

## LIMITATIONS OF THE ARRHENIUS METHODOLOGY

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## ABSTRACT

The Arrhenius methodology has been utilized for many years to predict polymer lifetimes in various applications. Unfortunately, there are numerous potential limitations associated with this methodology, many of which can lead to non-Arrhenius behavior. This paper will review several of these limitations, including a brief mention of diffusion-limited oxidation (DLO) effects and a more extensive discussion of the implication of changes in the effective Arrhenius activation energy  $E_a$  or in the dominant reactions as the temperature changes. Changes in  $E_a$  or in the dominant reactions with temperature can happen for any material, making extrapolations beyond the experimental temperature range problematic. Unfortunately, when mechanistic changes occur, they invariably result in a reduction in effective Arrhenius activation energy, leading to lower than expected material lifetimes. Thus it is critically important to derive methods for testing the Arrhenius extrapolation assumption. One approach that we have developed involves ultrasensitive oxygen consumption measurements. Results from the application of this approach will be reviewed.

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## INTRODUCTION

The Arrhenius methodology is commonly used to analyze thermal aging data and to extrapolate the data to temperatures outside the range of experimental temperatures. In nuclear power plants, it has been used extensively for polymeric materials and components both as a means of simulating degradation caused by decades of ambient aging and as a method for compressing time scales during LOCA and post-LOCA simulations. In this paper, we describe some of the problems that can result in non-Arrhenius behavior, potentially leading to apparent changes in the Arrhenius activation energy  $E_a$  with temperature. Since changes in  $E_a$  with temperature can significantly influence predicted lifetimes at temperatures below the lowest experimental conditions used in the Arrhenius analysis, methods are needed for determining whether the  $E_a$  changes in the extrapolation region. For polymers that are dominated by oxidation effects, we have introduced the first approach capable of achieving this objective. It is based on the use of ultrasensitive oxygen consumption measurements. For the interested reader, more detailed discussions on the problems associated with the Arrhenius approach and on the use of the ultrasensitive oxygen consumption method to test the Arrhenius extrapolation assumption have been published previously [1-2].

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## RESULTS AND DISCUSSION

Whenever oxygen is available during the aging of polymeric materials, oxidation chemistry typically dominates the degradation. For the simplest possible example, suppose a polymer  $P$  chemically reacts directly with oxygen dissolved in the polymer, leading to a degradation product  $D$ . In chemical kinetic terms, we can write this reaction as



where classical chemical rate theory gives the rate constant  $k$  in terms of  $E_a$ , the absolute temperature  $T$  and the universal gas constant  $R$  as

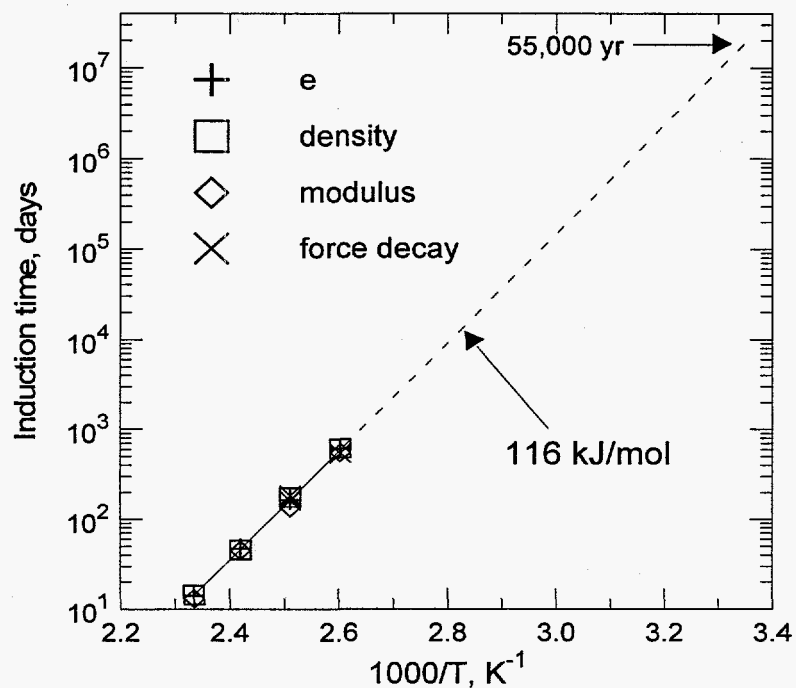
$$k \propto \exp\left[\frac{-E_a}{RT}\right] \quad (2)$$

Since mechanical properties are typically destroyed after oxidation of 1-2% of the polymer, the concentration of  $P$  will remain essentially unchanged during the degradation. This leads to the following expression for the rate of oxygen consumption and, equivalently, the rate of growth of the degradation product  $D$

$$\frac{dO_2}{dt} = \frac{dD}{dt} = k[O_2][P] = k' = A \exp\left[\frac{-E_a}{RT}\right] \quad (3)$$

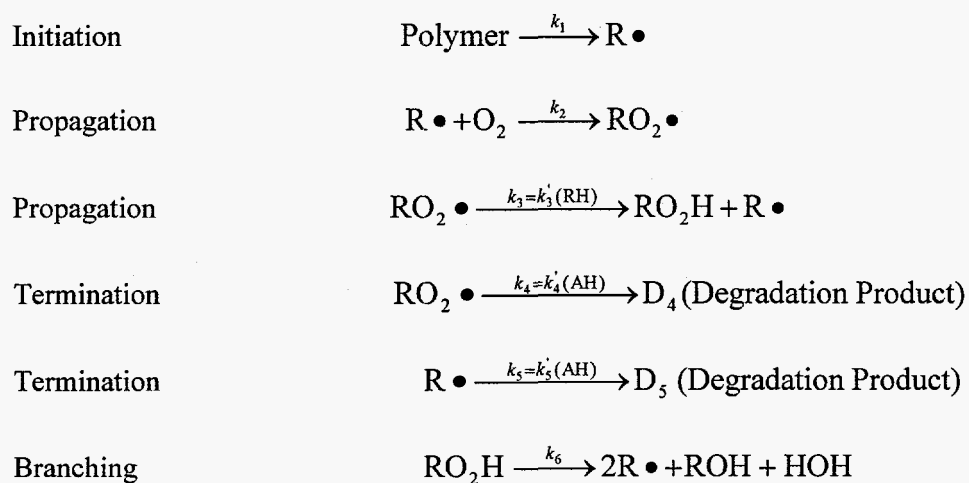
Equation (3) implies that the rate of degradation and the rate of oxygen consumption will be given by the same Arrhenius dependence on temperature and that this dependence will not change as the temperature is changed ( $E_a$  remains constant). If we therefore measure failure times at various aging temperatures for a property related to the buildup of degradation products and plot the log of the failure time versus inverse absolute temperature, we would expect linear behavior. Figure 1 shows such a plot for an EPDM material. In this plot, the induction (failure) times for several properties are in agreement and consistent with Arrhenius behavior (the  $E_a$  of 116 kJ/mol is derived from the slope of the line through the experimental results). From the figure, it is clear that the experimental time required for obtaining data at the lowest temperature probed by conventional measurements (111°C) is approximately 2 years. To make predictions at lower temperatures, it is assumed that the Arrhenius behavior remains constant, so that the linear behavior can be extrapolated (dashed line). This leads to a prediction of a 55,000-year lifetime at 25°C. Although a long lifetime is predicted at room temperature from the extrapolation shown in Fig. 1, it is clear that the distance of extrapolation is very large relative to the data range. This means that a drop in  $E_a$  below 110°C could have a profound effect on the extrapolated prediction. Thus, without a method for determining whether  $E_a$  remains unchanged, little confidence exists in such extrapolations.

It turns out that there are numerous phenomena that can lead to changes in  $E_a$  as the temperature changes [1]. Perhaps the easiest to understand comes from the fact that the oxidation chemistry underlying degradation is seldom as simple as that described by eqs. (1) – (3). In fact, the simplest realistic kinetic scheme for the oxidation of stabilized polymers is given by the following set of chemical reactions [1,3,4]



**Figure 1.** Arrhenius plot of the log of the induction times for the indicated experimental variables versus the inverse absolute aging temperature for an EPDM seal material. The data show Arrhenius behavior with an  $E_a$  of 116 kJ/mol. An extrapolation of this behavior (dashed line) to 23°C predicts a room temperature lifetime of 55,000 years.

**Scheme 1.** Classical oxidation scheme.



Although this scheme has similarities to the earlier scheme ( $O_2$  is used up by the second reaction eventually resulting in the creation of degradation products  $D_4$  and  $D_5$ ), kinetic analysis leads to very different conclusions concerning the constancy of  $E_a$ . By applying steady-state analyses to the free radical species and ROOH, one obtains [1]

$$\phi = \frac{d[O_2]}{dt} = \frac{C_1[O_2]}{1 + C_2[O_2]} \quad (4)$$

where

$$C_1 = \frac{k_1 k_2}{k_5} \quad (5)$$

$$C_2 = \frac{k_2(k_4 - 2k_3)}{k_5(k_3 + k_4)} \quad (6)$$

At low concentrations of  $O_2$

$$\frac{dO_2}{dt} = \frac{k_1 k_2 [O_2]}{k_5} \sim \frac{\exp\left[\frac{-E_1}{RT}\right] \exp\left[\frac{-E_2}{RT}\right] \exp\left[\frac{-\Delta H_s}{RT}\right]}{\exp\left[\frac{-E_5}{RT}\right]} \quad (7)$$

implying that the effective activation energy  $E_{\text{eff}}$  is given by

$$E_{\text{eff}} = E_1 + E_2 + \Delta H_s - E_5 \quad (8)$$

where  $\Delta H_s$  is the heat of solution for oxygen in the polymer. It is clear from eq. (8) that a constant effective value of  $E_a$  is predicted for low oxygen concentrations. On the other hand, at high oxygen concentrations, eqs. (4) – (6) lead to

$$\frac{dO_2}{dt} = \frac{k_1(k_4 + k_3)}{(k_4 - 2k_3)} \quad (9)$$

which, in general, predicts that the effective  $E_a$  will change with temperature. In addition, kinetic analysis of the rate of product formation gives for example

$$\frac{dD_4}{dt} = \left[ \frac{k_4}{k_4 + k_3} \right] \frac{dO_2}{dt} \quad (10)$$

This result predicts not only non-constant values of  $E_a$  for the degradation product  $D_4$  regardless of whether the oxygen concentration is low or high, but also differences in the values of  $E_a$  dependent upon which species ( $O_2$  consumption,  $D_4$  production) are being followed.

Although the above discussion indicates that non-Arrhenius behavior and differing values of  $E_a$  for different degradation variables might be anticipated from more realistic kinetic schemes, eqs. (9) and (10) show that the changes of the effective  $E_a$  with temperature may not be large if  $E_4$  is similar to  $E_3$  and  $E_1$  is considerably larger than either of the other two. This is in fact often the case, implying that the non-Arrhenius character may only show up as a gradual change with temperature. Nonetheless, given the large extrapolations often carried out, even a slowly changing  $E_a$  may have profound effects on extrapolated predictions.

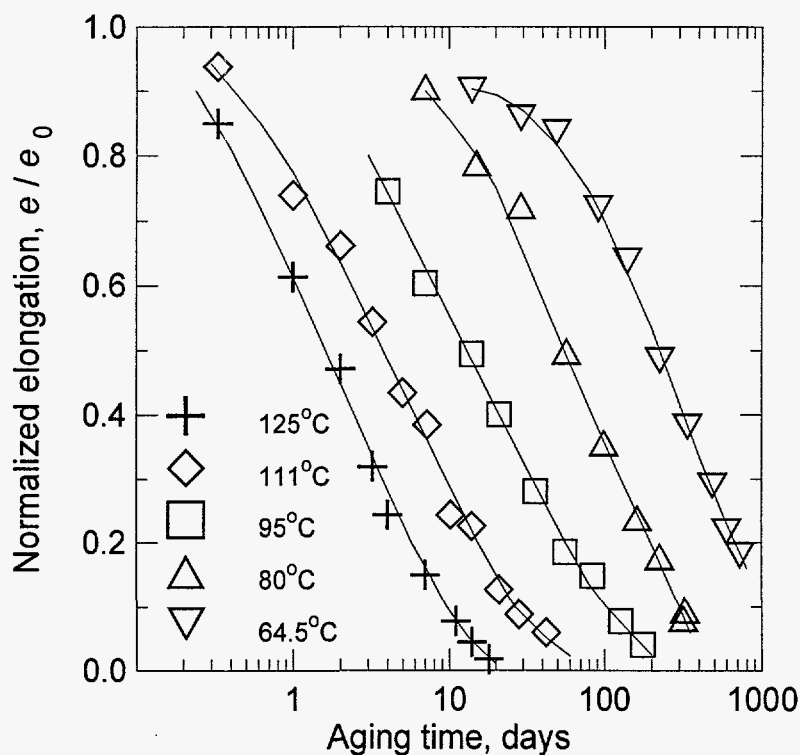
Another important mechanism that can lead to non-Arrhenius behavior involves diffusion-limited oxidation (DLO). At the high temperatures typically used for accelerated laboratory experiments, the consumption of dissolved oxygen in the polymer will often occur faster than the oxygen can be resupplied by diffusion from the surrounding air-atmosphere. Although oxidation at the sample surface will be at equilibrium and unaffected by the presence of DLO effects, the amount of oxidation will drop at positions deeper within the sample. Important DLO effects are commonly observed for typical, air-oven aging studies of numerous elastomers, as illustrated by comprehensive studies on SBR [5], nitrile [6], neoprene [5,6], EPDM [7,8] and hypalon [9]. Even though the importance of DLO effects has a complex dependence on time and temperature, these studies show that tensile elongation measurements are typically consistent with Arrhenius behavior. The reason stems from the fact that oxidative degradation of most elastomers leads to hardening of the material. If DLO effects are present, the hardening is greatest at the sample surface. Cracks would be expected to initiate at the hardened surface during tensile testing. Once initiated, if these cracks immediately propagate through the material, the tensile elongation will be determined by the surface degradation, which represents the true equilibrium oxidation rate (uninfluenced by DLO effects). Therefore, quite accidentally, tensile elongation measurements often lead to Arrhenius behavior even in the presence of important DLO effects. If cracks do not immediately propagate through the material, non-Arrhenius behavior can often be observed, as noted for a Kerite hypalon jacket material [9]. Similarly, properties that depend on the entire sample cross-section will not be amenable to Arrhenius analyses when DLO effects are important [2, 9].

Several other mechanisms can lead to important non-Arrhenius behavior. If, for instance, two distinct oxidation pathways underlie the degradation of a material, the mechanism of lower  $E_a$  will become dominant when the temperature drops sufficiently. This lower  $E_a$  mechanism will not be apparent until the Arrhenius degradation plot begins to curve at lower temperatures, therefore representing an unanticipated surprise if the curvature starts in the extrapolation region. Another problem can occur when the data region or the extrapolation range encompasses a polymer transition region, such as the crystalline melting point region characteristic of many EPDM and crosslinked polyolefin materials [1]. Several non-Arrhenius complications can arise from antioxidant interactions, caused by such things as solubility changes with temperature and various evaporation effects [10,11].

From the above discussion, it is apparent that many possible phenomena can result in non-Arrhenius behavior. It is therefore clear that methods need to be developed to provide more confidence in extrapolated predictions. We will describe one viable method of accomplishing this, involving the use of ultrasensitive oxygen consumption measurements, after we briefly review the concept of time-temperature superposition. The formalism used for time-temperature superposition analysis is needed and is ideally suited for discussing the ultrasensitive oxygen consumption approach.

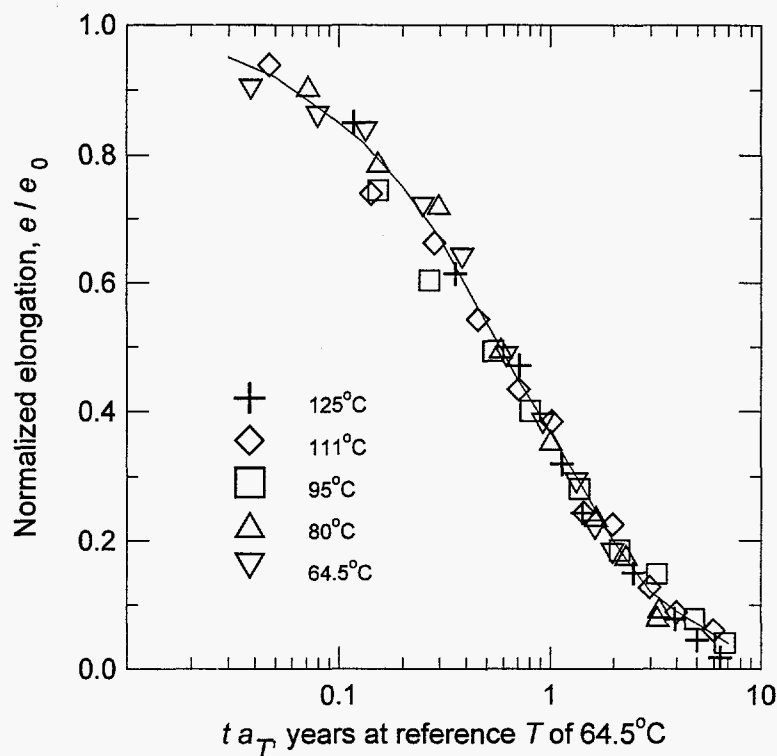
Earlier in Fig. 1, we used one processed point (the induction time) per temperature to test the Arrhenius equation. This means that most of the data generated versus time at each temperature were eliminated from the analysis. However, if the rate of degradation is constant at each aging temperature, an important consequence is the expectation that the time-dependent degradation curves at any two temperatures will be related by a constant multiplicative factor. This means that the curves at different temperatures should have the same shape when plotted versus the log of the aging time. Normalized elongation results for a nitrile rubber at five different aging temperatures [2] are consistent with this picture, as seen in Fig. 2. Instead of selecting only one point per temperature for the analysis, we apply the principal of time-temperature superposition [1,2,9,12]. We first select the lowest temperature (64.5°C) as the reference temperature. Then for each set of data at a higher temperature  $T$ , we multiply the experimental times by a constant shift factor,  $a_T$  chosen to give the best overall superposition with the reference temperature data ( $a_T = 1$  at the reference temperature). The results of this procedure are shown in Fig. 3, where the time-axis gives the superposed results at the reference temperature. Unlike the analysis given in Fig. 1, this approach utilizes every raw experimental point and yields empirical shift factors that can then be tested by models such as the Arrhenius. If, in fact the empirical shift factors are consistent with the Arrhenius equation, then they would be given by

$$a_T = \exp\left(\frac{1}{T_{ref}} - \frac{1}{T}\right) \quad (11)$$



**Figure 2.** Ultimate tensile elongation ( $e$ ) of a nitrile rubber normalized to its unaged value ( $e_0$ ) versus air-oven aging time and temperature.

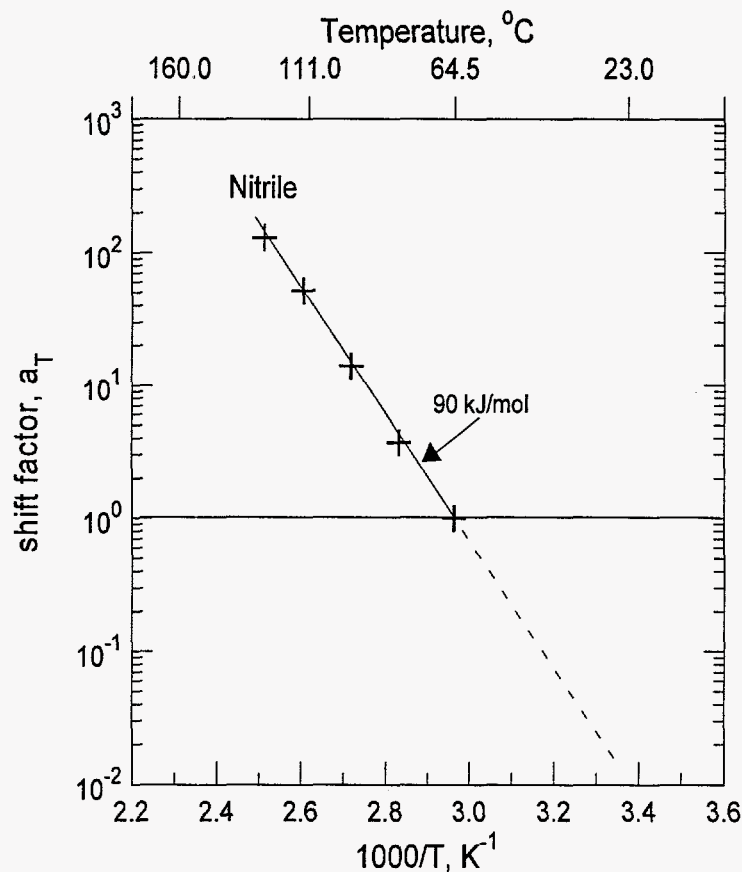




**Figure 3.** Time-temperature superposition of the data from Fig. 2 using empirically derived shift factors,  $a_T$ .

This would predict that a plot of  $\log(a_T)$  versus inverse temperature would give linear behavior. When the empirical shift factors are plotted in this fashion in Fig. 4, such linear behavior is in fact observed, with a corresponding  $E_a$  of approximately 90 kJ/mol determined from the slope. To make predictions at temperatures lower than 64.5°C ( $a_T = 1$ ), the normal procedure would then be to extrapolate (dashed line extension). For instance the extrapolated  $a_T$  at 22°C would be  $\sim 0.01$ , implying a lifetime approximately 100 times longer than at 64.5°C.

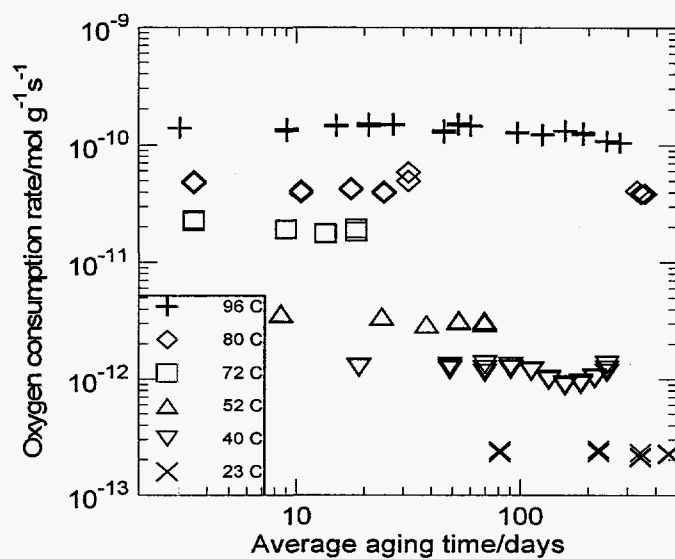
Given the distinct possibility that non-Arrhenius effects will be important for the extrapolations shown by the dashed lines in Figs. 1 and 4, it would be extremely useful to have methods that give more confidence in any attempted extrapolations. At the lowest temperatures utilized for conventional measurements (111°C for the EPDM material, 64.5°C for the nitrile material), several years of aging were required to see measurable property changes. Thus any technique that accesses lower temperatures must be an ultrasensitive monitor of the degradation. In addition, it needs to measure a property closely correlated to the chemistry dominating the mechanical degradation. One approach that we have developed for thermally oxidized materials involves ultrasensitive oxygen consumption measurements based on gas chromatography techniques [2]. With experimental care, this approach results in sensitivity capabilities of better than  $10^{-13}$  mol/g/s, which typically allows access to temperatures corresponding to expected mechanical property lifetimes of greater than 100 years. One might expect the oxygen consumption rate to be closely related to the tensile elongation since 1) oxidation chemistry is expected to dominate the degradation and 2) surface oxidation leads to the initiation of cracks that quickly propagate and therefore determine the elongation.



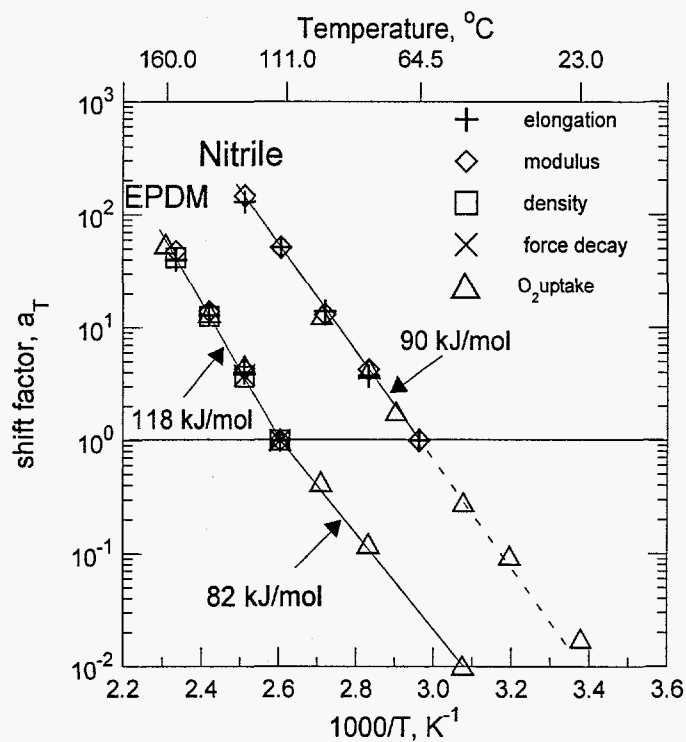
**Figure 4.** Arrhenius plot of the empirical values of  $a_T$  used to achieve the superposition shown in Fig. 3.

To confirm this correlation for the nitrile material, the oxygen consumption rate measurements (Fig. 5) are made at temperatures overlapping the temperatures used for the mechanical property experiments (96°C, 80°C and 72°C) as well as at lower temperatures in the extrapolation region (52°C, 40°C and 23°C). The oxygen consumption results of Fig. 5 were integrated and then time-temperature superposed at 64.5°C so that the shift factors could be directly compared with the mechanical property shift factors given earlier in Fig. 4. The resulting oxygen consumption shift factors are plotted as the triangles shown for the nitrile data on Fig. 6. The results show that the higher temperature oxygen consumption results are consistent with the mechanical property shift values, offering evidence that the two properties are dependent upon the same underlying chemistry. Since the oxygen consumption shift factors at the three lower temperatures are reasonably consistent with an unchanged Arrhenius slope (dashed line) in the extrapolation region, these results offer increased confidence in the validity of the extrapolation.

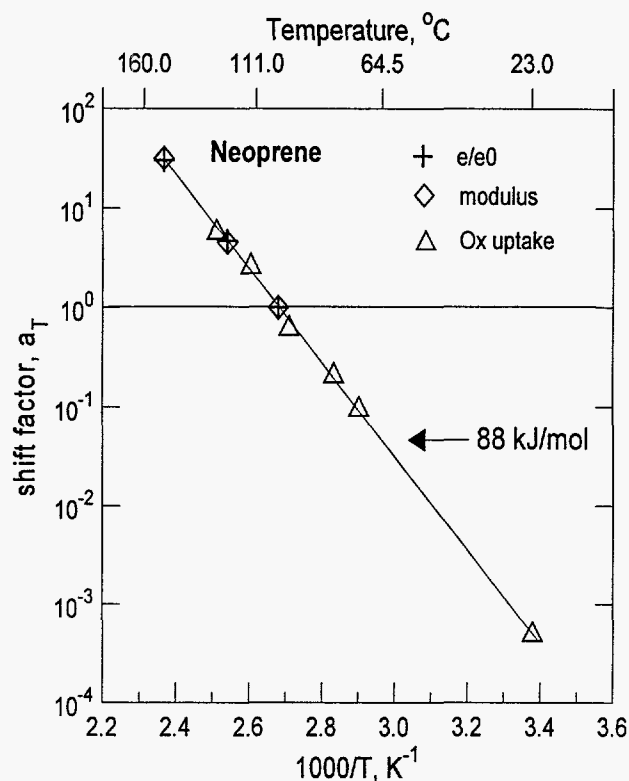
Similar oxygen consumption measurements spanning the temperature region where conventional measurements were made and continuing into the lower temperature "extrapolation regions" were made for the EPDM material (left set of triangles in Fig. 6) and for a neoprene material (triangles in Fig. 7). For the neoprene material, the results indicate that the Arrhenius behavior determined at high temperatures can be extrapolated with confidence all the way down to room temperature. For the EPDM material, the



**Figure 5.** Oxygen consumption rates for the nitrile rubber as a function of time at the indicated temperatures.



**Figure 6.** Arrhenius plot of the empirical values of  $a_T$  for the indicated conventional parameters and for oxygen consumption measurements (triangles) for the EPDM and the nitrile materials. The results are normalized ( $a_T = 1$ ) to a reference temperature of 64.5°C for nitrile and a reference temperature of 111°C for EPDM.



**Figure 7.** Arrhenius plot of the empirical values of  $a_T$  for the indicated conventional parameters and for oxygen consumption measurements (triangles) for a neoprene material.

oxygen consumption measurements at  $111^{\circ}C$  and above give shift factors consistent with the conventional results ( $E_a \sim 118$  kJ/mol), but a change in mechanism leads to an activation energy reduction to  $\sim 82$  kJ/mol below  $111^{\circ}C$ . Therefore, the straight-line extrapolation used in Fig. 1 is not warranted and the predicted EPDM lifetime is significantly reduced.

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#### REFERENCES

1. K. T. Gillen, M. Celina, R. L. Clough and J. Wise, Trends in Polymer Science, Vol 5, No. 8, 250 (August, 1997).
2. J. Wise, K. T. Gillen and R. L. Clough, Polym. Degrad. & Stabil., 49, 403 (1995).
3. J. L. Bolland, Proc. R. Soc. London, A186, 218 (1946).
4. L. Bateman, Q. Rev. (London), 8, 147 (1954).

5. R. L. Clough and K. T. Gillen, *Polym. Degrad. Stabil.*, 38, 47 (1992).
6. J. Wise, K. T. Gillen and R. L. Clough, *Polymer*, 38, 1929 (1997).
7. B. Mattson, B. Stenberg, K. T. Gillen, R. L. Clough and E. Ostman, *Polym. Degrad. Stabil.*, 41, 211 (1993).
8. 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", SAND98-1942 (September, 1998).
9. K. T. Gillen, R. L. Clough, M. Celina, J. Wise and G. M. Malone, Proceedings of the 23<sup>rd</sup> Water Reactor Safety Information Meeting, NUREG/CP-0149, Vol. 3, p. 133 (1995).
10. N. C. Billingham in Atmospheric Oxidation and Antioxidants, Vol. II, G. Scott, Ed., Elsevier, p. 219 (1993).
11. N. C. Billingham in Oxidation Inhibition in Organic Materials, Vol. II, J. Pospisil and P. P. Klemchuk, Eds., CRC Press, p. 249 (1990).
12. J. D. Ferry, Viscoelastic Properties of Polymers, 2nd Ed., Wiley, New York, 1970.