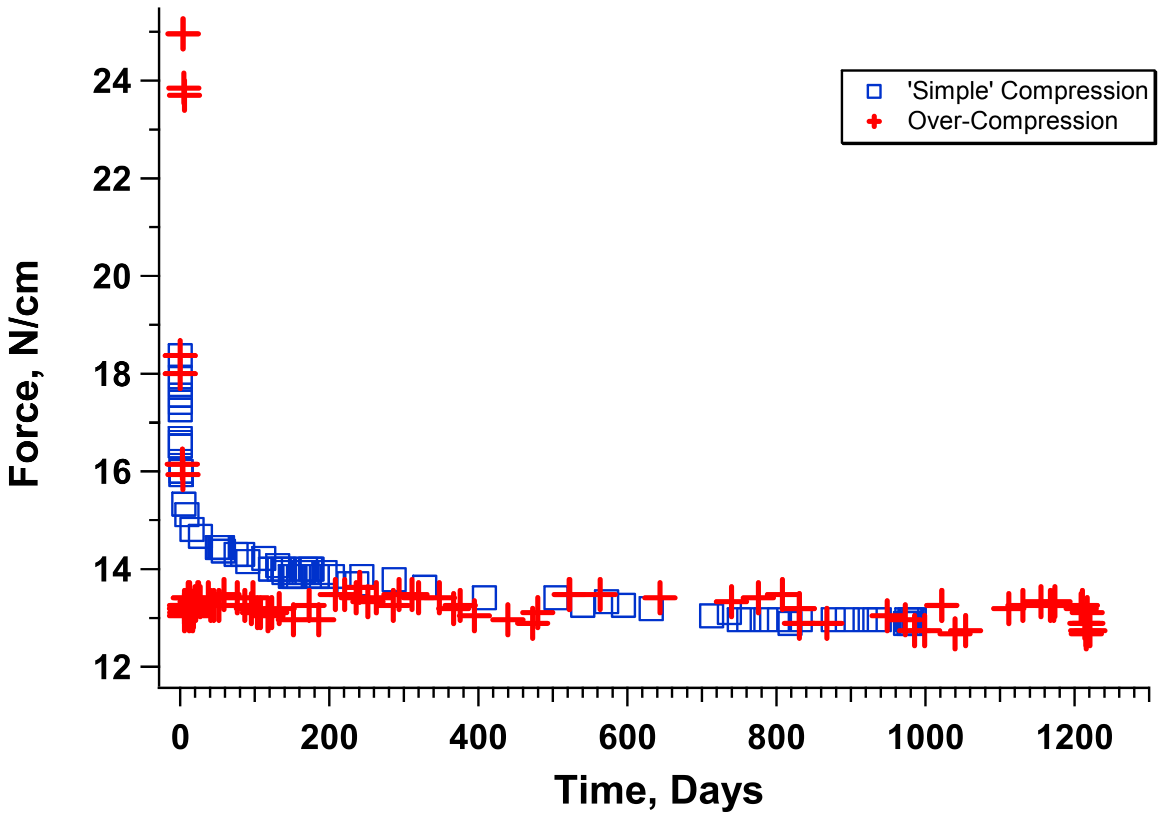


Figure 3: Comparison of simple versus over compression

Measurement of the variation (scatter) of the technique was desired, therefore, a single fluorosilicone o-ring was cut and used in six CSR jigs. Providing one o-ring for all the material for the study eliminated any issues from different material batches or different processing times. The gap size for all the jigs was initially set at ca. 25% compression which is ca. 2.64 mm (104 mils). The force was measured for each jig as a function of time. A rapid decrease in the force was observed followed by a slower longer-term force decrease. After a number of days the o-rings were 'over compressed' to ca. 30%, e.g., to approximately 2.46 mm (97 mils). The samples were allowed to sit for around three days, and then released back to the desired value of 2.64 mm (104 mils±1 mil). This technique is illustrated graphically in Figure 4 for a single jig as sealing force and gap size versus compression time.

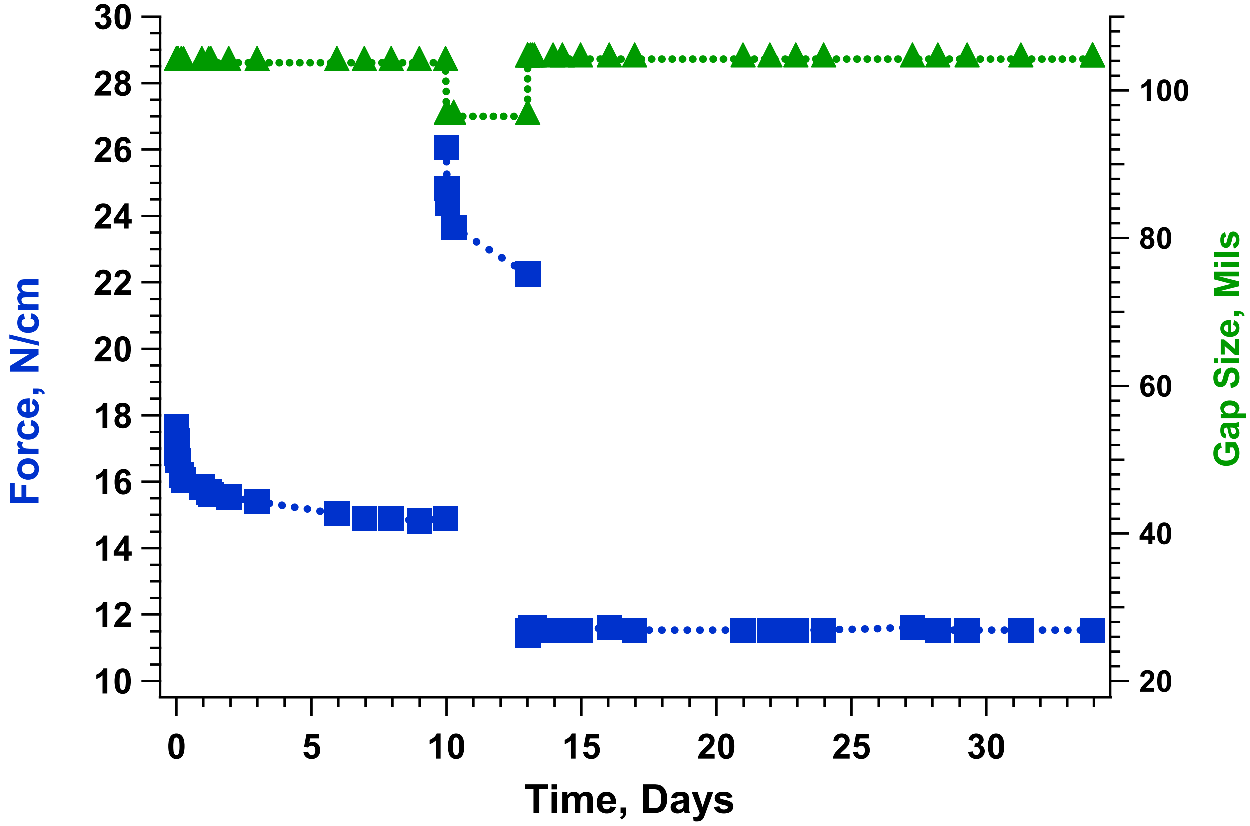


Figure 4: Representative o-ring sample displaying the sealing force (squares) and the gap size changes (triangles) as a function of compression time at 23 °C.

Interestingly all six jigs yielded a very tight force range for the estimated equilibrium values (Figure 5). It should be noted that numbers closer to the desired value for the gap size were achievable after the over-compression based on the measurements taken from the first squeeze, which undoubtedly is the explanation for the tighter data set after the over-compression. As can be seen from the sample with no over-compression, the time to achieve equilibrium values would have been extremely lengthy without the over-compression step.

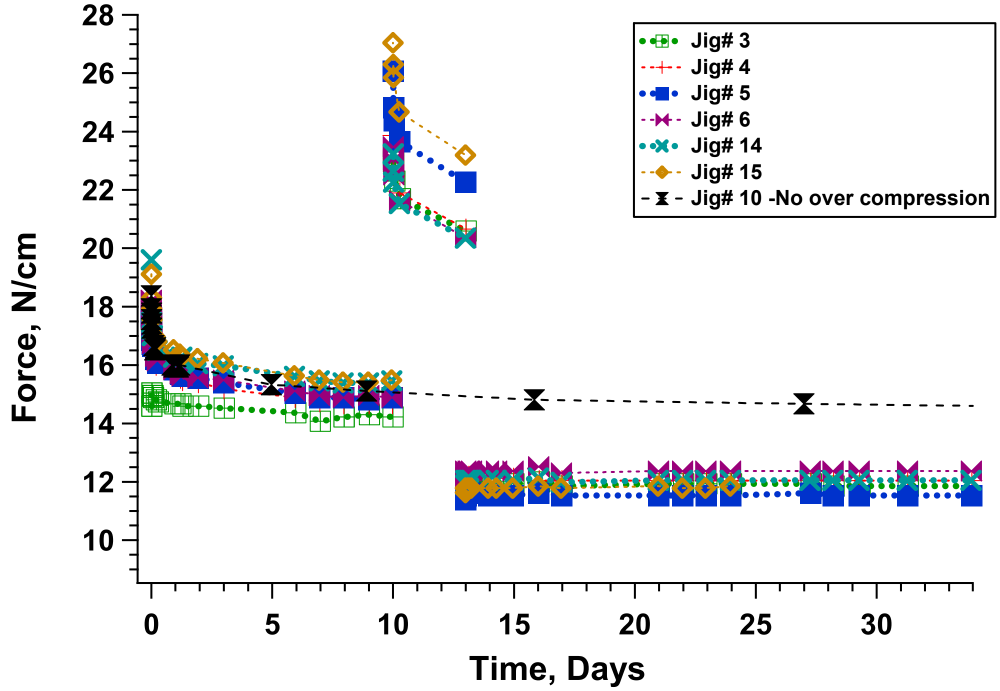


Figure 5: Seven sample jigs of the same material graphed as sealing force versus time.

When a second o-ring was used in the study, it yielded similar but not exactly the same numbers, highlighting the variations (presumably in the equilibrium modulus value) from o-ring to o-ring (Figure 6).

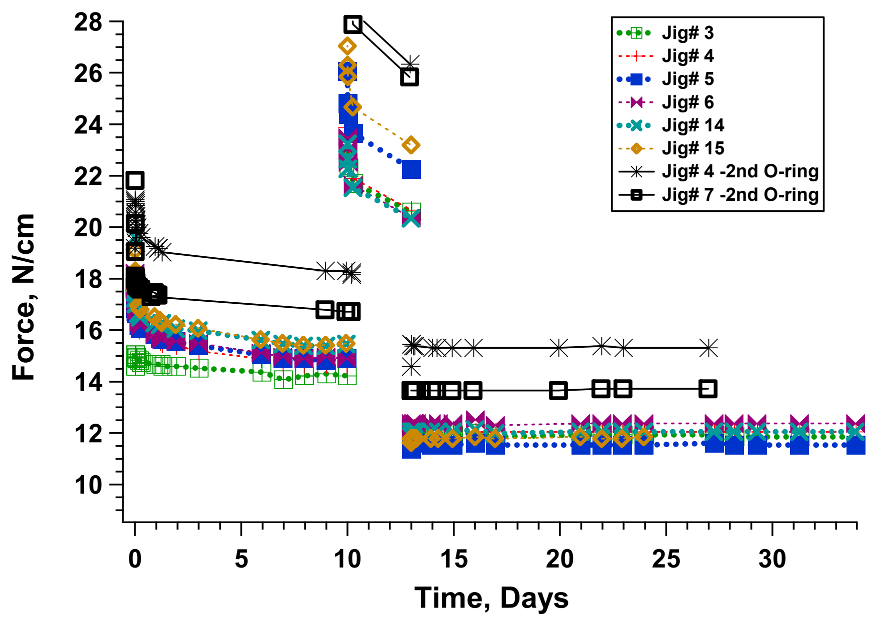


Figure 6: Comparison of inter and intra o-rings

When the data from the different o-rings are compared it is readily observed that there is some degree of scatter in the initial (10 day) force value. However, the percent drop in sealing force after the over compression cycle is roughly similar (Table 2).

Table 2: Comparison of jig values

	Force Value		
Jig#	~ 10 day	~ After over compression	% drop
3	14.2	11.9	16
4	14.67	12.04	18
5	14.89	11.53	23
6	14.89	12.37	17
14	15.4	12.05	22
15	15.4	11.78	24
4	18.3	15.3	16
7	16.7	13.7	18

This demonstrates that while there is a real variance in the data, a general statement can be made that for fluorosilicone material under 25% compression, an approximate 20% drop in force is expected after 10 days due to continuing physical relaxation towards equilibrium of the virgin material.

Accelerated Aging

After the over-compression study was completed, a number of the samples were used as part of an accelerated aging study. The samples were aged at elevated temperatures to begin chemical degradation and the loss in force was monitored. It can be seen that by raising the temperature the force value of the o-ring rises dramatically (Figure 7). This is a direct result of the coefficient of thermal expansion and other physical factors associated with the temperature change. The accelerated aging data utilized only the data obtained after the samples were placed at the elevated temperatures. The early elevated temperature results were extrapolated back to "time zero" at elevated temperature in order to get the initial force value at the elevated aging temperature (F_0).

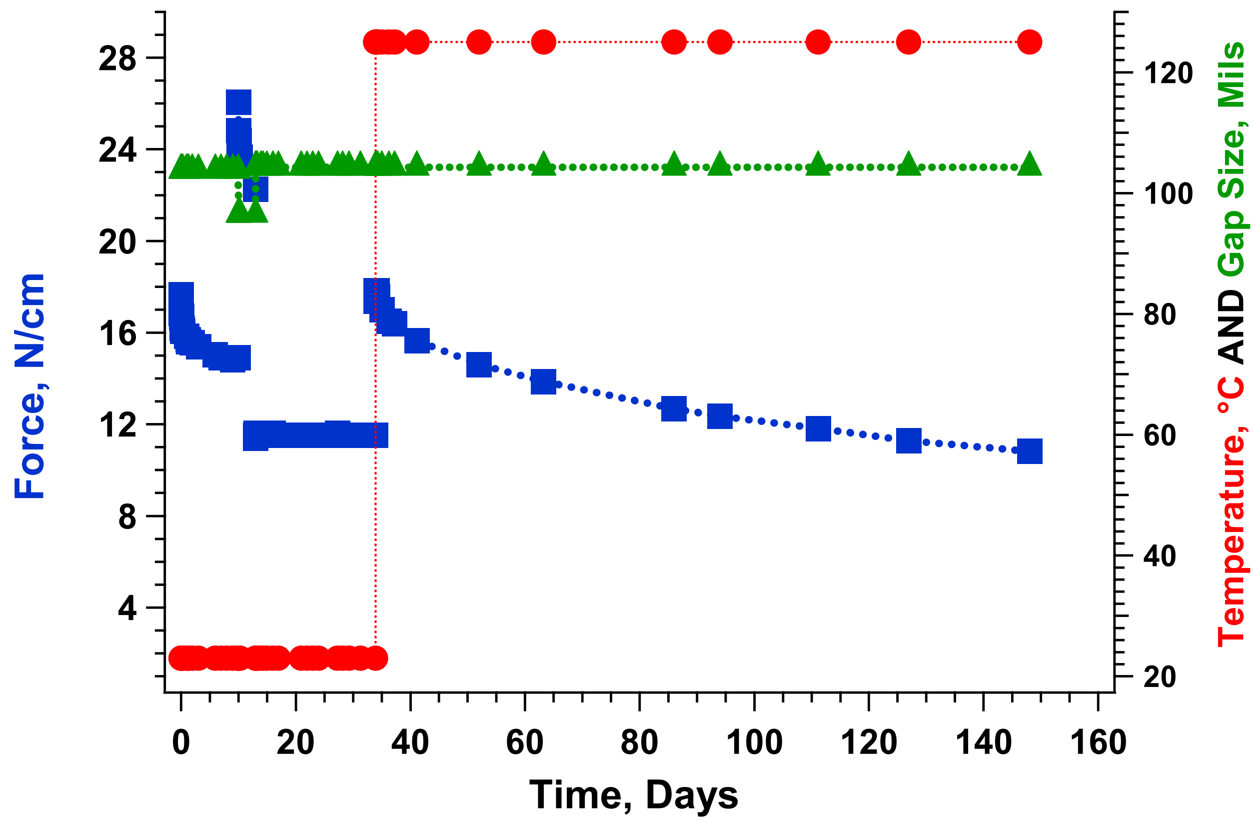


Figure 7: Representative sample of physical and then chemical aging (124 °C) of o-ring material

A number of samples were aged at different temperatures to accelerate the force loss at different rates. The data for the accelerated aged samples (138, 124, 109, and 80 °C) was normalized (relative to their F_0 values at each elevated temperature) to give the percent force remaining as a function of time at temperature (Figure 8).

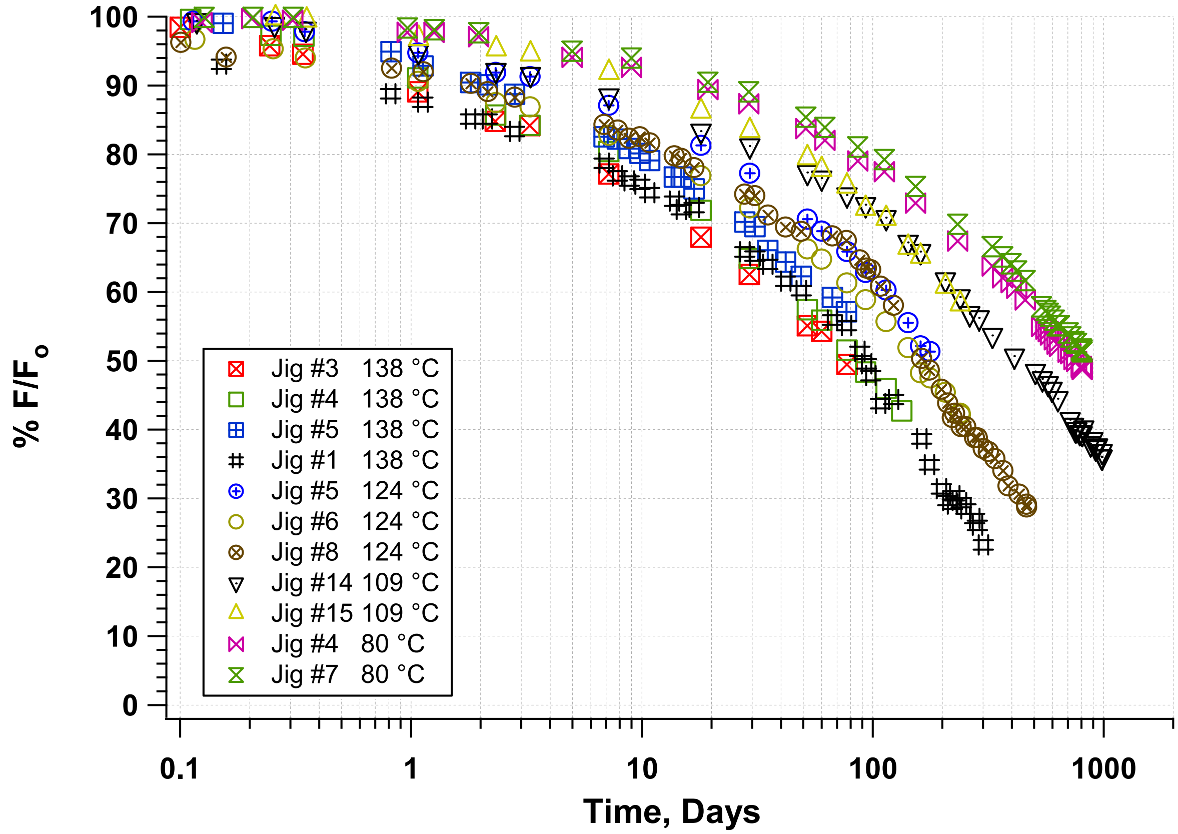


Figure 8: Accelerated aging results for the fluorosilicone at various temperatures.

The resulting curves had similar shapes when plotted on a log time graph, which suggested that time-temperature superposition was possible. The time-temperature superposition was maximized for overlap between 70-80% force values and resulted in excellent overlap for all of the temperatures (Figure 9).

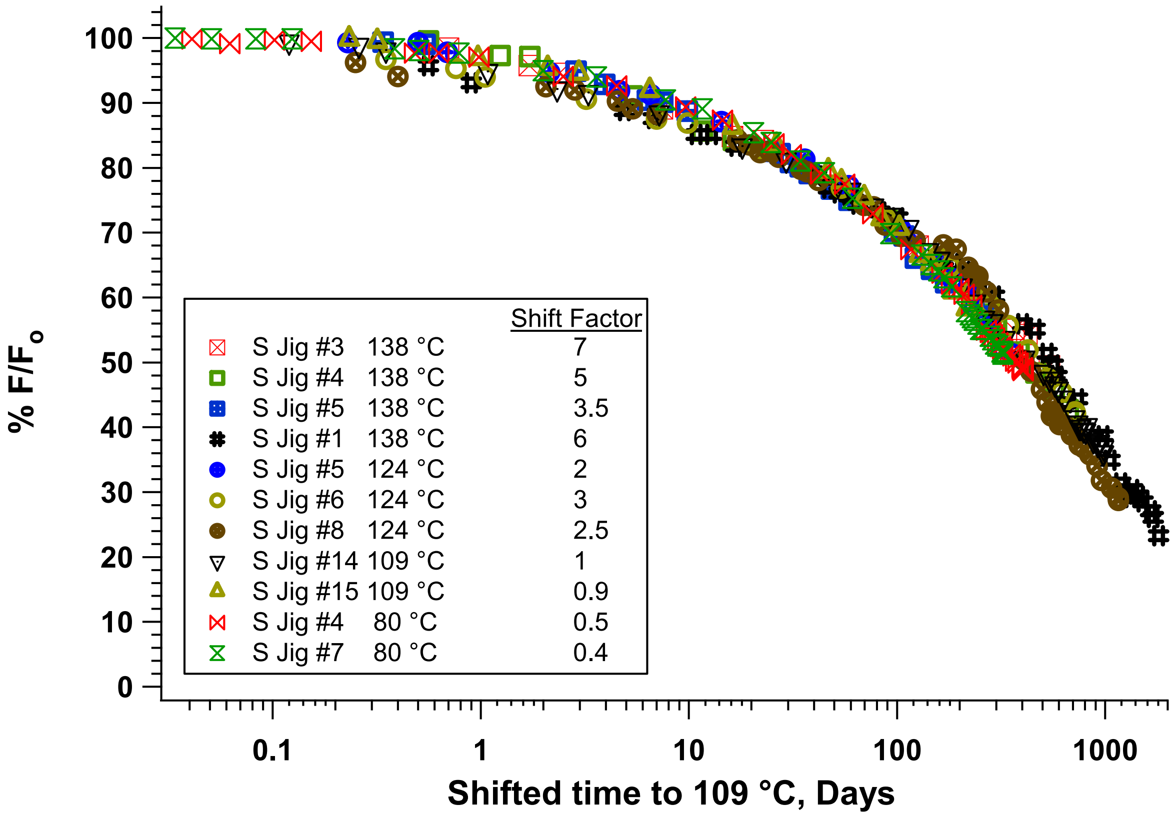


Figure 9: Time-temperature superposed data (shifted to 109 °C) of the data from Figure 8.

The shift factors used to superpose the data (see insert in Figure 9) was then graphed in an Arrhenius plot (Figure 10).

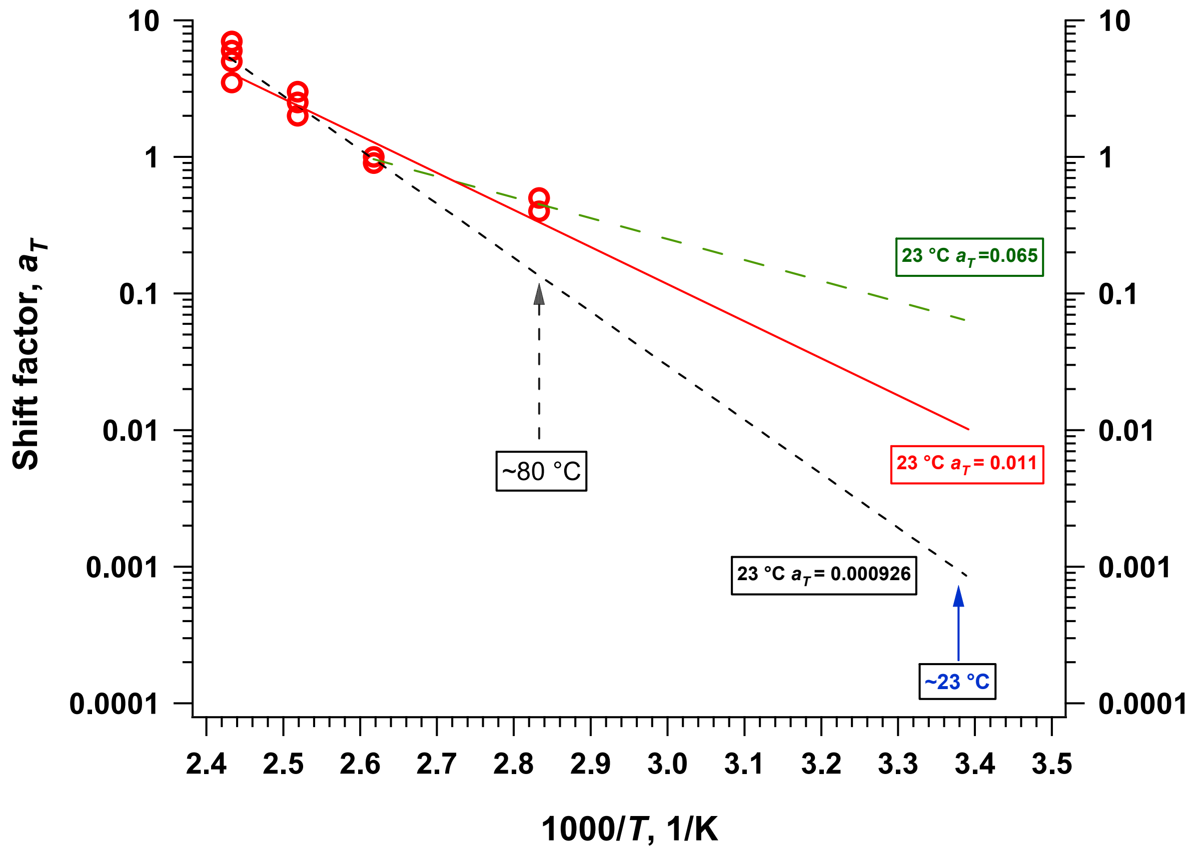


Figure 10: Shift factor plot; three lines illustrate different fits of the data

Depending upon how the data is perceived, multiple interpretations can be obtained from the data set; for example, three different lines can be drawn which lead to three very different predictions. They will all be discussed to demonstrate why long term and low temperature studies are of critical importance to any accelerated aging program. The first line (short dashed line), which ignores the 80 °C data set, demonstrates the danger in not taking data to the lowest temperature possible. The second (solid line) involves the best fit line to all the data obtained, which assumes linear Arrhenius behavior together with data scatter effects. Lastly, the third (long dashed line) assumes a mechanism change, and hence a change in the activation energy at 109 °C. The 109 °C and 80 °C data are used to fit the third line. Each one of these scenarios is graphed below to highlight the potential problems with accelerated aging studies.

Using just the high temperature data and ignoring the 80 °C data (using the short dashed line from Figure 10) results in predictions that suggest incredible lifetimes for fluorosilicone o-rings (Figure 11). These predictions result in a time scale at 23 °C that comes from dividing the 109 °C time scale of Figure 9 by the 23 °C shift factor for the short dashed line (a_T = 0.000926 as indicated on Fig. 10). Approximately 50% force loss is predicted at 23 °C in ~1000 years. Clearly this is wrong, but it demonstrates just how dangerous accelerated aging studies can be when they are incomplete and rushed.

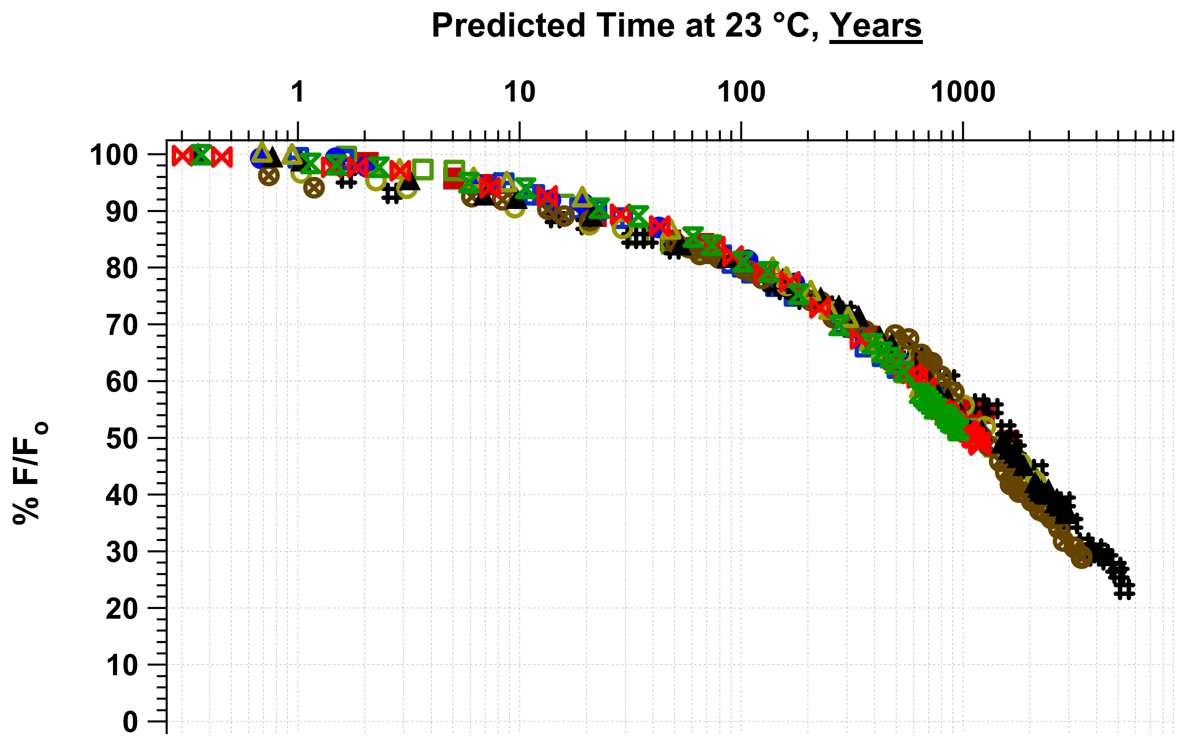


Figure 11: Data set of Figure 9 shifted to 23 °C ignoring the 80 °C data.

The second fit (solid line from Figure 10), which uses all of the data, results in much quicker drop in the sealing force with ~50% force value reached in ~100 years at 23°C. Although this prediction is closer to expectations, it disregards the obvious curvature in the Arrhenius plot of the shift results. This curvature is indicative of a mechanistic change in the degradation chemistry that appears to be occurring at lower temperatures.

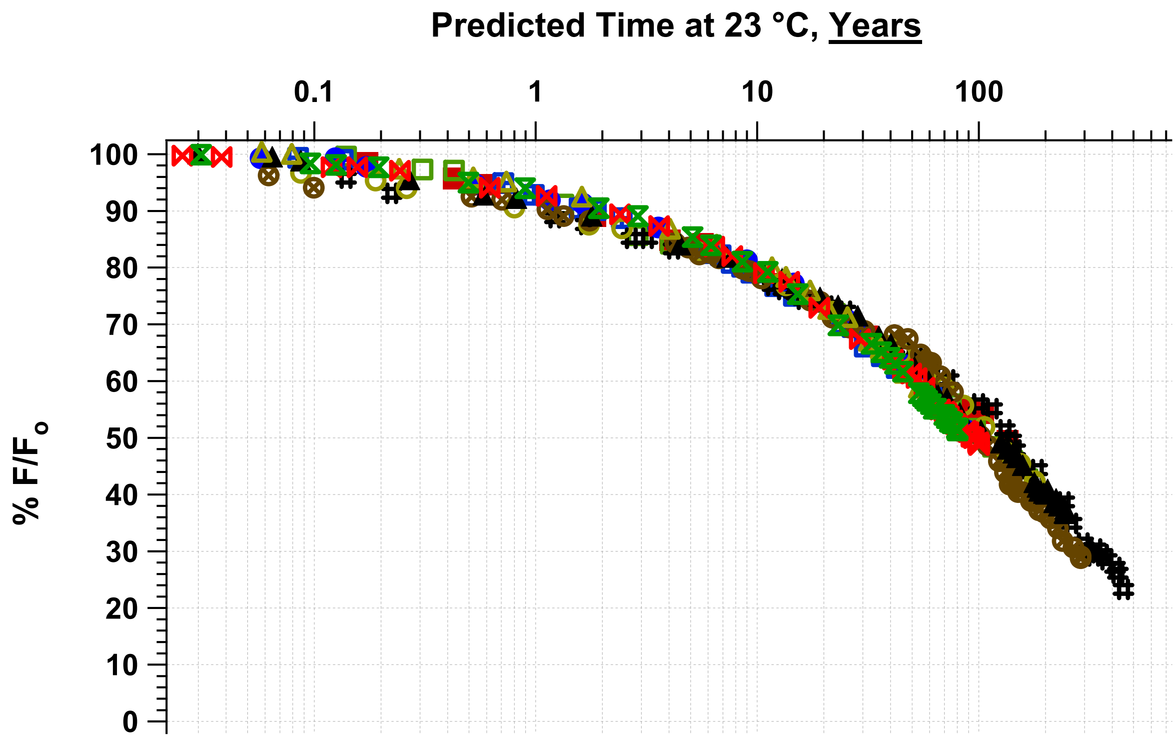


Figure 12: Data set of Figure 9 shifted to 23 °C using the best straight line through all of the data.

The best and most defensible approach is the one that takes advantage of the lower temperature data that is demonstrating curvature from linearity of the rest of the shift factor data. This prediction (long dashed line in Figure 10) is based solely on using the experimental shift factor difference between the 109 °C and 80 °C data sets (Figure 13).

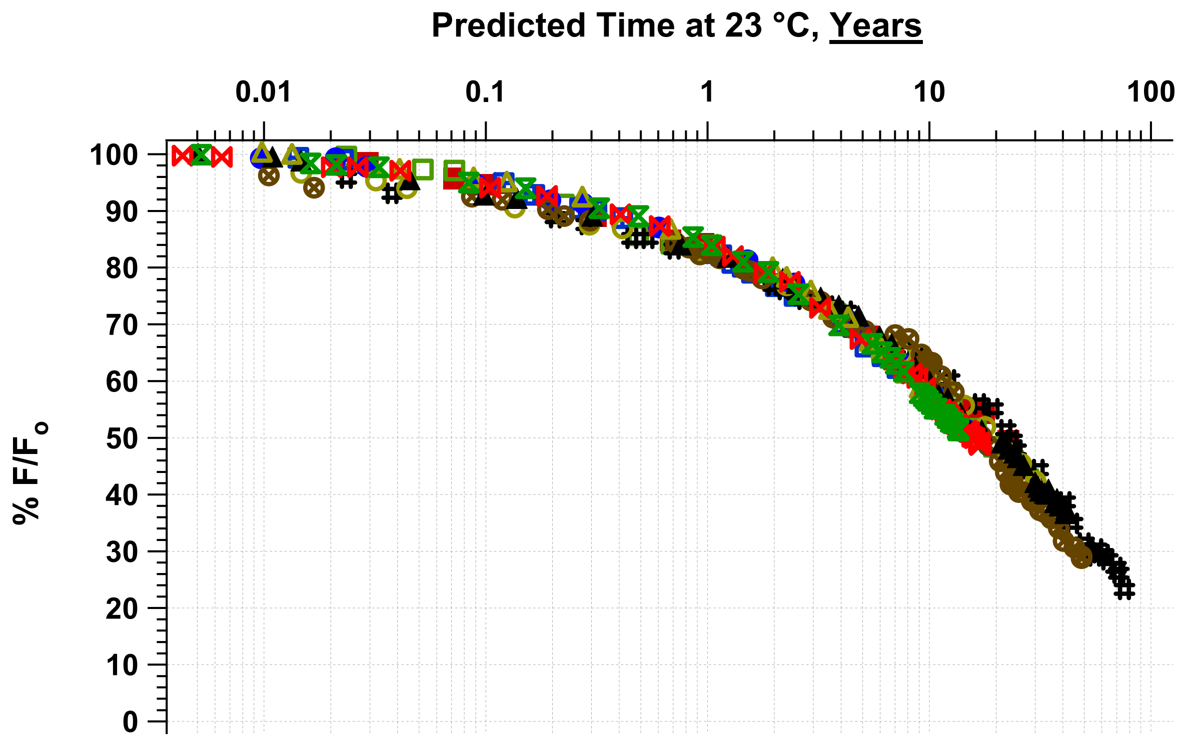


Figure 13: Most reasonable prediction; data set of Figure 9 shifted to 23 °C using only the 109 °C and 80 °C shift factor data.

This predicts that the force value reaches ~50% in ~20 years at 23 °C. Even lower temperature studies would be desirable in order to give a better 23 °C prediction; however, the time required at the lower temperatures was beyond the timescale and funding allotted for this project.

The third approach used (Figure 13) assumes the existence of non-Arrhenius behavior where the Arrhenius activation energy drops as the temperature drops. Such behavior turns out to be common and has been well documented by many recent careful studies that examined the large accelerated aging temperature ranges required to obtain compelling evidence for non-Arrhenius effects. These include studies of a butyl o-ring,[1] a chloroprene cable jacket,[9] a chlorosulfonated PE cable jacket,[10] an HNBR elastomer,[11] a polypropylene,[12] and a nylon material.[13] Most previous literature and manufacturer studies that claimed to "confirm" Arrhenius behavior (no evidence of curvature) for many different elastomers and polymers utilized a limited temperature range where it would be difficult to see compelling evidence of non-linear effects.

Force Loss Correlated to Compression Set

Compression set can be defined as the 'shape change' (set) of an o-ring based on the aging in a compacted position (i.e. forming the seal). Mathematically it is defined as

$$CS= [(t_0-t_f)/(t_0-t_w]x100\%$$

Where t_0 is defined as the original nominal thickness (o-ring cross section), t_f is the measured final thickness, and t_w is the nominal compressed thickness of the o-ring in the application.

Compression set for accelerated aged fluorosilicone study

This study involved the accelerated aging of fluorosilicone o-rings, hence direct comparison of compression set to force remaining is difficult. The reason is that at the elevated temperature, the o-ring will change in dimension due to coefficient of expansion. However, this can be corrected for based on some reasonable assumptions as highlighted below.

Suppose a 100 mil o-ring (room temperature diameter) was compressed to 75 mil at room temperature, then aged at 125 °C. After aging, it is released and then placed in an 80 °C oven for a day to physically relax. If it ends up at 87.5 mil, the simple set calculation would give a set of

$$C.S. = 100\left(\frac{100-87.5}{100-75}\right) = 50\%$$

Assuming a typical linear coefficient of expansion of 2e-4/°C, the room temperature 100 mil o-ring becomes 102 mil at 125 °C. Since the metal holding the o-ring at 75 mil has very little expansion, the actual situation during 125 °C aging is a 102 mil o-ring compressed to 75 mil. Since the 87.5 mil final dimension is measured at room temperature, one can assume that the coefficient of expansion remains at 2e-4/°C. With this assumption, the 87.5 mil final dimension would be 89.25 mil at 125 °C.

Therefore the corrected C.S. would be

$$C.S. = 100\left(\frac{102-89.25}{102-75}\right) = 47.2\%$$

Or a correction factor of 47.2/50= 0.944

One can do similar calculations for any other value of the final room-temperature measurement, and it will turn out that the correction factor is always 0.944 for this change in temperature. For example, if the final value is 77.5 mil, conventional analysis would give

$$C.S. = 100\left(\frac{100-77.5}{100-75}\right) = 90\%$$

Whereas the corrected analysis would give

$$C.S. = 100\left(\frac{102-79.05}{102-75}\right) = 85\%$$

Where the correction factor is 85/90= 0.944

Note, if desired the actual coefficient of expansion numbers can be measured for the unaged material and the aged materials.

Using this correction approach (and the estimate for the coefficient of expansion) the percent force remaining at temperature can be compared to the corrected equilibrium compression set for the fluorosilicone o-rings used in the accelerated aging studies (Figure 14). For each aging condition (a single value of % force remaining), set measurements were taken on each of the five o-ring segments removed from the aging jig, resulting in five set measurements for each force value.

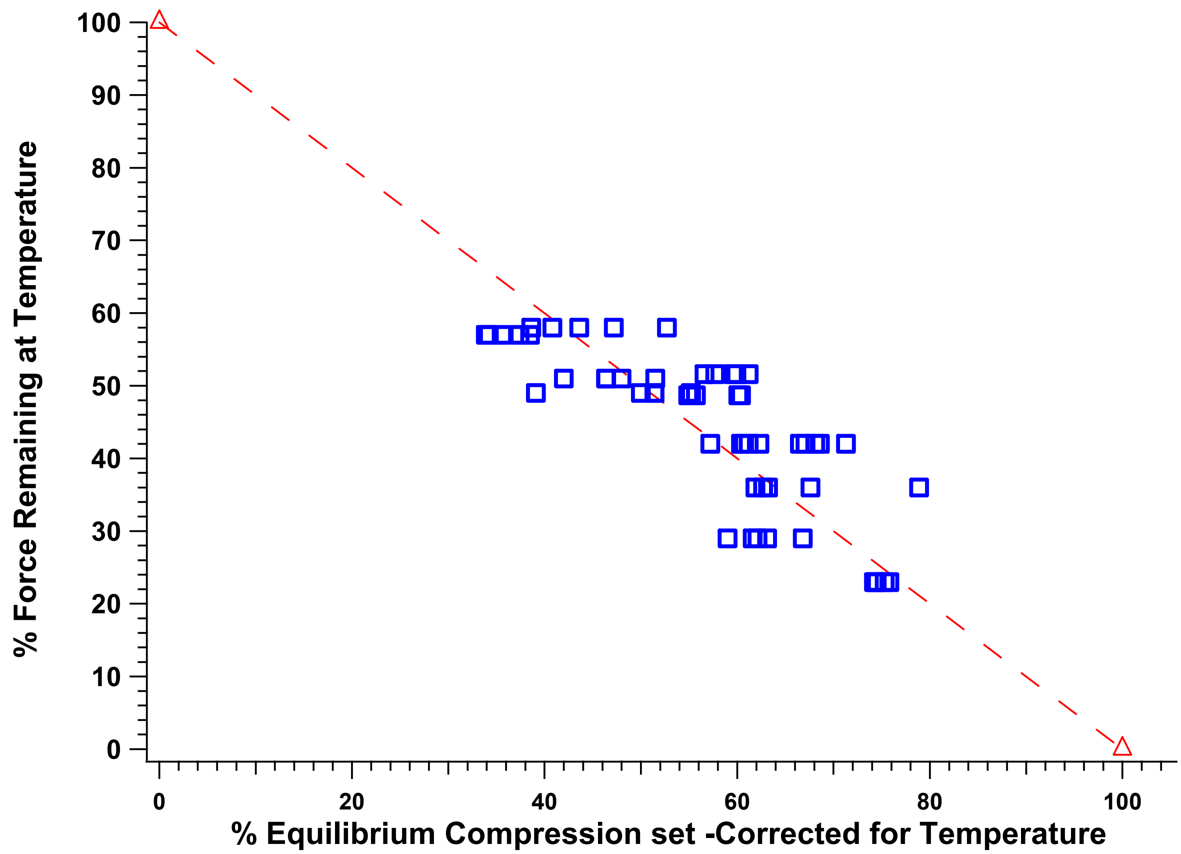


Figure 14: Corrected compression set comparison to % force remaining. The dashed line is an artificial line and not a curve fit.

Although there is a fair amount of scatter, what can be clearly seen is a reasonable linear correlation between the two measurements. A line is drawn from 100%, 0 to 0, 100% to illustrate for the eye what would be a perfect straight line correlation. Use of the average set data (one set value for each force value) would give a better fit, however that is not done here to highlight the high degree of scatter possible from real world measurements. When field samples are returned, several compression set measurements are typically made by probing different positions on the o-ring so typical scatter is available.

The observation in Figure 14 of an approximately linear relationship between compression set and sealing force reduction implies that the accelerated aging predictions of Figure 13 can be compared to surveillance compression set measurements obtained on similar fluorosilicone materials. This will be done in the next section of this report. It also should be pointed out that a linear relationship between compression set and force decay corresponds theoretically to a situation where the modulus of a material does not change very much as the material ages.[2] This conclusion could be verified by modulus measurement comparisons between unaged and aged fluorosilicone materials.

Surveillance results for fluorosilicone material

The W69 was dismantled approximately 10 years ago. This weapon system used several fluorosilicone o-rings, including J-1 (Design Agency Part No. 874452), J-2 (Design Agency Part No. 876662) and J-8 (Design Agency Part No. 876295). The material for all three of these o-rings was “fluorosilicone rubber per Dow Corning Compound No. LS-53 or Parker Seal Co. Compound No. L449-65”. Based on conversations with Parker Seal Co. it appears that the o-ring (due to color) is most likely the Dow Corning compound (e.g. the one that is used in the accelerated aging study) but this fact can not be proven beyond a doubt. During surveillance activities, the compression set for these o-rings was obtained at Pantex. The measurements were taken at four locations on the o-ring (at ~0°, 90°, 180° and 270°) at two times after o-ring removal (at ~30 minutes and at 16-24 hours). We were able to obtain several of the older surveillance reports covering ~ 15 units from SLT-7, SLT-8 and SLT-9 (measurements taken in 1978-1980) that were in the field ranging from ~3 years to 7 years. The compression set values reported at that time averaged ~10% with a maximum value of 22.9%. Such low values of compression set alleviated any aging concerns. Unfortunately, the reports used an incorrect definition of compression set and the real values were actually ~4 times greater. These higher correct values imply a reasonable amount of aging occurred over a fairly short field exposure. We have also received some more recent Pantex data for two units examined in 1994 (6 years and 17 years exposure, respectively). Figure 15 plots the average compression set value for the four locations on each J-1, J-2 and J-8 o-ring for the above Pantex measurements taken 16-24 hours after removal from the weapon versus time in the field. The additional data at ~25 years came from 1997 Sandia measurements made on one of the dismantlement units described below several months after the o-rings were removed from the unit.

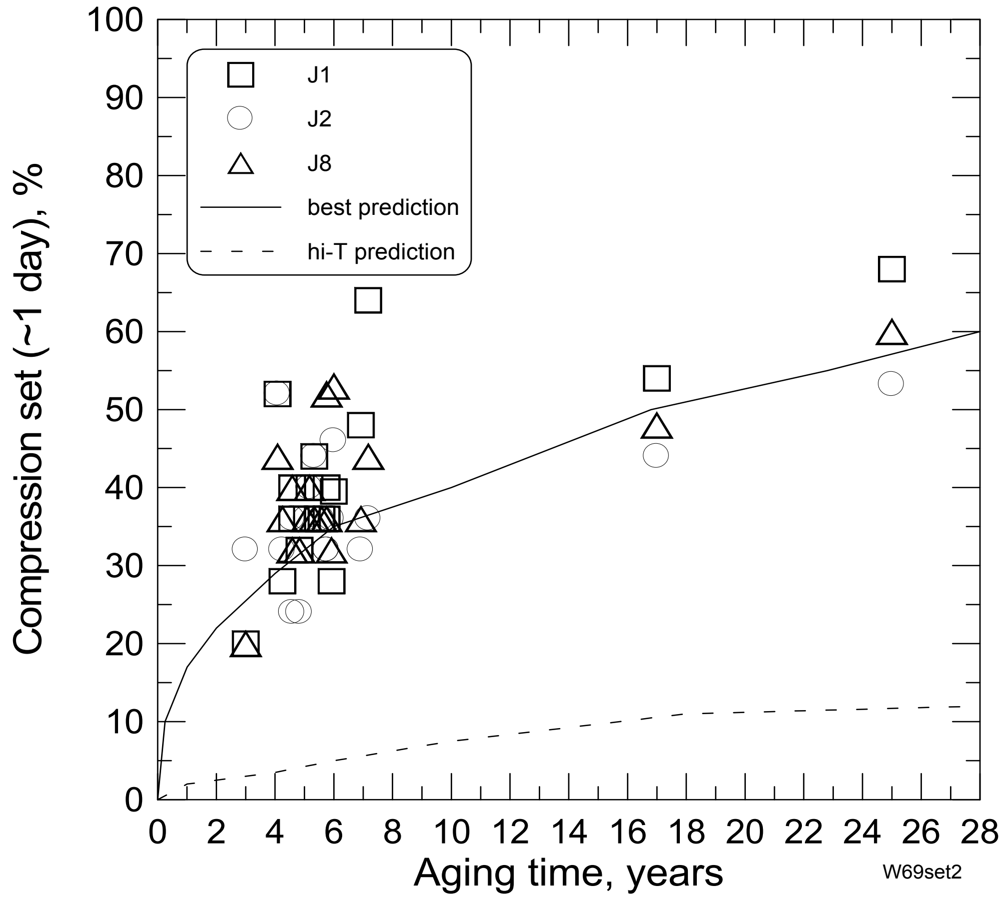


Figure 15: Pantex compression set measurements of three fluorosilicone o-rings taken on W69 surveillance units approximately 1 day after removal from the unit. The solid curve and the dashed curve come from Figure 13 and Figure 11, respectively assuming a linear relationship between set and force decay.

It is clear from the results shown that the compression set increases fairly quickly with aging time. Assuming that the linear correlation between compression set and force decrease (Figure 14) is approximately valid, we can transform the accelerated aging results of Figure 11 and Figure 13 into compression set predictions. The results are plotted in Figure 15 as a dashed curve (transformation of Figure 11 results) and a solid curve (transformation of Figure 13 results).

The dashed curve, based on the dangerous extrapolation of only the high temperature aging results, predicts very slow buildup of compression set values. The more realistic solid curve is in quite good agreement with the experimental results. Since the compression set values taken 1 day after removal are not at equilibrium, the equilibrium set values are likely to be somewhat lower than those shown in Figure 15. In fact, in 1997 during the dismantlement of the W69, we were sent the J-1, J-2 and J-8 o-rings from several units which had been in the field for 15 to 25 years. Compression set measurements were recently obtained for these o-rings. Since these o-rings had sat at room temperature in unstrained conditions for the past ten years, the set measurements can be considered at equilibrium. The results from these measurements are shown in Figure 16 together with the predicted response from accelerated aging obtained from Figure 13 out to 80 years.

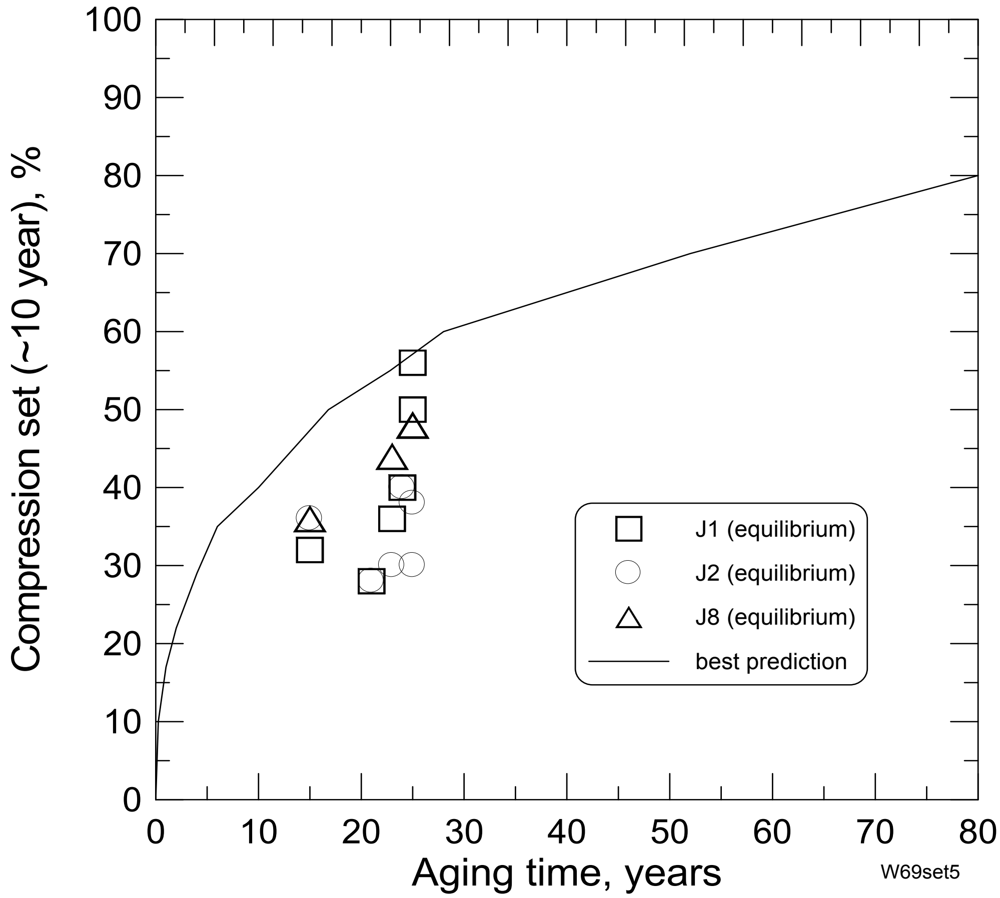


Figure 16: Compression set results for W69 o-rings aged in the field for times up to 25 years. The compression set measurements were taken ~ 10 years after the o-rings were removed from their units.

These recent compression set results indicate that equilibrium set values change somewhat slower than the best accelerated prediction. Since the accelerated prediction indicates ~20% force remaining (80% set- see Figure 13 and Figure 16) after 80 years and the actual field results out to 25 years appear to change at a slower rate (Figure 16), these results give us good confidence in the long-term viability of fluorosilicone o-rings under room temperature conditions.

It is clear from the results of Figure 15 and Figure 16 that non-Arrhenius extrapolation (results of Figure 13) leads to a much more accurate estimate of the degradation rate than conventional straight-line Arrhenius extrapolation of high temperature data. Thus, as has been shown repeatedly,[1,2,6,7] curvature of Arrhenius plots to lower activation energies at lower temperatures is not only quite common but also consistent with long-term, real-time aging results. This again shows the power and necessity of running long-term accelerated aging experiments to temperatures as low as possible.

Compression set for silicones

Silicone elastomers are also frequently used for weapon sealing applications. Similar to fluorosilicone materials, silicone materials have always had a reputation for robust lifetimes at lower temperatures. These conclusions for both materials are typically based on oven-aging exposures conducted on mechanically unstrained materials, of limited relevance to sealing materials expected to perform under mechanical strain. Since fluorosilicone seals appear to degrade substantially faster than expected at room temperature, one might wonder if the same conclusion is operative for silicone seals. Although we have not conducted accelerated aging studies on silicone seals, previous Sandia work indicates that silicone seals do in fact degrade at rates similar to fluorosilicone seals at room temperature. The previous work conducted approximately 30 years ago by Ed Salazar and John Curro, collected a massive amount of compression set data versus temperature, time at temperature, time after release of strain and amount of strain. Part of the data from this study was analyzed in a memo dating back to 2001.[14] In this memo, Gillen graphed the compression set data measured 10,000 h after strain release versus aging temperature and aging time. (Figure 17).

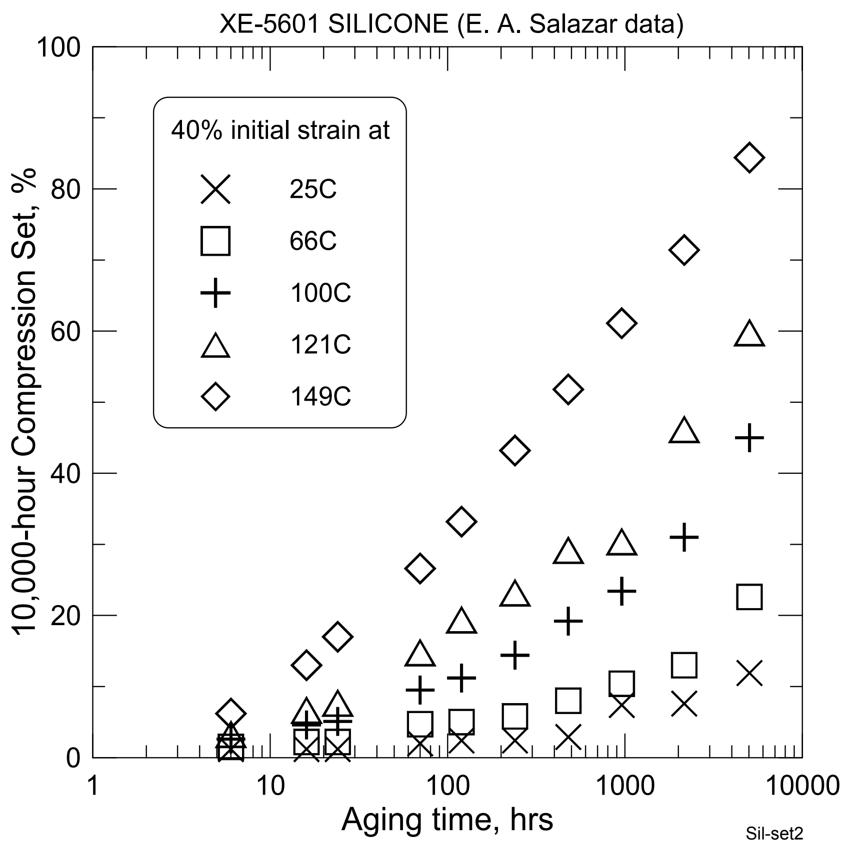


Figure 17: Compression set measured 10,000 after strain release as a function of previous aging time at different temperatures.[14]

He then analyzed the data to make predictions about room temperature aging of the o-rings (Figure 18).[14]. Interestingly, his predictions were in excellent agreement with 40-year field-aging results obtained by a British group on a different silicone o-ring material.

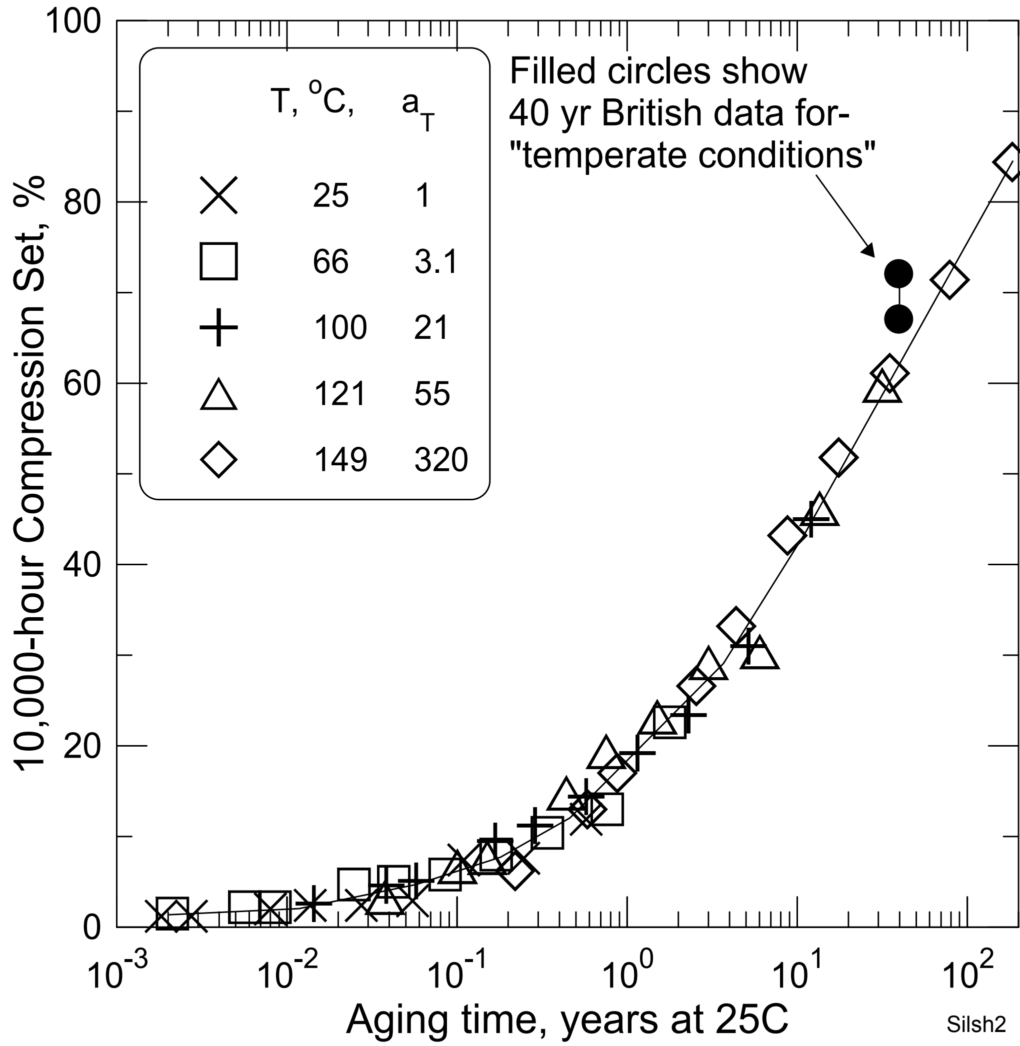


Figure 18: Prediction of silicone o-ring compression set at room temperature[14]

It is also interesting to note that the shift factors obtained for this data (shown on Figure 18) show the now familiar non-Arrhenius character with a drop in activation energy occurring as the temperature is reduced (Figure 19).

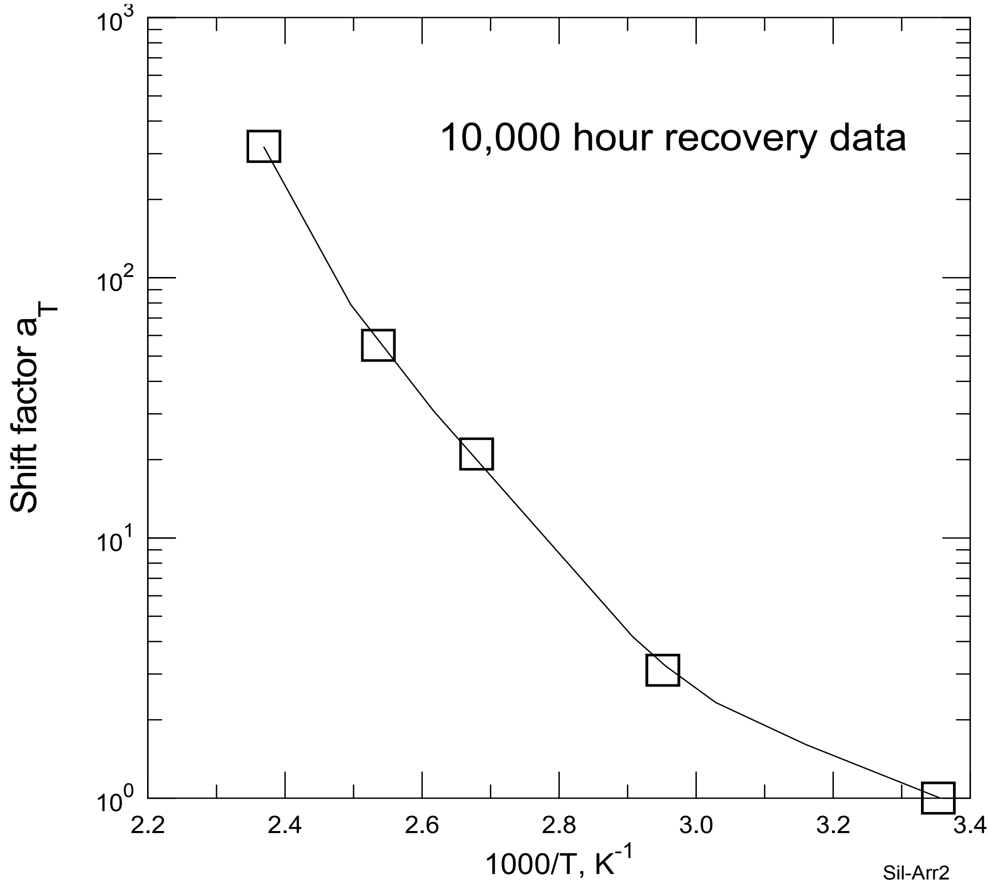


Figure 19: Arrhenius plot of the shift factors for silicone compression set (data from Figure 18)

The silicone data of Figure 18 can now be compared to the Figure 13 predictions obtained in this study. The force values obtained were correlated to the compression set values. Although the data was obtained by different groups, on different materials, with different cross sections, and predictions were made to 25 °C (instead of the 23 °C used in this study), the comparison of compression set to force percent resulted in a excellent correlation (Figure 20). Thus it is apparent that silicone and fluorosilicone elastomers have similar degradation rates at low temperatures from a force decay/compression set perspective and similar non-Arrhenius behavior.

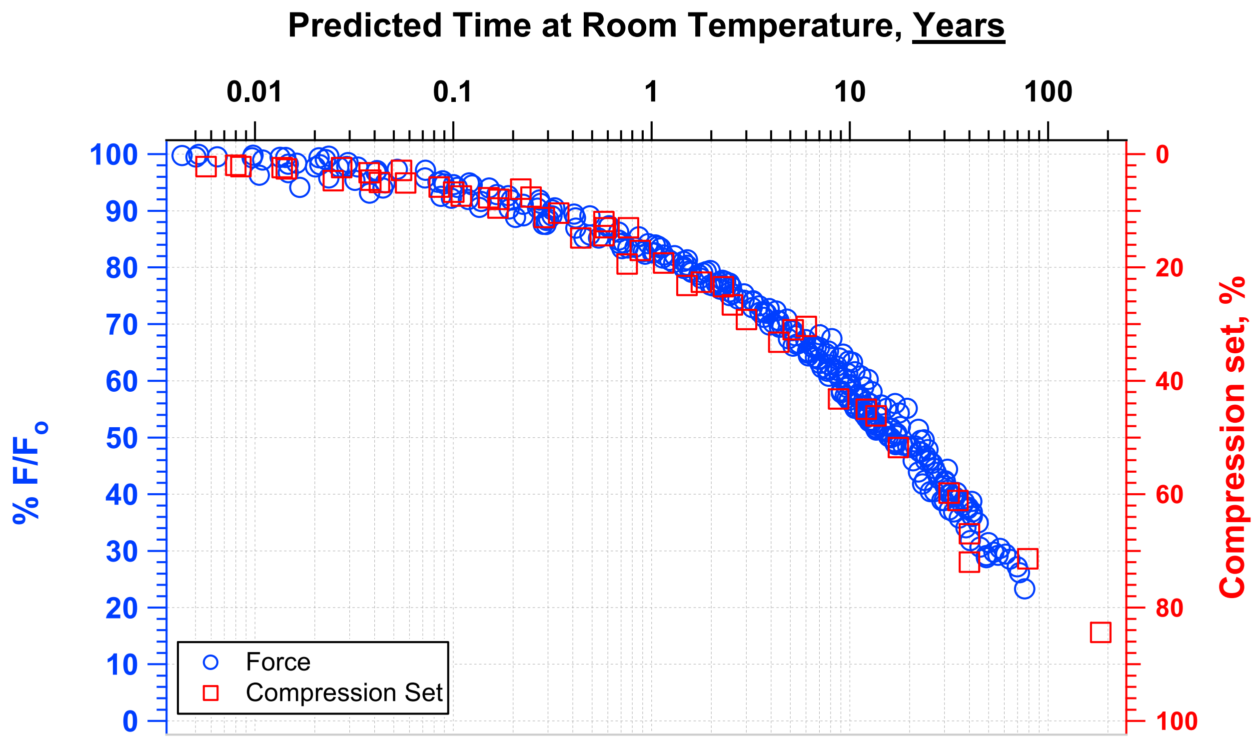


Figure 20: Comparison of compression set (silicone o-rings) versus percent force (fluorosilicone o-rings).

Conducting silicone; compression set versus force

A limited study was performed on a conducting silicone o-ring material. This o-ring was a silicone base, heavily filled with carbon particles to render it conducting. The o-ring was Tecknit 07700-86-30039, a 103 mil o-ring made from Tecknit compound 862, which is a silicone elastomer filled with carbon particles (S/O 95026 DKMT070127). Since the two sections above, demonstrated what appeared to be a linear relationship between force decay and compression set for silicone and fluorosilicones, it was of interest to see how this heavily filled silicone o-ring would behave. Comparison of the compression set versus the force remaining for the conducting silicone o-ring resulted in a graph that was not linear (Figure 21).

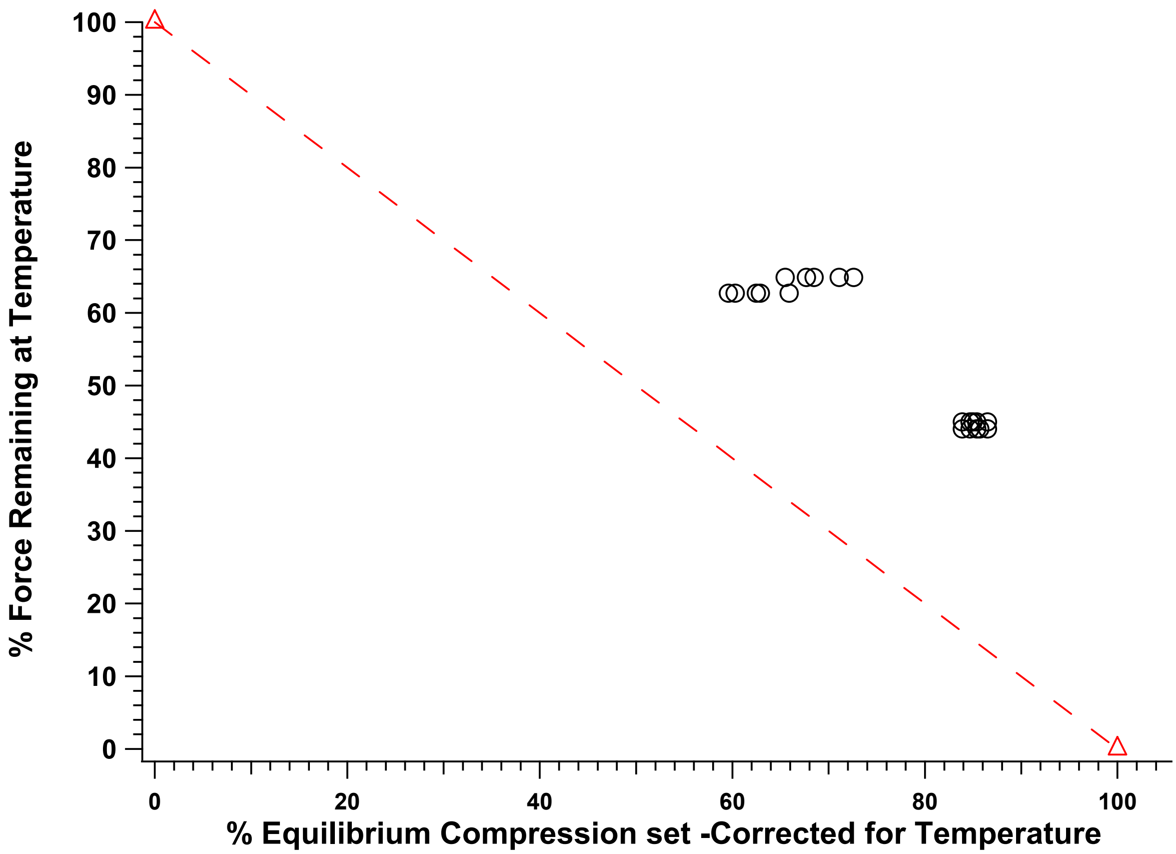


Figure 21: Conducting o-rings compression set versus force remaining

As noted earlier, theoretical treatments expect such non-linear behavior when the modulus of the material changes substantially during the aging.[2] It would be interesting to follow the changes in modulus values for this material with aging to see how closely the theory predicts the results found in Figure 21. In any case, these results demonstrate the caution that should be maintained when making general correlation statements about polymers. In this case, the conducting silicone o-ring material demonstrates very different behavior from the other materials discussed in this publication (possibly due to the high filler content needed to achieve the conductivity). Care must always be taken to understand the material before any predictions can be made.

Conclusions

This data from the current study validates that the technique developed for rapidly achieving the equilibrium sealing force for butyl material appears applicable to fluorosilicone materials. The over-compression methodology removes the physical component for fluorosilicone in the same manner as butyl material which suggests universality in this methodology for elastomers (the amount of time and over compression to achieve reasonably stable force values may vary with material). These samples were accelerated aged at various temperatures to gain insight into the force loss of the material as a function of aging temperature and time in order to aid in lifetime predictions.

Accelerated aging resulted in significant curvature when the time-temperature superposed shift factors were plotted on an Arrhenius plot. Comparison of force loss predictions based on using the non-Arrhenius extrapolation of the results are in reasonable accord with field-aged compression set results obtained on similar fluorosilicone materials. The results from both accelerated aging and field compression set results imply that the degradation of fluorosilicone seals occurs much more quickly than anticipated. The strong non-Arrhenius character of the data is consistent with numerous recent studies showing very similar non-Arrhenius character when data is taken over large enough temperature ranges. These results show the power and necessity of running long-term accelerated aging experiments to temperatures as low as possible.

Silicone compression set predictions at room temperature from old Sandia data correlated well with the room temperature sealing force predictions for fluorosilicones generated by this study. This implies that silicone seals have force degradation rates at room temperature that are similar to those found for the fluorosilicone. Although it is clearly advantageous to directly obtain the correlation between force decay and compression set, it is clear that as a first approximation, the compression set value can be used to approximate the sealing force.

Currently no future work is scheduled due to funding and time constraints. If future work were to be performed, it might involve such things as (1) modulus measurements versus aging time to test whether the theoretical relationship[2] can be used to explain the experimental correlations found between set and force loss in Figure 14 and Figure 21, (2) accelerated force decay measurements on silicone o-ring materials as well as equilibrium compression set measurements and modulus versus time measurements to obtain lifetime predictions, correlations between set and force loss and tests of the theoretical relationship, and (3) density studies to see if there is a correlation between the density and the force loss.

Acknowledgement.

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References

(1) Gillen, K. T.; Celina, M.; Bernstein, R. *Polymer Degradation and Stability,* Validation of Improved Methods for Predicting Long-Term Elastomeric Seal Lifetimes from Compression Stress-Relaxation and Oxygen Consumption Techniques **2003**, *82*, 25-35.

(2) Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polymer Degradation and Stability,* Predicting and Confirming the Lifetime of O-rings **2004**, *87*, 257-270.

(3) Chavez, S. L.; Domeier, L. A. "Laboratory Component Test Program (LCTP), Stockpile O-rings," BB1A3964, 2004.

(4) Gillen, K. T.; Green, P. F. "Moisture Permeation of Environmental Seals Used in Weapons," SAND92-2651, 1993.

(5) Adolf, D. "Nonlinear Viscoelastic Response of Carbon Black-Filled Butyl Rubber and Implications for O-Ring Aging," SAND97-2630, Sandia National Laboratories, 1997.

(6) Gillen, K. T.; Celina, M. "New Methods for Predicting Lifetimes. Part 2: The Wear-out Approach for Predicting the Remaining Lifetime of Materials," SAND2000-0715, 2000.

(7) Gillen, K. T.; Celina, M.; Clough, R. L.; Malone, G. M.; Keenan, M. R.; Wise, J. "New Methods for Predicting Lifetimes in Weapons. Part 1: Ultrasensitive Oxygen Consumption Measurements to Predict the Lifetime of EPDM O-Rings," SAND98-1942, 1998.

(8) Bernstein, R. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry),* Fluorosilicone O-Ring Equilibrium Force Determination Study **2005**, *46*, 650-651.

(9) Gillen, K. T.; Bernstein, R.; Derzon, D. K. *Polymer Degradation and Stability,* Evidence of Non-Arrhenius Behavior from Laboratory Aging and 24-Year Field Aging of Chloroprene Rubber Materials **2005**, *87*, 57-67.

(10) Gillen, K. T.; Bernstein, R.; Celina, M. *Polymer Degradation and Stability,* Non-Arrhenius Behavior for Oxidative Degradation of Chlorosulfonated Polyethylene Materials **2005**, *87*, 335-346.

(11) Gillen, K. T.; Celina, M. C.; Bernstein, R., *Methods for Predicting Lifetimes and Remaining Lifetimes of Polymers*; In -Service Life Prediction: Challenging the Status Quo; Martin, J. W., Ryntz, R. A., Dickie, R. A., Eds.; Federations of Societies for Coatings Technology: Sedona, AZ, 2005; pp 67-78.

(12) Celina, M.; Gillen, K. T.; Assink, R. A. *Polymer Degradation and Stability,* Accelerated Aging and Lifetime Prediction: Review of Non-Arrhenius Behavior Due to Two Competing Processes **2005**, *90*, 395-404.

(13) Bernstein, R.; Derzon, D. K.; Whinery, L. D.; Shedd, M. M.; Gillen, K. T. "Parachute Aging Studies; Nylon and Kevlar," 2007.

(14) Gillen, K. T. "Silicone Seal Analysis," Internal Memo, SNL, 2001.

Appendix

Drawing 267970

BX--------------------PRINTED 09/29/89--------------U-N-C-L-A-S-S-I-F-I-E-D--------------DRAWING NUMBER---267970 ISSUE--- F

TITLE---SEAL,RUBBER ROUND SECTION

DESIGN AGENCY CODE IDENT---14213

TIE ---SC/BX/ DRC---2

DRAWING LOCATION---BX DATE---09-29-89

RELEASED BY DA RELEASED DATE---10-3-89

--SHEET--001 OF 001

FOR EXPLANATION OF CODES SEE END OF CALLOUTS SECTION.

	GENTRY, F N 907/DAVIS,R 5114/MESSINA, M 834	00100
*** OTHER REQUIREMENTS ARE ***	8962895X C REV 1	00101
9900000 GENERAL REQUIREMENTS	1. DELETED LINE 02840 AND NOTE 1.	00102
	--	00199

NL CODE -QTY-	-QTY-	-QTY-	-QTY-	-QTY-	UNIT OF MEASURE -QTY-	PRODUCTION AGENCY NUMBER /PENTAGON M/	CODE IDENT	DESIGN AGENCY PART NUMBER / PART OR CONTROL NO	DESCRIPTION	PART CLASS	T	LINE NO
					-101	267970-101		267970-00		N		02000
					NA	AY267970-004		AY267970-004	SEAL,RUBBER ROUND SECTION			02500
					NA	9943014-01		9943014-01	PACKAGING,PREFORMED PACKING,RUBBER SEALS AND PIECE PARTS			02830 RT081
					ARS	4155220-02		4155220-02	ELASTOMER,FLUOROSILICONE, FUEL RESISTANT		1	02900 RT081

---END OF CALLOUT SECTION---

EXPLANATION OF CODES.

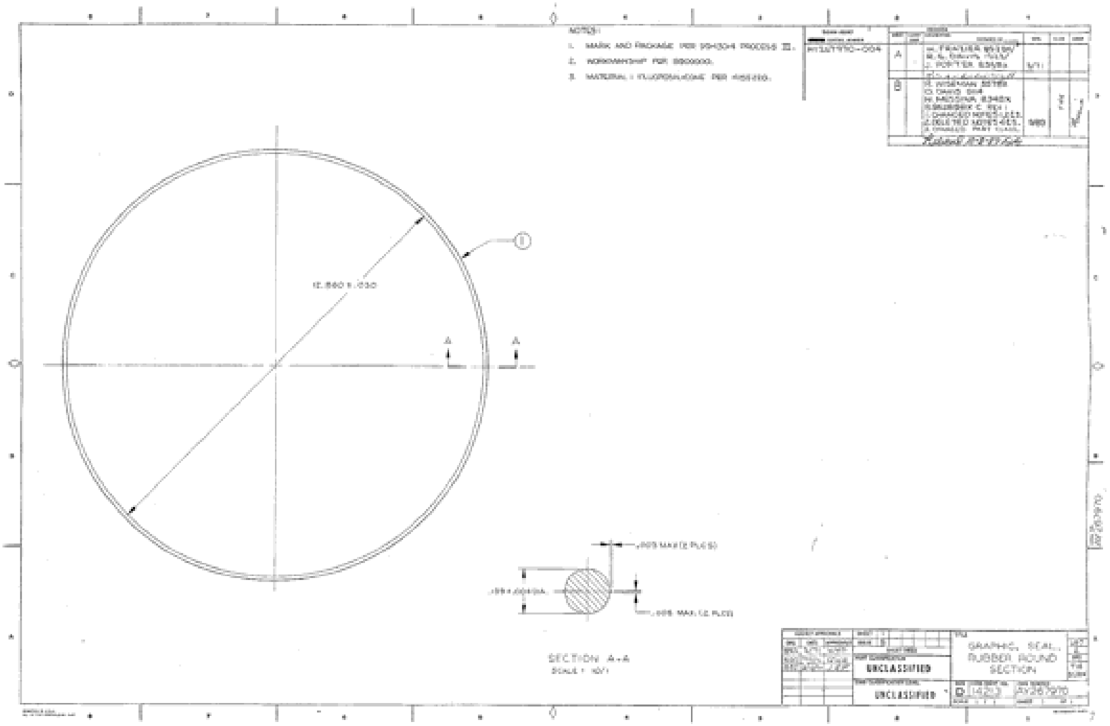
QUANTITY CODE/S--- AR-AS RQRD ARS-AS RQRD PER ASSY NA-DOCUMENTS PM-PROCESS MATERIEL EM-EXPENSE MATERIEL ALT-ALTERNATE

UNIT OF MEASURE CODE/S---IN-INCHES LB-POUNDS OZ-OUNCES AVOIRDUPOIS TZ-OUNCES TROY G-GRAMS FT-FEET PC-PER CENT M-METRE MM-MILLIMETRE KG-KILOGRAM

PART CLASSIFICATION CODES: UNCLASSIFIED---N UNCLASSIFIED CONTROLLED NUCLEAR INFORMATION---R

BX--------------------PRINTED 09/29/89--------------U-N-C-L-A-S-S-I-F-I-E-D--------------DRAWING NUMBER---267970 ISSUE--- F

Drawing AY267970



Sandia National Laboratories

Operated for the U.S. Department of Energy by

Sandia Corporation

Albuquerque, New Mexico 87185-1411

date: 9 April, 2001 (Distributed by email)

to: R. D. Holt, MS-0479 (2113) and L. A. Andrews, MS-0523 (1733)

from: K. T. Gillen, MS-1411 (1811)

subject: Silicone Seal Analyses

Recently you requested us to make estimates of lifetimes and remaining lifetimes of several silicone seals used in the W76. No information appears to be available concerning the type of silicone used for the seals and, in fact, available samples removed from MC3034 and MC3024 connectors after 9 to 17 years in the field are found to be white for the 17 year-old seals and red for the others. We have located some unpublished compression set measurements carried out ~30 years ago by Ed Salazar on an XE-5601 silicone seal material and carried out crude analyses of these old results in order to get a ballpark estimate of expected lifetimes. This memo summarizes our conclusions as well as compression set measurements made on the W76 seals obtained from the MC3034 and MC3024 connectors.

Ed Salazar's experiments comprised compression set measurements made using fixtures and specimens per ASTMD-395. Samples were compressed to initial strains of 10%, 20%, 30% and 40%, placed in air-circulating ovens at 5 temperatures (room temperature, 65.6°C, 100°C, 121.1°C and 148.9°C) for times ranging from 6 h to 210 days. Upon extraction from a given aging condition (comprising initial strain, temperature and time), the strain was released and the sample recovery height was measured after 1 hour at room temperature and after 10,000 h at room temperature. Since the strains appropriate to the W76 seals of interest vary between approximately 20 and 45% and since degradation is usually most severe at higher strains, we analyzed Salazar's data for 40% strain. Figures 1 and 2 show the compression set results versus aging time and temperature for 1-hr recovery (Fig. 1) and 10,000-h recovery (Fig. 2).

In general, compression set results are more difficult to interpret than compression stress relaxation measurements since the former depend in a complex manner on the interplay between scission and crosslinking, whereas the latter primarily reflect only scission events. In addition, both types of measurements are influenced by both physical (reversible polymer chain motions) and chemical (irreversible) effects which must be separated in a proper analysis. Although this is impossible in the present case, the presence of the 10,000-h recovery data will minimize the importance of physical effects. With the above in mind, we feel that an analysis based on time-temperature superposition (horizontal shifting of the curves by multiplicative factors that give the best overlap of the degradation curves) will lead to a semi-quantitative estimate of seal lifetime at room temperature. The results of this procedure lead to reasonably good superposition as shown in Fig. 3 (1-h recovery) and Fig. 4 (10,000-h recovery). The main difference in the two superposed curves is the expected observation that, at any time, the 10,000-h recovery results give compression set values less than the 1-h recovery. The differences average around 5 to 10%, reflecting the enhanced physical recovery expected for the longer recovery time. Clearly chemical degradation effects dominate compression set values above 20 to 30%. These results imply that the XE-5601 silicone compressed to 40% at room temperature will reach compression set values of around 70% after ~40 years. It is interesting to note that recent 40-year silicone seal compression set data reported by British workers (R. P. Brown and T. Butler, "Natural Aging of Rubber", Rapra Technology Ltd., 2000) were in excellent agreement with the predictions shown in Figs. 3 and 4 (the British results are plotted on the figures). Even though the British silicone was different from the silicone studied by Ed Salazar, the agreement of real data with our crude extrapolated analyses of Salazar's data lends some confidence to the predictions shown in Figs. 3 and 4.

There are several silicone seals of concern to the W76, used on connectors for the MC3347 isolator, the MC2912 AF&F and the CF2253 Load. The isolator seals are exposed to air whereas the other seals are in inert environments (no oxygen). We received seals from the MC2912 AF&F to evaluate. Three came from the MC3034 connector and three from the MC3024 connector. Details on the seals obtained and their colors are shown in the first two columns of Table 1. The initial seal thicknesses are 44±2 mil and the seals were compressed to a minimum thickness of 25 mil, a nominal thickness of 30 mil and a maximum thickness of 34 mil. We measured the thickness of the 6 seals after they spent times in the field ranging from 9 to 17 years. Table 1 summarizes the field times and the measured thickness upon return from the field in columns 3 and 4. Columns 5 and 6 estimate the maximum compression set (C. S.) found (assumes an initial thickness of 46 mil compressed to 34 mil) and nominal C. S. (assumes an initial thickness of 44 mil compressed to 30 mil).

Table 1. Seals and calculated compression set values.

Identity	Color	Time in field, yr	Measured thickness, mil	Max. C. S., %	Nominal C. S., %
MC3034-01 1828-B80	White	17	44	16.7	0
MC3034-02 4207-B86	Red	12	44	16.7	0
MC3034-02 3512-A84	Red	9	44	16,7	0
MC3024-02 4207-B86	Red	12	44	16.7	0
MC3024-01 1828-B80	White	17	43	25	7
MC3024-01 2217-A80	Red	11	43	25	7

It is clear from the results shown in Table 1 that little degradation is apparent for these six seals, much less than the 40-50% set predicted for the XE-5601 material exposed to air (see Fig. 4). However, because these seals were not exposed to air, degradation would be expected to be much less severe. If the predictions in Figs. 3 and 4 are reasonably accurate, they would suggest that room temperature silicone seal lifetimes in air should exceed 50 years. However, if a seal is removed after 10-20 years in the field and then reused in another unit for further field time, the range in possible compressed thicknesses could lead to little or no compression for the second cycle. For example, if a 42-mil o-ring (minimum size) is compressed in its first cycle to 25 mil (maximum compression) and has 50% set after 20 years, it would have a thickness of ~33.5 mil after its first cycle. If it were then placed in a unit with a minimum compressed spacing of 34 mil, the seal would start out without any compression. One way around this problem would be to measure seal thickness before reusing a seal. Only seals above a certain thickness would be reused.

It is also important to note that the rate of degradation of silicones from different manufacturers and different formulations will vary. As an example, silicone o-rings exposed for 20 years under inert conditions in the MC2854 Inertial Switch experienced nominal compression set values in the 30-40% range (memo from K. T. Gillen to G. T. Randall dated September 13, 1999). These results are in reasonable agreement with the air-aging predictions shown in Fig. 4, but quite different from the results shown in the Table.

We therefore conclude that it is difficult to make sound conclusions on expected lifetime behaviors without having proper data (e.g., in air or inert environments as appropriate) on the particular silicone used in the application. Since this information may not be available, the best approach may be to obtain more seals from surveillance units to assess their condition. If a representative group of seals (including those exposed to air) show evidence of minimal degradation similar to that observed for the seals studied in Table 1, confidence in the continued viability of the seals of interest would increase. Difficult to procure seals that show very little evidence of degradation could be seriously considered for reuse.

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R. L. Clough, MS-0888
R. Bernstein, MS-1411

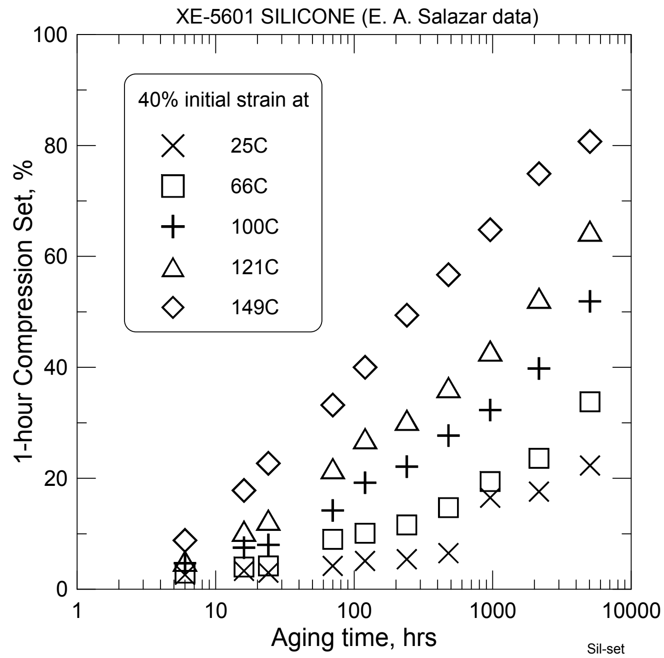

Figure 1. Compression set data after 1-hr recovery.

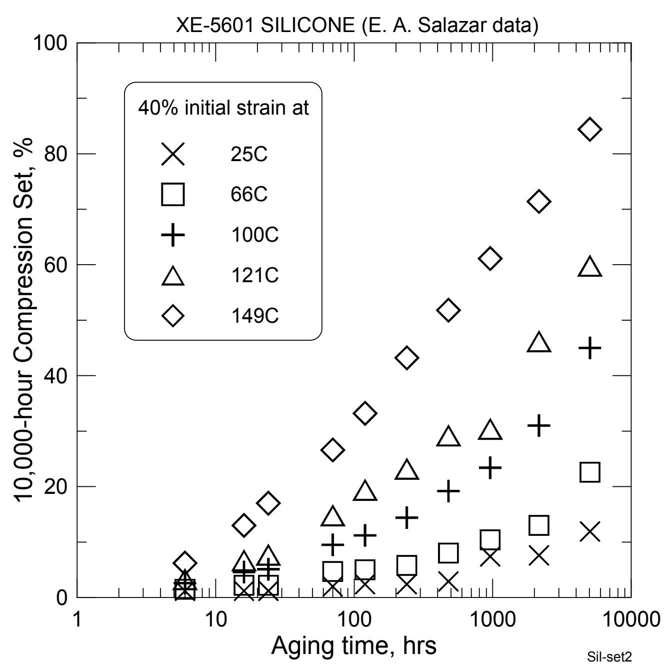

Figure 2. Compression set data after 10,000-hr recovery.

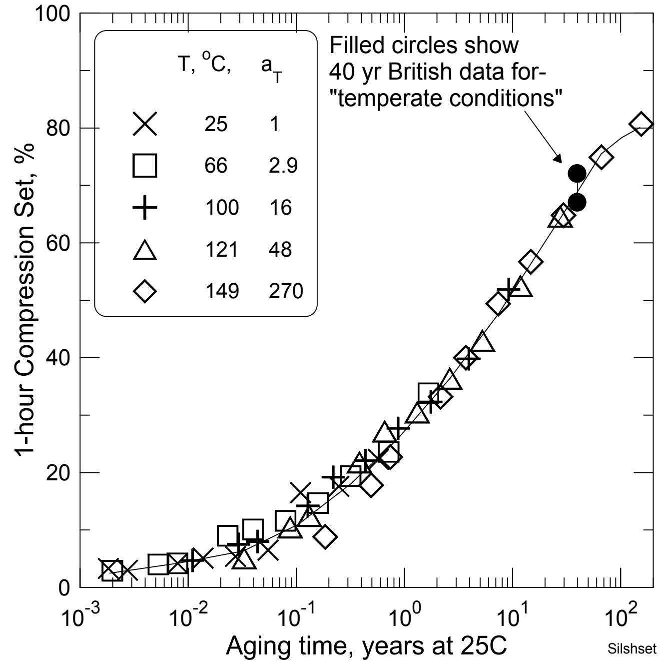

Figure 3. Time-temperature superposed data using the results from Fig. 1.

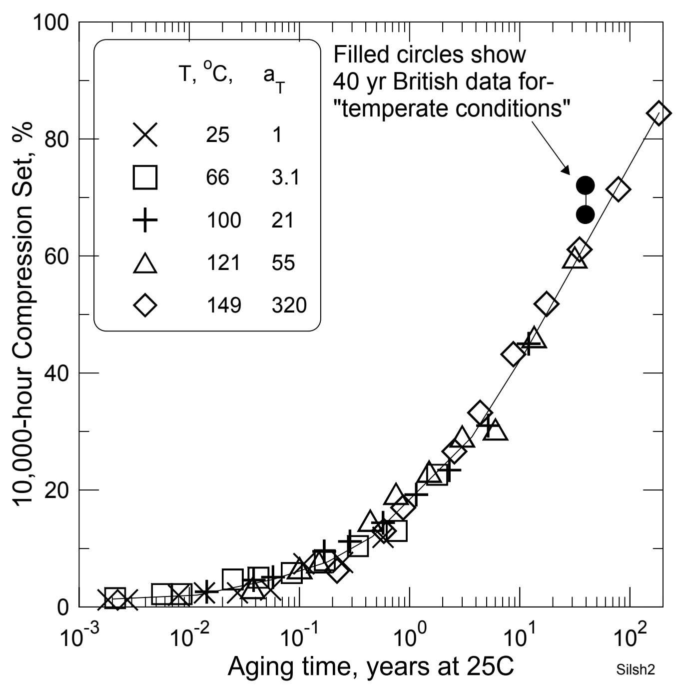

Figure 4. Time-temperature superposed data using the results from Fig. 2.

Distribution

1	MS-2C43	Mark Wilson		
1	MS 1322	Aidan Thompson	1435	
1	MS 0372	David Lo	1524	
1	MS 1411	Joanne Budzien	1814	
1	MS 0888	Douglas Adolf	1821	
1	MS 0888	Gregory Jamison	1821	
1	MS 0886	Jim Aubert	1821	
1	MS 1411	Ken Gillen	1821	
5	MS 0888	Robert Bernstein	1821	
1	MS 1411	David Tallant	1822	
1	MS 0886	Mike Keenan	1822	
1	MS 0888	Jeff Braithwaite	1826	
1	MS 0447	Paul Hooper	2111	
1	MS 0479	Scott Brumbaugh	2138	
1	MS 0344	Elizabeth Schexnayder	2626	
1	MS 0311	George Clark	2626	
1	MS 0344	William Nance	2626	
1	MS 0634	Pamela Walker	2951	
1	MS 0611	Siviengxay Limary	2957	
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