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LIFETIME PREDICTIONS FOR ELASTOMERS FROM ACCELERATED AGING EXPERIMENTS

K. T. Gillen and R. L. Clough*

Organic Materials Department
Sandia National Laboratories
Albuquerque, NM 87185-1411, USA

Introduction

Prediction of polymer lifetimes is an important challenge for the polymer industry, particularly for materials expected to perform reliably for extended time periods (e.g., decades). It is also critically important for comparing new material formulations during their development. This paper briefly reviews some of the state-of-the-art lifetime prediction methods available for commercially formulated elastomers exposed to oxygen, humidity and/or high-energy radiation environments. Important complications and pitfalls associated with such methods are highlighted.

Discussion

Simplistic Arrhenius Approach. Historically, the vast majority of accelerated aging studies have utilized the so-called Arrhenius methodology. In the simplest instance, this approach assumes that a chemical reaction is responsible for the degradation and uses classical chemical rate theory to predict that the reaction rate ~ $\exp(-E_a/RT)$, where E_a is the activation energy of the reaction, R is the gas constant and T is the absolute temperature. Plots of the log of the rate constant (or the failure time for a degradation variable) versus inverse T are predicted to give linear behavior. If confirmed, the linear behavior is then extrapolated to the use T to predict use lifetime. Figure 1 shows induction (failure) time data analyzed in this fashion for three degradation parameters of an EPDM material. Arrhenius behavior is confirmed for the induction time data and the linearity is extrapolated to 25°C, leading to a predicted lifetime of 55,000 years.

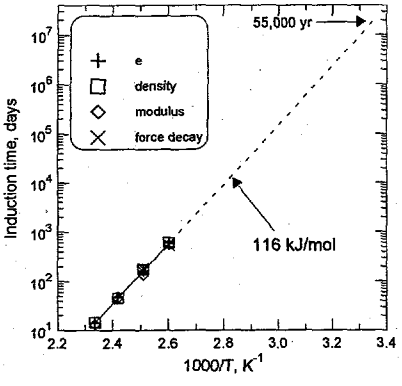

Figure 1. Arrhenius plot and extrapolation of EPDM induction times.

Although long life is predicted from the extrapolation, the large extrapolation distance gives little confidence in the result. In fact, there are numerous phenomena that can lead to non-Arrhenius behavior. Several of these will be discussed briefly below, including the presence of more realistic reaction kinetics that can lead to or predict non-Arrhenius behavior[1] and physical subtleties involving the sorbed concentration of reactant gas (heat of solution effects for hydrolysis[2], diffusion effects for oxidation[3,4]). Many other phenomena that can lead to non-Arrhenius behavior will not be covered. These include changes that often occur when the data region or extrapolation range encompasses a polymer transition (T_g or T_{mp}) and antioxidant complications caused by solubility changes with T and evaporation effects.[5,6]

Solubility Effects. For aging in air, if $[O_2]$, the concentration of dissolved O_2, affects the oxidation rate, changing T usually leads to a change in $[O_2]$. Because Henry's Law, which predicts a linear relationship between $[O_2]$ and gas phase O_2 partial pressure holds at each T, Arrhenius behavior is not impacted (the measured activation energy will equal the true E_a plus the O_2 heat of solution). A more complicated situation occurs when hydrolysis dominates the degradation of a material since Henry's Law behavior is often inappropriate. By understanding how water vapor sorption curves depend on temperature, Arrhenius behavior can be recovered as long as data are taken and analyzed at constant relative humidity (Fig. 2).[2]

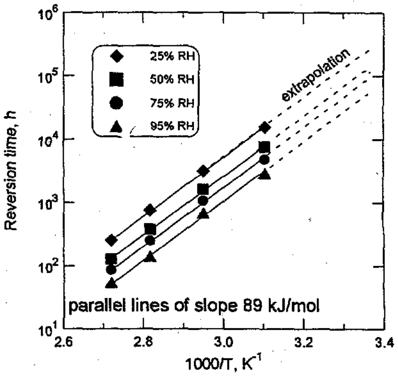

Figure 2. Arrhenius plot at constant RH of reversion times for a polyurethane.

Realistic Oxidation Scheme for Stabilized Polymers. When oxygen is present during degradation of polymers, oxidation effects normally dominate degradation. Typical kinetic oxidation schemes are based on variants of the so-called basic auto-oxidation scheme (BAS) derived many decades ago by Bolland[7], Bateman[8] and co-workers. Analysis of this scheme[1] for stabilized polymers leads to the following expression for the oxidation rate

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

C_1 and C_2 are constants involving the rate constants of the individual reactions in the kinetic scheme and $[O_2]$ is the dissolved O_2 concentration. This implies that the oxidation rate will generally depend upon the concentration of dissolved O_2. At low $[O_2]$, the rate will be proportional to $[O_2]$; at the other limit of high $[O_2]$, the rate will be independent of $[O_2]$. It is easy to show that rigorously-Arrhenius behavior only occurs at the low $[O_2]$ limit.[1]

Time-temperature Superposition. Equation (1) implies a constant oxidation rate at each aging T; this is consistent with experimental observations on many stabilized elastomers.[9] Since this implies a constant acceleration of the degradation when T increases, the time-dependent degradation curves at two temperatures should be related by a constant multiplicative shift factor defined as a_T. This leads to a concept called time-temperature superposition,[9,10] where all of the data (as opposed to a typical analysis which uses one processed data point per curve- see Fig.1) at the experimental Ts are superposed to a reference T with empirically chosen shift factors. Figure 3 shows superposed results for elongation data of a nitrile rubber at a reference T of 64.5°C (the empirically derived a_T values are noted on the figure). When the empirical a_T values are plotted on an Arrhenius plot (Fig. 4, squares), the observed linearity confirms Arrhenius behavior.

Diffusion-Limited Oxidation (DLO) Effects. We saw above that the oxidation rate can depend and, in fact, does depend[1,9] on the dissolved O_2 concentration for stabilized elastomers. This implies that DLO effects can occur whenever the rate of oxidation in the material exceeds the rate at which the dissolved O_2 can be replenished by diffusion from the surrounding air atmosphere.[3,4,9] It turns out that such DLO effects are commonly observed for accelerated aging of elastomers.[1,4,9] These effects can be monitored experimentally by several methods,[11] including modulus profiling.[12] Modulus profiling results[9] showing important DLO effects are plotted in Fig. 5 for the nitrile rubber material aged for selected times at 125°C. Such DLO effects can also be predicted quantitatively from modeling if estimates or measurements of the O_2 consumption rate and permeability coefficient are available.[4,13] It may at first seem surprising that the nitrile material gives excellent t-T superposition (Fig. 3) and Arrhenius behavior (squares in Fig. 4) given the importance of DLO effects (Fig. 5). This turns out to be fortuitous for this and many other oven-aged elastomers since the elongation is usually dominated by surface hardening, which is unaffected by DLO.[1,9]

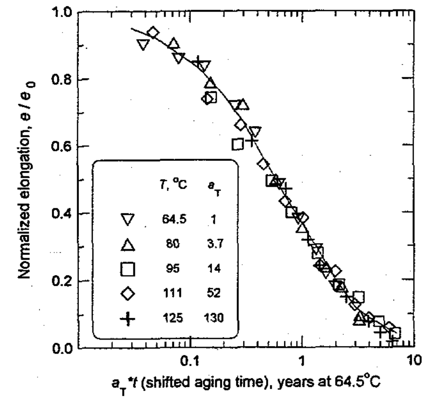

Figure 3. Time-temperature superposed elongation results for a nitrile rubber.

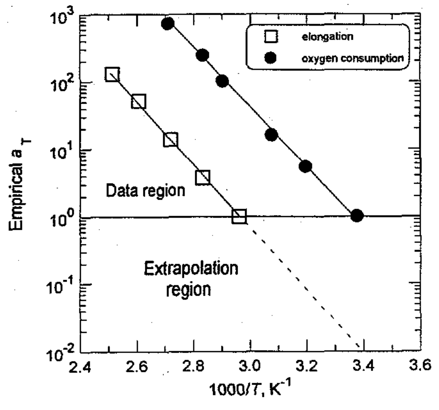

Figure 4. Arrhenius plots of nitrile rubber shift factors for elongation and oxygen consumption.

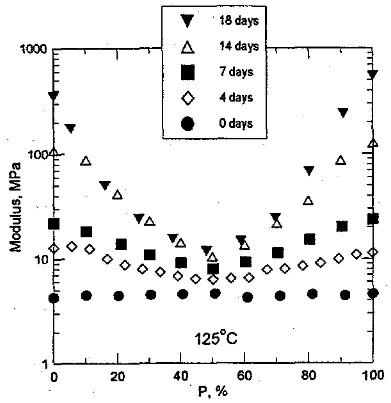

Figure 5. Modulus profiles for nitrile rubber versus aging time at 125°C.

Ultrasensitive O_2 Consumption to Test Extrapolation Assumption. A final problem with the Arrhenius approach is the unconfirmed extrapolation of high *T* accelerated results to much lower *T*s (Figs. 1 and 4). To minimize the extrapolation, long-term accelerated data should be obtained, as was done (up to ~2 year exposures) for the EPDM (Fig. 1) and the nitrile (Fig. 3) materials. Clearly, an ultrasensitive analytical technique related to the degradation mechanism is needed to access *T*s in the extrapolation regions. One approach that has been successful is O_2 consumption measurements that typically allow data to be taken at *T*s 40 to 60°C lower than the lower *T* limit of conventional measurements.[1,9] Such measurements were made from 96°C down to 23°C for the nitrile material.[9] After *t-T* superposition of the results, shift factors for O_2 consumption were derived. When plotted on Fig. 4 (solid circles), it is clear that the oxidation mechanism has the same E_a down to room temperature, confirming the extrapolation of mechanical properties. Similar experiments on the EPDM material showed that the E_a dropped substantially in the extrapolation region, leading to a significant reduction in the predicted room temperature lifetime.[1]

Combined Radiation and Temperature Environments. Predicting lifetimes can get even more complex when an additional environmental stress enters in addition to *T* and gaseous reactant (e.g., O_2 or H_2O). For example, for materials aging in nuclear power plants, high-energy radiation can become significant in addition to *T* and O_2. Even though such situations would seem to be intractable, it is often possible to derive sufficient knowledge of the underlying chemistry[14] such that quantitative models for multi-stress environments can be derived and confirmed.[15] This work allowed us to explain degradation rates that were observed to occur 10 to 100 times faster than expected.

Conclusions

Regardless of the stress environments acting on polymers, it should be clear that *t-T* superposition is the analysis method of choice when attempting to understand and extrapolate the *T* dependence of degradation. It is also critically important to monitor/understand DLO effects, minimize extrapolation distances and use ultrasensitive analytical techniques to probe the extrapolation region. Although a great deal has been learned about better methods for predicting polymer lifetimes, much more research needs to be accomplished in this important area. More work focussing on understanding the complex chemical pathways underlying degradation will aid in developing better extrapolation approaches. Additional ultrasensitive methods for following degradation at low temperatures will allow more confident extrapolations.

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