LIFETIME PREDICTIONS FOR ELASTOMERS FROM ACCELERATED AGING EXPERIMENTS

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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 \( \text{exp}(-E_r/kT) \) where \( E_r \) is the activation energy of the reaction, \( k \) 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.

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 and physical subtleties involving the sorbed concentration of reactant gas (heat of solution effects for hydrolysis, diffusion effects for oxidation). 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 \( T_m \)) and antioxidant complications caused by solubility changes with \( T \) and evaporation effects.

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 \( E_r \) 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).

![Figure 2. Arrhenius plot at constant RH of reversion times for a polyurethane.](image)

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

Integrated oxidation rate analysis. Underlying such superposition principles have been derived and used mainly for fatigue life and the establishment of failure criteria. Assuming a reasonable correlation between a constant extent of oxidation (i.e. 20% for the damage required to result in a given failure criterion (i.e. 20%) and the damage parameter versus fractional degradation lifetime, regardless of the type of damage parameter, the integrated oxidation rate analysis can be considered a model for predicting residual lifetimes of polymeric materials. Time-temperature superposition, which allows us to evaluate kinetic "interaction effects" and establish failure criteria, is expected to show good agreement with the model. The model is expected to show good agreement with the model and the model is expected to show good agreement with the model.
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.19

![Graph 1](image1.png)

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

![Graph 2](image2.png)

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

![Graph 3](image3.png)

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

**Ultrasonic Oxygen Consumption to Test Extrapolation Assumption.** A final problem with the Arrhenius approach is the unconfirmed extrapolation of high T accelerated results to much lower Ts (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 Ts in the extrapolation regions. One approach that has been successful is O2 consumption measurements that typically allow data to be taken at Ts 40 to 60°C lower than the lower T limit of conventional measurements.16 Such measurements were made from 98°C down to 23°C for the nitrile material.17 After r-T superposition of the results, shift factors for O2 consumption were derived. When plotted on Fig. 4 (solid circles), it is clear that the oxidation mechanism has the same Ea down to room temperature, confirming the extrapolation of mechanical properties. Similar experiments on the EPDM material showed that the Ea dropped substantially in the extrapolation region, leading to a significant reduction in the predicted room temperature lifetime.18

**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., O2 or H2O). For example, for materials aging in nuclear power plants, high-energy radiation can become significant in addition to T and O2. Even though such situations would seem to be intractable, it is often possible to derive sufficient knowledge of the underlying chemistry14 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 focusing 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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**References**


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