CONF-970982--
SAND97-2181C
SAND--97-2181C

Evidence that Arrhenius High-Temperature Aging Behavior for an EPDM O-ring Does Not Extrapolate to Lower Temperatures

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SEP 2 3 1997
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Because of the need to significantly extend the lifetimes of weapons, and because of potential implications of environmental o-ring failure on degradation of critical internal weapon components, we have been working on improved methods of predicting and verifying o-ring lifetimes. In this report, we highlight the successful testing of a new predictive method for deriving more confident lifetime extrapolations. This method involves ultrasensitive oxygen consumption measurements. The material studied is an EPDM formulation (designated SR793B-80) used for the environmental o-rings on the W88. Conventional oven aging (155°C to 111°C) was done on compression molded sheet material; periodically, samples were removed from the ovens and subjected to various measurements, including ultimate tensile elongation, density and modulus profiles [1]. Compression stress relaxation (CSR) measurements were made at 125°C and 111°C on disc-shaped samples (12.7 mm diameter by 6 mm thick) using a Shawbury-Wallace Compression Stress Relaxometer MK II. Oxygen consumption measurements were made versus time, at temperatures ranging from 160°C to 52°C, using chromatographic quantification of the change in oxygen content caused by reaction with the EPDM material in sealed containers [2].

In general, changes in mechanical properties with aging determine the lifetime of polymeric materials. When oxygen is present during aging, oxidation chemistry will usually dominate the degradation, implying that measurements such as oxygen consumption should be closely correlated with mechanical property changes and provide mechanistic insights of the underlying chemistry. Figure 1 shows oxygen consumption results versus aging time at 125°C. Except for a small initial drop, the oxygen consumption rate is relatively constant for the first 150 days or so, after which it rapidly increases. This is often termed "induction-time" behavior, with the drastic rate increase at the induction time (t_{ind}) occurring after the protective antioxidant in the material has been consumed by degradation reactions. It turns out that this induction-time behavior, recognized from the oxygen consumption measurements, totally dominates the degradation of all other properties. For instance, surface modulus results at 125°C (also plotted in Fig. 1), obtained from modulus profiling experiments, show minor changes up to t_{ind}. Once the oxidation rate begins to rapidly increase, the modulus quickly rises by an order of magnitude. Figure 2 plots tensile elongation results at four aging temperatures; the 125°C data clearly show that a rapid decrease in tensile properties occurs after t_{ind}. Even for the CSR experiments, where mechanical stress is added to the aging environment, the same t_{ind} determines the loss of properties, as seen in Fig. 3.

By selecting a failure criterion for each parameter monitored (see Table 1), we can derive the times required to reach this value; these times, which we define as t_{ind}, are summarized in Table 1

Table 1. Summary of t_{ind} estimates.

Aging temperature, °C	*155*	*140*	*125*	*111*
elongation- time to reach 50% absolute, days	14	47	165	610
density- time to reach 1.16 g/cc, days	14.3	45.5	175	610
Surface modulus- time to double the unaged value, days	13	45.5	135	550
Normalized force (F/F_0)- time to reach 0.1, days			162, 184	540

The conventional analysis approach involves the Arrhenius model. This model predicts that $t_{ind} \sim \exp(-E_a/RT)$, where E_a is the Arrhenius activation energy and T is the absolute temperature. The results from Table 1, when shown on an Arrhenius plot, give the expected linear behavior (E_a equals 116 kJ/mol), as seen in Fig. 4. Normally, the next step is to extrapolate the Arrhenius line to lower temperatures to make long-term predictions at experimentally inaccessible temperatures; in the present case (dashed line) this procedure predicts a 55,000 year lifetime at 23°C.

In the conventional Arrhenius analysis above, only one data point per temperature (the induction time) was used. A better approach, time-temperature superposition, uses the complete data set to test the Arrhenius or other acceleration models [2]. We first select 111°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 5 shows the superposed results for the elongation data plotted in Fig. 2. The a_T values used for elongation and a_T values similarly derived for the density, modulus, and force decay data are summarized in Table 2 and plotted on an Arrhenius plot as crosses, squares, diamonds and Xs, respectively in Fig. 6. These results again give Arrhenius behavior with an E_a of 118 kJ/mol, virtually identical to the result in Fig. 4; they can also be linearly extrapolated to lower temperatures in a similar manner.

Table 2. Summary of time-temperature shift factors, a_T

Temperature	a_T *- elongation*	a_T *-surface modulus*	a_T *- density*	a_T *- F/F₀*	a_T *- O₂ consumption*
160°C					55.7
155°C	40	48	42		
140°C	13	14	12.7		13.7
125°C	4	4.3	3.7	3.8	4.7
111°C = T_{ref}	1	1	1	1	1
96°C					0.433
80°C					0.124
52°C					0.0103

We determined above that the EPDM o-ring material appeared to have reasonable Arrhenius behavior at temperatures of 111°C and higher, and then extrapolated this behavior in a conventional manner to predict very long lifetimes at 25°C. Unfortunately, this can be quite dangerous, since degradation mechanisms can change in the extrapolation region [2,3]. Better extrapolation methods are clearly needed and, by necessity, they must involve an ultrasensitive analytical method which follows a parameter intimately correlated with the mechanical degradation. Oxygen consumption clearly fits the latter requirement. In recent studies developing this technique, we determined that measurements could easily be made down to levels of sensitivity better than 1×10^{-13} mol/g/s. For most polymers, this sensitivity allows measurements to be made at temperatures which correspond to 100 or more years of mechanical property lifetime, sufficient for most predictive purposes [2]. This sensitivity allowed us to make oxygen consumption measurements down to 52°C for the EPDM material. When the data were time-temperature superposed to the T_{ref} of 111°C, the resulting values of a_T are shown in Table 2 and plotted as triangles on Fig. 6. At 111°C and above, the activation energy for the oxygen consumption shift factors is consistent with the conventional measurements. Below this temperature, the activation energy drops by approximately 30% to 82 kJ/mol, implying that changes are occurring in the underlying oxidation mechanisms. This change in slope will significantly reduce the lifetimes predicted from any extrapolation. For instance, at the lowest experimental temperature of 52°C, the experimental shift factor of ~0.01 coupled with the ~600 day mechanical property lifetime at 111°C (Fig. 5) leads to a predicted lifetime of ~150 years. If no additional mechanistic changes occur below 52°C, extrapolation of the 82 kJ/mol activation energy results in a predicted lifetime at 25°C of greater than 2000 years; even though this represents an approximate factor of 30 reduction from the predictions given earlier based on the conventional Arrhenius analyses, much more confidence exists in the result. It is of course possible that the effective activation energy will become less than 82 kJ/mol below 52°C, which would cause a further reduction in the 2000 year estimated lifetime. However, since no cases are known for thermoxidative aging in which the activation energy drops below zero, we conclude, with high confidence, that the EPDM o-ring will have a lifetime of at least 150 years for temperatures less than 52°C, a temperature that is much higher than typical weapon aging conditions.

References

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Acknowledgments

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

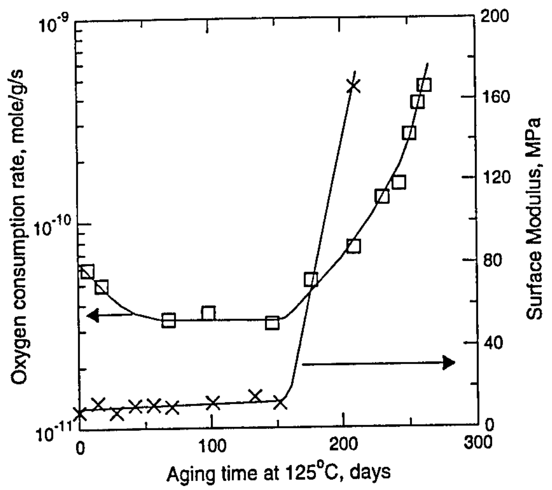

Fig. 1. Oxygen consumption rate & modulus vs. time at 125C.

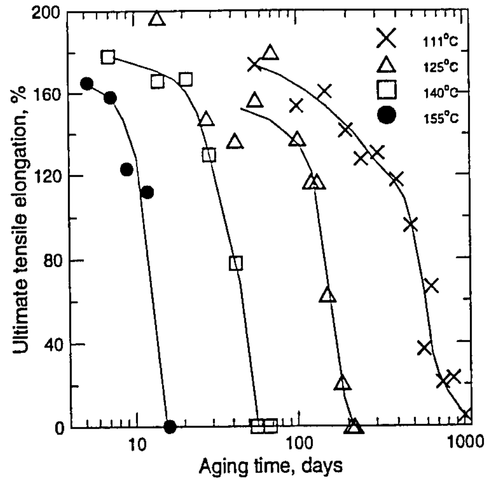

Fig. 2. Elongation vs. time and temperature.

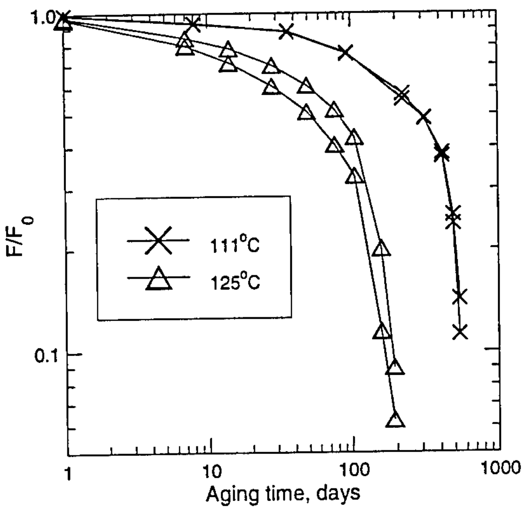

Fig. 3. Normalized force results vs. time and temperature (two samples were studied at each temperature).

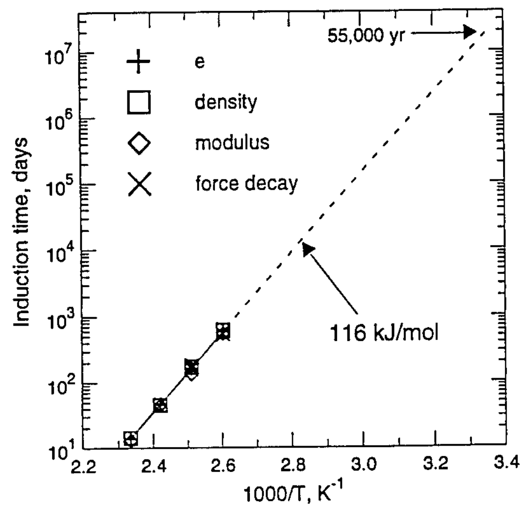

Fig. 4. Arrhenius plot of induction times from Table 1.

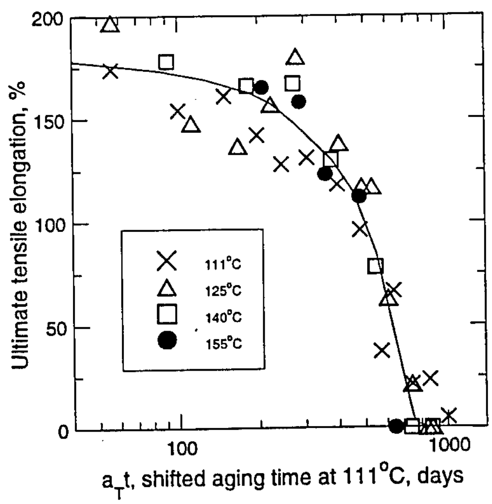

Fig. 5. Superposition of elongation data from Fig. 2.

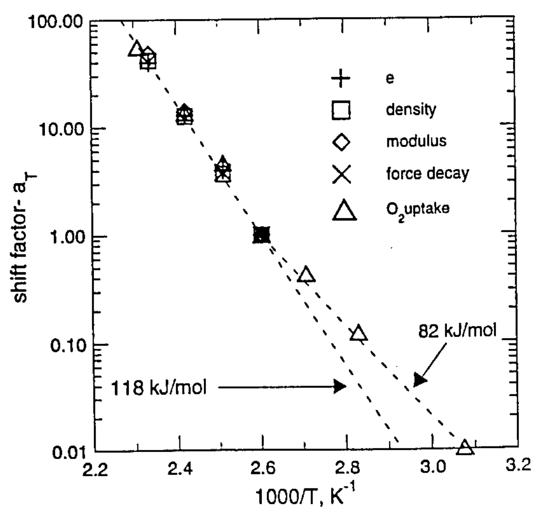

Fig. 6. Arrhenius plot of shift factors from Table 2.

M98000201

Report Number (14) SAND--97-2181C

CONF-970982--

Publ. Date (11) 199709

Sponsor Code (18) DOE/DP, XF

UC Category (19) UC-700, DOE/ER

DOE