SAND99-0623C

Better Methods for Predicting Lifetimes of Seal Materials

Kenneth T. Gillen, Mat Celina and Michael R. Keenan
Sandia National Laboratories, Albuquerque, NM 87185-1407

Introduction

We have been working for many years to develop better methods for predicting the lifetimes of polymer materials. Because of the recent interest in extending the lifetimes of nuclear weapons and the importance of environmental seals (o-rings, gaskets) for protecting weapon interiors against oxygen and water vapor, we have recently turned our attention to seal materials [1,2]. Perhaps the most important environmental o-ring material is butyl rubber, used in various military applications. Although it is the optimum choice from a water permeability perspective, butyl can be marginal from an aging point-of-view. The purpose of the present work was to derive better methods for predicting seal lifetimes and applying these methods to an important butyl material, Parker compound B612-70.

Results and Discussion

For seal materials, the property that is most correlated to eventual failure is the sealing force between the seal and its metal mating surface. The experimental approach most closely related to sealing force decay involves compression stress-relaxation (CSR) measurements. We conducted standard CSR experiments using a commercially available apparatus, the Shawbury-Wallace Compression Stress Relaxometer MK II. The standard approach involves compressing 0.5-inch (12.7-mm) diameter rubber discs between adjustable metal platens in special CSR jigs, aging the jigs at elevated temperatures and periodically measuring the sealing force. At the start of the experiments, the disks were compressed approximately 25%. From conservation of volume, this implies that the disks are ~14.7-mm diameter during the aging. Once jigs were placed in aging ovens, force measurements were made after 1 day and then periodically, dependent upon how fast the force was decaying. Extrapolating the force results back to time zero allowed us to obtain the normalized force results versus aging time at each temperature. Figure 1 plots the normalized sealing force results for experiments run on these 14.7-mm disks at the four indicated temperatures. Since ~1 year is required at 80°C for the force to decay substantially, lifetime predictions at lower temperature clearly require an extrapolation of the higher temperature data. The most common approach, involving the Arrhenius model, assumes that a chemical process, with rate proportional to $\exp(-E_a/RT)$, determines the degradation rate. To test this model, we select an arbitrary failure criterion of 75% loss in sealing force (dashed line in Figure 1), and plot the log of the failure times versus inverse absolute temperature (X's in Fig. 2). If the Arrhenius model were valid, this plot would be linear. In fact, the results are very non-linear. In addition, the instantaneous slopes give effective E_a values ranging from ~56 kJ/mol at 80°C to ~38 kJ/mol at 125°C, lower than the range normally expected for oxidation processes (80 to 120 kJ/mol).

Based on our past studies of diffusion-limited oxidation (DLO) effects for sheet materials [3] and the rather large diffusion distances appropriate to a 14.7-mm diameter disk, important DLO effects were suspected as the reason for these strange results. DLO effects occur whenever the rate of oxidation inside a material uses up dissolved oxygen faster than it can be replenished by diffusion from the surrounding air atmosphere. Since they become more important as the temperature is raised, they are consistent with the observed behavior for the CSR results. To more quantitatively test this hypothesis, we derived a theoretical DLO model for the disk-shaped

geometry appropriate to CSR experiments by using an expression for the oxygen consumption rate in the diffusion-reaction equation appropriate to radial coordinates. With standard finite element methods, we obtained solutions [2] for the integrated relative oxidation (IRO) versus model parameters related to the disk diameter, the oxygen permeability coefficient and oxygen consumption rate. By then measuring the oxygen consumption rates (Fig. 3) and the oxygen permeability coefficient as functions of temperature, we were able to estimate IRO values as a function of disk diameter and aging temperature (Fig. 4). These results show that the IRO (the percentage of oxidation relative to a homogeneously oxidized material) for the 14.7-mm diameter CSR experiments varied from ~30% at 125°C to ~62% at 80°C, consistent with expectations.

An easy method for eliminating anomalous DLO effects involves reducing the CSR disk diameter. At 70°C and 80°C, we ran CSR experiments on 6-mm diameter disks, since Fig. 4 shows that such experiments should have IRO values greater than 90%. Since a single smaller disk would substantially reduce the force in the jigs, four were strained in parallel. Initially, the four disks were placed sufficiently far apart on the metal platen such that they would not touch when the 25% strain was imposed. Above 80°C, even smaller disks are required to minimize DLO effects. We therefore used disks of 2-mm diameter (50 strained in parallel) for experiments at 95°C, 110°C and 125°C. Figure 5 shows the results obtained for these parallel, mini-disk experiments. As expected, the decays are much faster than found for the 14.7-mm diameter samples, especially at the higher temperatures. The Arrhenius plots for force drops of 50% and 75% for these experiments are plotted as the triangles and diamonds respectively on Fig. 2. The results now indicate Arrhenius behavior, independent of the amount of degradation (parallel lines) with a reasonable E_a of 80 kJ/mol.

For conventional Arrhenius analyses, typically one or two processed data points per temperature are used. A better approach, time-temperature superposition, uses the complete data set [4]. We first select the lowest temperature 70°C as the reference temperature, T_{ref}. If increasing the temperature to T equally accelerates all of the reactions underlying a given degradation variable, than the time decay of the degradation parameter will be accelerated by a constant multiplicative shift factor, a_T. For each higher temperature, we empirically determine the value of a_T that results in the best superposition with the data at T_{ref}. Figure 6 shows the superposed results for the CSR data of Fig. 5 and the a_T values used for shifting. These values, which are plotted on an Arrhenius plot as squares in Fig. 7, give Arrhenius behavior with the same E_a determined earlier from Fig. 2. The normal approach is to extrapolate the line through this data to make predictions at lower temperatures (dashed extension). Unfortunately, degradation mechanisms can change as the temperature drops [5], making this extrapolation problematical without confirmatory evidence. We have recently showed that oxygen consumption measurements are sensitive enough to probe this low temperature region and therefore can be used to test this extrapolation assumption [1,4,5]. Since oxidation dominates the drop in force for the butyl material, it should be sufficiently correlated to the force drop to allow a test of this extrapolation. The oxygen consumption results shown in Fig. 3 were taken at three high temperatures overlapping the range of temperatures used for the CSR experiments. In addition, measurements were made at three temperatures in the extrapolation region, including room temperature. These measurements were integrated and then time-temperature superposed at a 25°C reference temperature, yielding the excellent superposition shown in Fig. 8. The empirical shift factors needed to achieve this superposition are plotted as triangles in Fig. 7. The results are Arrhenius over the entire temperature region from 110°C down to 25°C with an E_a of 82 kJ/mol, essentially identical to that of the CSR experiments. This correlation offers good evidence that the CSR data can be extrapolated to 25°C, yielding the result shown by the upper x-axis in Fig. 6. If we assume that "failure" of the butyl seals represents a 75% decrease in the sealing force, these results imply a lifetime of greater than 100 years at room temperature.

Acknowledgments

The authors thank G. M. Malone for assistance in the experimental measurements. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

References

1. K. T. Gillen, M. Celina, R. L. Clough, G. M. Malone, M. R. Keenan and J. Wise, "New Methods for Predicting Lifetimes in Weapons. Part 1: Ultrasensitive Oxygen Consumption Measurements to Predict the Lifetime of EPDM O-Rings", Sandia Report SAND98-1942 (September 1998).
2. K. T. Gillen, M. R. Keenan and J. Wise, Die Angewandte Makromolekulaire Chemie, 261/262, 83 (1998).
3. J. Wise, K. T. Gillen and R. L. Clough, Polymer, 38, 1929 (1997).
4. J. Wise, K. T. Gillen and R. L. Clough, Polym. Degrad. & Stabil., 49, 403 (1995).
5. K. T. Gillen, M. Celina, R. L. Clough and J. Wise, Trends in Polymer Science, 5, 250 (1997).

Figure 1. Normalized force decay versus temperature for standard disk samples.

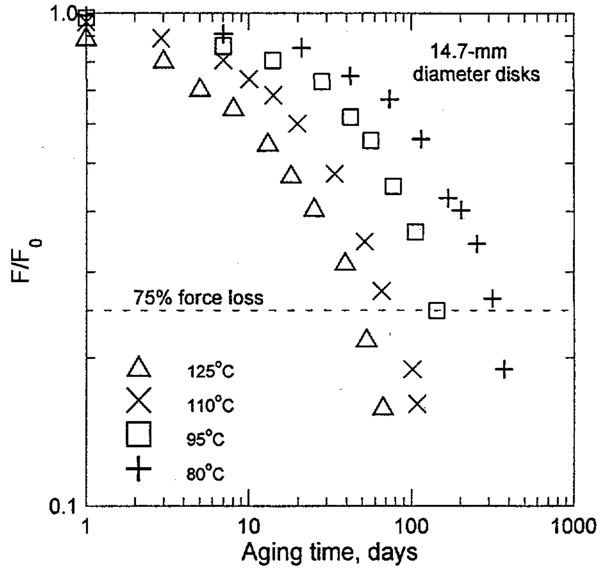
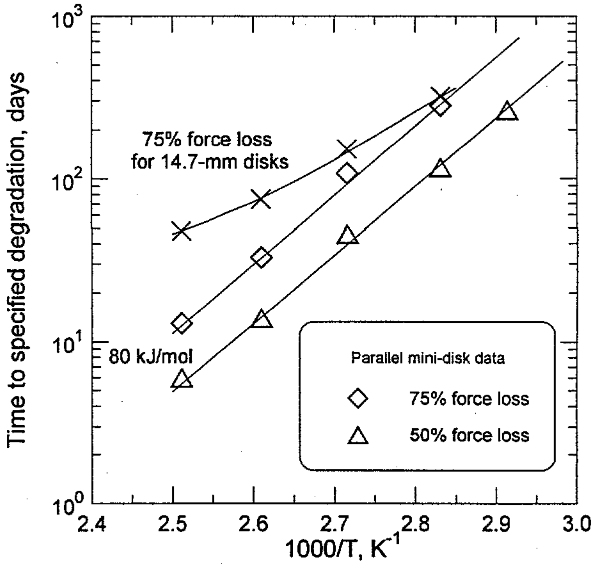


Figure 2. Arrhenius plots of CSR results as indicated.



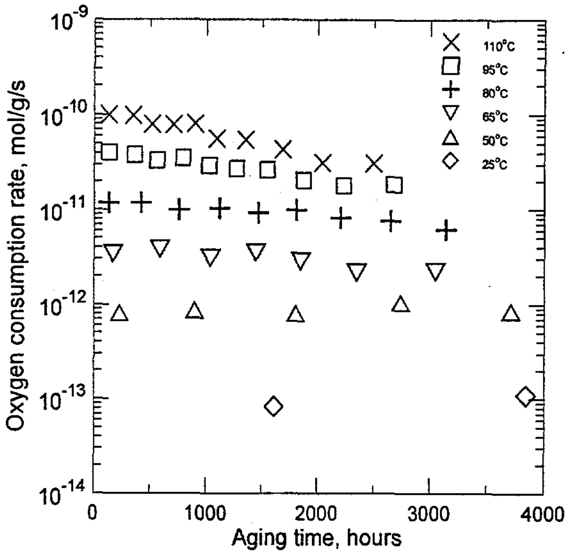


Figure 3. Oxygen consumption results versus time at the indicated temperatures.

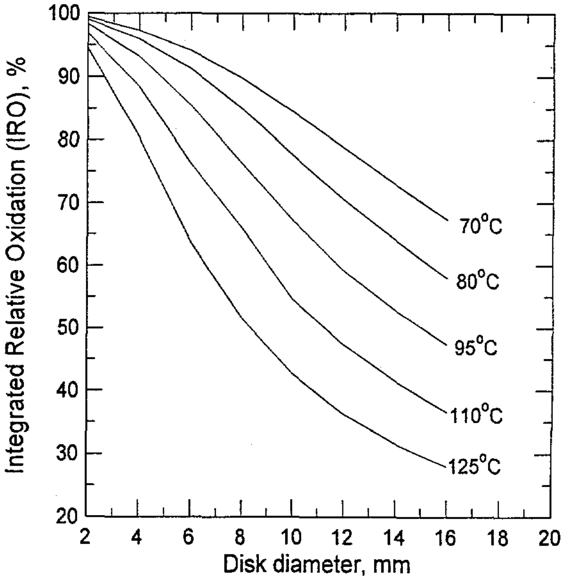


Figure 4. Predicted IRO values versus disk diameter and aging temperature.

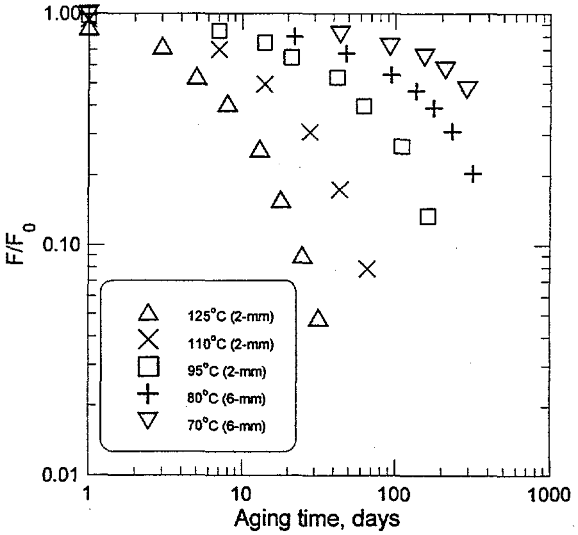


Figure 5. Normalized force decay versus temperature for parallel mini-disk samples.

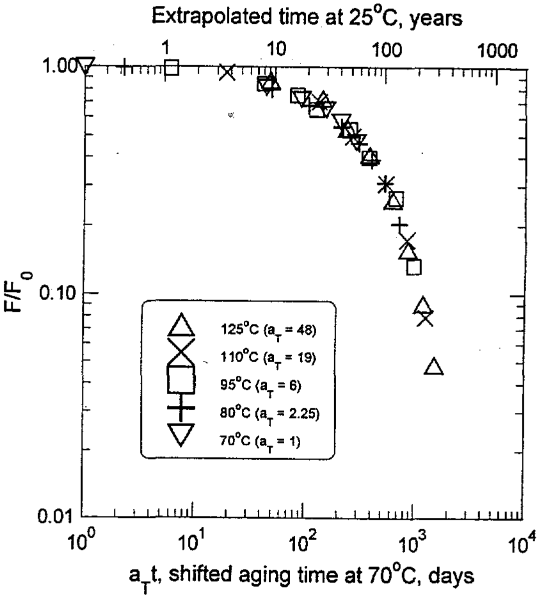


Figure 6. Time-temperature superposed results using data from Fig. 5.

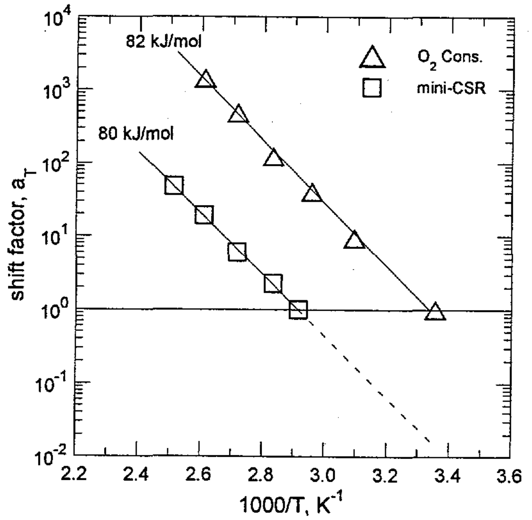


Figure 7. Arrhenius plots of shift factors.

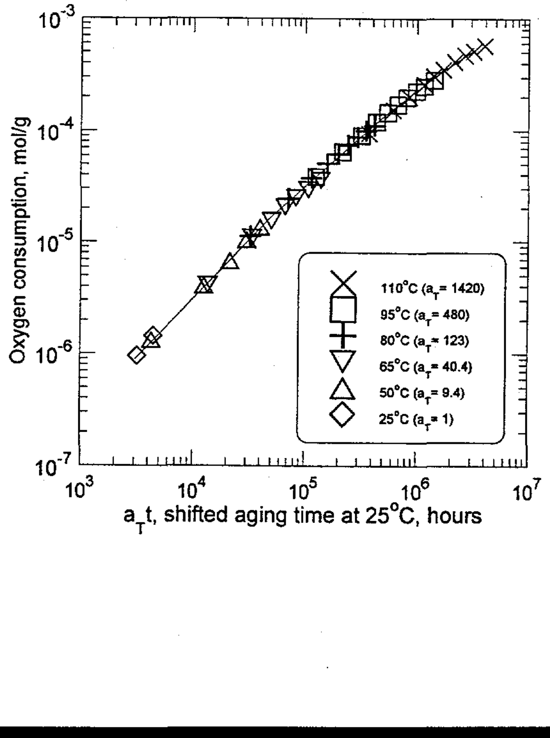


Figure 8. Time-temperature superposed oxygen consumption data.