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A TEST OF THE ARRHENIUS EXTRAPOLATION ASSUMPTION FOR A NITRILE RUBBER*

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The Arrhenius relationship predicts a linear relationship between the log of the time to a certain amount of material property change and the inverse absolute temperature, with the Arrhenius activation energy E_a defined from the slope of this line. Data are typically analyzed over a range of elevated temperature exposures to determine if this linearity occurs. When it does, long-term predictions can be attempted by assuming that the linearity continues beyond the temperature range of the data, i.e., by extrapolating the Arrhenius behavior to lower temperatures. In recent years, we have been critically examining the Arrhenius approach to better understand its capabilities and limitations[1-3]. The current paper attempts to address the validity of this important extrapolation assumption.

For a nitrile rubber material, we have shown that Arrhenius behavior can be observed for tensile elongation results, even in the presence of complex diffusion-limited oxidation anomalies[2,3]. Figure 1 shows the normalized elongation results versus air-oven aging temperature for this material. To test for Arrhenius behavior, we select several levels of degradation (e/e_0 equal to 0.75, 0.5 and 0.25 in the present case) and plot at each level the relationship between log time and inverse absolute temperature. Figure 2 shows that the results are linear (E_a = 22 kcal/mol from the slope) and independent of degradation level, indicating Arrhenius behavior. This implies that the data of Fig. 1 should superpose when shifted to a common reference temperature using the Arrhenius functionality. Figure 3 shows the superposed results at 23°C, where long lifetimes (hundreds of years) are predicted.

Critical to such predictions at low temperatures is the assumption that E_a remains constant in the extrapolation region (see Fig. 2). The reliance on extrapolations can be reduced, and confidence in predicted lifetimes increased, however, by measuring degradation at temperatures in the extrapolation region or, preferably, at the service temperature. Achieving this goal requires ultra sensitive techniques that measure processes directly related to the reactions responsible for macroscopic degradation. Oxygen consumption measurements fit these requirements, since they can be very sensitive and oxidation reactions were found to dominate the deterioration of mechanical properties for this nitrile material[2,3]. Measurements were made at six temperatures ranging from ambient to 95°C, with three temperatures in the extrapolation region and three temperatures in the range used for the tensile data; the results are shown in Fig. 4. Using the 23°C data as a reference, the other results were horizontally shifted by a constant shift factor a_T appropriate to each temperature to empirically obtain the best overall superposition of the data. Figure 5 shows the resulting superposed data; the empirically derived values of a_T are plotted versus inverse temperature in Fig. 6. From 95°C to 52°C, the E_a for oxygen consumption is identical to the E_a appropriate to the elongation (Fig. 2), offering further evidence that the oxidation processes are responsible for the degradation in macroscopic tensile properties. Below 52°C, however, the E_a for oxygen consumption appears to drop slightly to around 18 kcal/mol, implying that the Arrhenius extrapolation assumption probably overestimates the tensile property lifetime by a factor of approximately two at 23°C. These results demonstrate the feasibility of measuring degradation rates at temperatures approaching ambient. Further, the change in E_a observed for the nitrile rubber, while not necessarily universal, highlights the value of measuring degradation at or near service temperatures.

[1]R. L. Clough and K. T. Gillen, Polym. Degrad. & Stabil., **38**, 47 (1992).
[2]K. T. Gillen, R. L. Clough and J. Wise, Polymer Preprints, **34, No. 2**, 185 (Aug., 1993).
[3]K. T. Gillen and R. L. Clough, Proceedings of the 18th DOE Conference on Compatibility, Aging and Service Life, Savannah River, April, 1993.

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Fig. 1. Nitrile rubber elongation divided by its unaged value (e/e_0) versus aging time in air at the indicated temperatures.

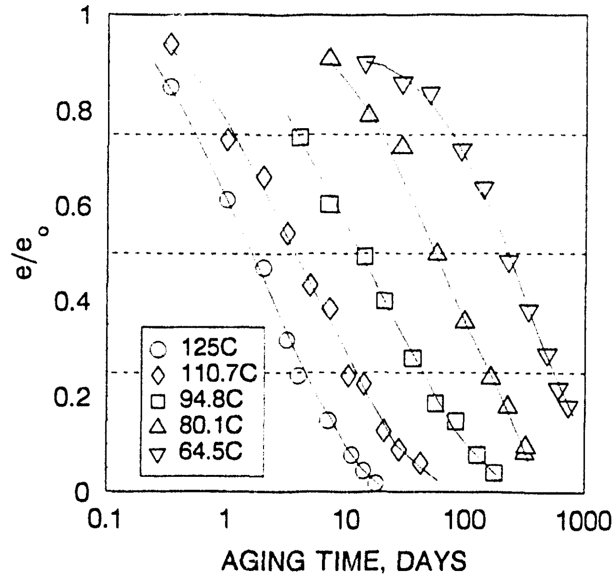


Fig. 2. Arrhenius plot of elongation results for the nitrile rubber.

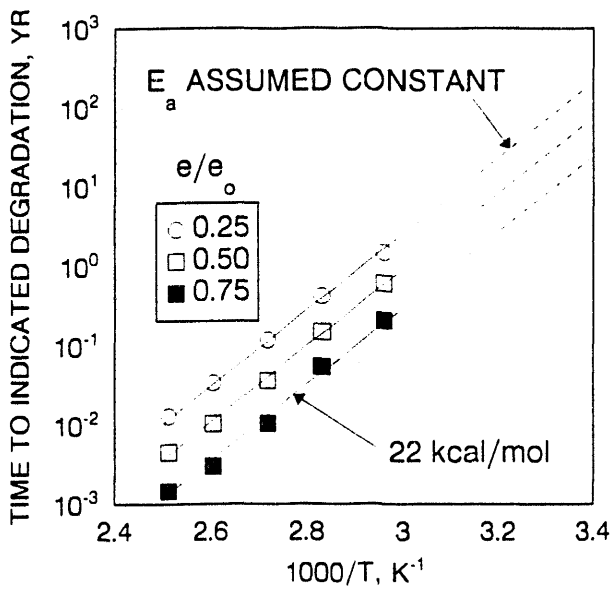
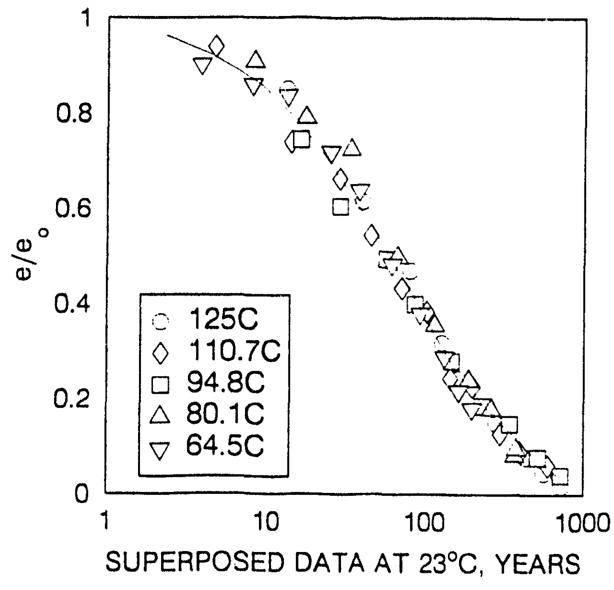


Fig. 3. Time-temperature superposition of the e/e_0 data from Fig. 1 at a reference temperature of 23°C using E_a = 22 kcal/mol.



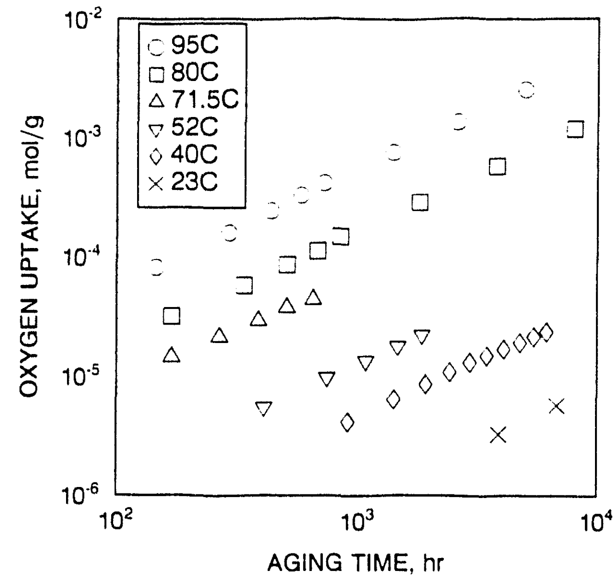


Fig. 4. Oxygen consumption results for the nitrile rubber versus aging time at the indicated temperatures.

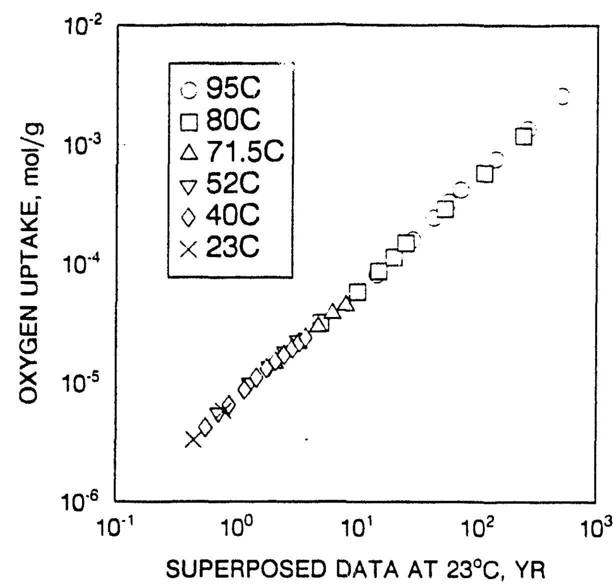


Fig. 5. Empirical time-temperature superposition of the oxygen consumption results from Fig. 4 at a reference temperature of 23°C.

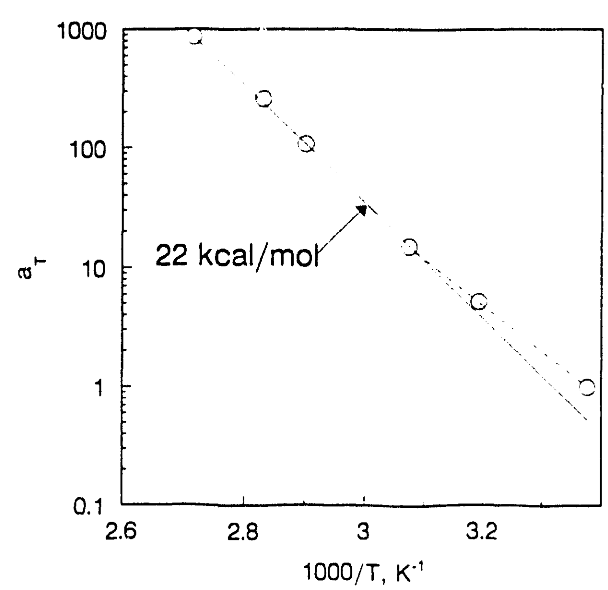


Fig. 6. Arrhenius plot of the empirical shift factors a_T used to obtain the superposed oxygen consumption results of Fig. 5.

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