METHODS FOR PREDICTING MORE CONFIDENT LIFETIMES OF SEALS IN AIR ENVIRONMENTS

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ABSTRACT

We have been working for many years to develop improved methods for predicting the lifetimes of polymers exposed to air environments and have recently turned our attention to seal materials. This paper describes an extensive study on a butyl material using elevated temperature compression stress-relaxation (CSR) techniques in combination with conventional oven aging exposures. The results initially indicated important synergistic effects when mechanical strain is combined with oven aging, as well as complex, non-Arrhenius behavior of the CSR results. By combining modeling and experiments, we show that diffusion-limited oxidation (DLO) anomalies dominate traditional CSR experiments. A new CSR approach allows us to eliminate DLO effects and recover Arrhenius behavior. Furthermore, the resulting CSR activation energy (E_a) from 125°C to 70°C is identical to the activation energies for the tensile elongation and for the oxygen consumption rate of unstrained material over similar temperature ranges. This strongly suggests that the same underlying oxidation reactions determine both the unstrained and strained degradation rates. We therefore utilize our ultrasensitive oxygen consumption rate approach down to 23°C to show that the CSR E_a likely remains unchanged when extrapolated below 70°C, allowing very confident room temperature lifetime predictions for the butyl seal.

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INTRODUCTION

A continuing major objective for the polymer industry is better predictions of polymer lifetimes. It is especially important to have reliable predictive methods for materials expected to perform for extended time periods (e.g., many years to decades). These methods are also useful for guiding the development of new or modified formulations. The most common approach for modeling chemical degradation effects is the so-called Arrhenius methodology which assumes that a chemical process governed by a rate proportional to $\exp(-E_a/RT)$ underlies the degradation (E_a is the Arrhenius activation energy, R the gas constant and T the absolute temperature). A degradation parameter is followed at several elevated (accelerated) temperatures and its dependence on temperature is tested with the Arrhenius functionality. If Arrhenius behavior is confirmed over the accelerated temperature range, the next step is to extrapolate this behavior to make predictions under lower-temperature, experimentally inaccessible conditions. For commercially formulated polymers, many potential problems can lead to non-Arrhenius behavior [1]. Some of these are dependent on physical effects such as 1) changes in chemistry caused by taking data or extrapolating across a polymer transition [2], 2) diffusion-limited oxidation [3-5] and 3) complex antioxidant behavior involving its redistribution by internal diffusion and evaporation/blooming at the sample surface [6-7]. Others are chemically based and result in changes in the effective activation energy brought about by such things as a switch in the dominant mechanism as the temperature is changed or a slow temperature-dependent change due to the complex form of the effective activation energy [1]. Careful studies are necessary to determine whether Arrhenius behavior holds over the normal accelerated data collection region. Although extrapolation of accelerated Arrhenius behavior has historically been an act-of-faith, we have recently outlined how ultrasensitive oxygen consumption methods can be used to gain more confidence in such extrapolations [1,8].

For the current study, we are interested in developing better methods for predicting lifetimes of seal materials in oxygen-containing environments. For seal materials, the property of paramount interest is the sealing force, and the experimental approach most closely related to this property involves compression stress-relaxation (CSR) measurements [9-11]. Stress-relaxation in general results from a combination of so-called physical relaxation processes and chemical effects [12-14]. The physical relaxation (unrelated to the physical effects mentioned above) involves aspects like the movement of chains and entanglements. For elastomers in the absence of chemical changes, physical relaxation is a reversible process. The chemical processes, however, are irreversible, mainly involving scission and crosslinking phenomena. Our first goal was to determine whether the chemical processes underlying accelerated CSR measurements could be successfully modeled with the Arrhenius approach. If so, our next objective was to see whether our ultrasensitive oxygen consumption approach could be utilized to gain more confidence in extrapolating the accelerated data to much lower temperatures.

EXPERIMENTAL

Material

Compression molded sheets of a commercial, peroxide-cured butyl rubber were obtained from Parker Seal Company (Parker compound B612-70) in three thicknesses (~0.7 mm, ~1 mm and ~2 mm). The thinnest material was used for the elongation, modulus, density, solvent uptake/gel and oxygen consumption experiments in order to minimize the chances of diffusion-limited oxidation effects. Since ~6-mm thick cylindrical samples were needed for standard compression stress relaxation experiments, either three 12.7-mm diameter disk-shaped samples were cut from the 2-mm thick compression-molded sheets and stacked on top of one another or six 1-mm disks were stacked on top of one another. For the non-standard CSR experiments involving 2-mm diameter disks, sample were cut from the 1-mm thick material in order to keep the ratio of sample diameter to sample thickness approximately the same as in the standard CSR configuration. Similarly, for the non-standard CSR experiments involving 6-mm diameter disks, three sample cut from the 1-mm thick material were stacked together yielding a sample of ~6-mm diameter by 3-mm thickness.

Oven aging

Oven aging was carried out in air-circulating ovens ($\pm 1^\circ\text{C}$) equipped with thermocouples connected to continuous strip chart recorders.

Tensile tests

Tensile samples (~150 mm long by 6 mm wide) were cut from the ~0.7-mm thick compression molded sheets before aging. Tensile testing (5.1 cm initial jaw separation, 12.7 cm/min strain rate) was performed on an Instron 1000 tensile testing machine equipped with pneumatic grips; an extensometer clamped on the sample allowed ultimate tensile elongation values to be obtained.

Density measurements

Density measurements were made using the Archimedes approach [15-16], where the sample (typically 50 mg) is weighed in air and then in iso-propanol on a balance with a reproducibility of better than 10 micrograms.

Solvent uptake/gel measurements

Solvent uptake measurements were carried out by first exposing a known weight of sample (w_0) to refluxing p-xylene for a minimum of 24 hours. The sample was quickly recovered from the hot solvent and the weight of the swollen rubber (w_s) determined. The final weight w_f was determined after drying the swollen sample under vacuum. The solvent uptake factor is defined as the ratio of w_s to w_f . The percent gel is given by the ratio of w_f to w_0 .

Modulus profiles

Modulus profiles with a resolution of $\sim 50 \mu\text{m}$ were obtained on sample cross-sections using a computer-controlled, automated version of our modulus profiling apparatus, which has been described in detail previously [17]. This instrument measures inverse tensile compliance, which is closely related to the tensile modulus.

Compression stress-relaxation (CSR) measurements

Compression stress relaxation (CSR) measurements were made using a Shawbury-Wallace Compression Stress Relaxometer MK II. This instrument uses special Shawbury-Wallace jigs (CSR jigs) to compress the cylindrical samples between adjustable metal platens. The preparation of the standard 12.7-mm diameter disks was described above. To make the non-standard 2-mm diameter disks, a stainless steel circular die with very thin cutting surfaces was specially prepared. Since the area of a single 2-mm disk leads to a very small force when compressed, obtaining reasonable CSR force values requires the use of multiple mini-disks strained in parallel (the current series of experiments uses 50). To ensure that the 50 mini-disks for a given experiment had similar unstrained thicknesses, they were all cut from a small area of a sheet ($\sim 2 \text{ cm}$ by 2 cm), chosen such that little thickness variation occurred in the region used for cutting. To obtain mini-samples, whose sides were perpendicular to their base, it was found necessary to ensure that the 2-mm cutter was kept precisely perpendicular to the sheet during the cutting operation. This was accomplished by holding the square top of the 2-mm cutter securely against a press, which pushes perpendicular to the sample sheet. For the non-standard CSR experiments involving 6-mm diameter disks, three samples cut from the 1-mm thick material were stacked together yielding a sample of $\sim 6\text{-mm}$ diameter by 3-mm thickness. Four of these stacks were strained in parallel in order to increase the force being monitored.

The CSR jigs were used to first strain the cylindrical samples by 25% at room temperature. After watching the force decay for approximately 1 week at room temperature (physical relaxation), the jigs were placed in elevated temperature ovens. Periodically, the jigs were removed from the aging oven and allowed to equilibrate at room temperature, after which a sealing force measurement was made. The jigs were then returned to the oven for further aging. For the experiment conducted under nitrogen conditions, the samples were conditioned, then compressed in the jig and finally placed inside a sealed aging can all under inert atmosphere in a glove box. The nitrogen-filled aging can containing the jig was aged in a 125°C oven. Periodically, the aging can was removed from the oven and cooled to room temperature. As quickly as possible, the aging can was opened, the CSR jig removed, a force measurement obtained, immediately after which all components were quickly returned to the glove box. After waiting approximately one week to eliminate most of the oxygen that might have gotten into the sample during its short exposure to air during the force measurement, the jig was reassembled in the inert aging can for further elevated temperature exposure in the oven. This procedure was repeated several times to obtain inert force measurements versus time.

Compression set measurements

After the completion of the standard CSR experiments, the jigs were opened and the cylindrical samples removed to determine how much of their original height was recovered after aging. To speed up the physical relaxation process, the samples were placed in a 125°C oven for short times (on the order of 1 day) until the recovery appeared to stabilize. With h_0 , h_s and h_r representing the original unstrained sample height (disk thickness), the strained height and the recovery height, respectively, the percentage compression set was obtained as $100(h_0 - h_r)/(h_0 - h_s)$.

Oxygen permeation measurements

Oxygen permeation measurements were performed on an Oxtran-100 coulometric permeation apparatus (Modern Controls, Inc., Minneapolis, MN, USA), which is based on an ASTM Standard [18]. Several modifications, the most important of which was placing the sample holder in the oven, have been made to this instrument to permit data acquisition at higher temperatures (95°C for the present studies) with minimal temperature gradients (less than $\pm 0.5^\circ\text{C}$) across the sample during the experiment.

Oxygen consumption measurements

Oxygen consumption rates were measured using a technique that has been described in detail elsewhere [8]. This technique monitors the change in oxygen content caused by reaction with polymer in sealed containers using gas chromatographic detection.

RESULTS AND DISCUSSION

Conventional CSR measurements

For the compression stress-relaxation experiments at a given temperature, time-dependent values of Young's modulus $E(t)$ were obtained from rubber elasticity results as [19]

$$E(t) = \frac{3F(t)}{A\left(\lambda - \frac{1}{\lambda^2}\right)} \quad (1)$$

where $F(t)$ is the force versus time measured at room temperature, A is the unstrained area of the disk sample and λ is the stretch ratio (1.25 for the current experiments). For the standard CSR experiments (disks of 12.7-mm initial diameter), conservation of volume during a 25% compression implies that the disks have diameters of approximately 14.7 mm during aging. Since 14.7 mm is the effective diameter of the disk during aging, this diameter will be used for the remainder of the paper.

Representative CSR results at 110°C and 125°C are plotted in Fig. 1. The decays in modulus typically result from a combination of physical and chemical relaxation effects [20-23]. The earliest experimental times monitored in the CSR experiments are after 1

day at temperature. Using short-term, elevated-temperature shear relaxation data under nitrogen, we showed in an earlier conference paper that physical relaxation after 1 day is so small relative to the chemical relaxation that it can be ignored in the analyses [24]. We therefore extrapolate the chemically dominated CSR data the short distance back to time zero (see Fig. 1 for example) and use this procedure to normalize all of our CSR results.

Figure 2 compares normalized CSR results at 125°C for experiments conducted under air and under nitrogen. It is immediately clear from this comparison that oxidation will dominate the force decay when oxygen is available for reaction. Also plotted on this figure are ultimate tensile elongation results for tensile samples aged in a 125°C air-circulating oven. Since the force-decay for the CSR sample aged in air occurs approximately three times faster than the unstrained mechanical property samples, an important synergism occurs when mechanical strain is combined with air-oven aging.

Figure 3 plots normalized CSR results for standard disk samples (14.7-mm diameter) at four temperatures ranging from 125°C down to 80°C. Since we use the 1-mm thick sheets for other CSR experiments below, we wanted to make sure that experiments using these sheets gave similar aging behavior to those using 2-mm thick sheets. We therefore ran some of our 14.7-mm diameter standard CSR experiments on 6-mm (nominal initial thickness) sandwich samples made from stacking together three 2-mm disks and others made from stacking together six 1-mm disks. Experiments run under the two configurations gave consistent results.

The results shown in Fig. 3 indicate that approximately one year is required to observe significant degradation at 80°C, implying that accelerated aging below this temperature would typically be unrealistic. When long-term predictions are required at lower temperatures, the accelerated data need to be analyzed and somehow extrapolated to these temperatures. The most common approach involves the use of the Arrhenius equation which assumes that a chemical process governed by a rate proportional to $\exp(-E_a/RT)$ underlies the degradation (E_a is the Arrhenius activation energy, R the gas constant and T the absolute temperature). The normal procedure is to first select some level of degradation and then plot the log of the times required at each temperature to reach this amount of degradation versus the inverse absolute aging temperature. The plot should be linear if Arrhenius behavior holds. For instance, we can choose 75% loss of force as the failure criterion for the CSR data of Fig. 3 (dashed line) and find the times associated with this amount of degradation versus the aging temperature. These results are plotted as squares on an Arrhenius plot in Fig. 4. It is immediately apparent that non-linear (non-Arrhenius) behavior occurs, making it impossible to attempt any extrapolation of the results to lower temperatures. In addition, the results on the figure imply that the effective activation energies obtained from the instantaneous slopes of the curve through the data range from ~56 kJ/mol at the lowest temperature to ~38 kJ/mol at the highest temperature. These are much lower than the normally expected activation energy range for oxidation processes (~80 to 120 kJ/mol).

The low observed activation energies and the reduction in activation energy as the temperature increases suggests the presence of important diffusion-limited oxidation (DLO) effects. These effects can enter whenever the rate of oxidation in the material uses up dissolved oxygen faster than it can be replenished by diffusion from the surrounding air atmosphere. Since such effects become more important as the aging temperature increases [1,5] and any portion of the sample that is not oxidized will relax much slower (Fig. 2), the trend in the data is consistent with DLO effects. Another compelling piece of evidence for DLO effects comes from the compression set results taken on the samples after completion of the CSR measurements. While taking these measurements, we noticed that the samples aged at higher temperatures had non-uniform set values with substantially more set near the outside surface of the disk compared to the set at the center of the disk. If DLO is important, equilibrium oxidation will occur at the outside surface of the disk and reduced or non-existent oxidation will hold further into the disk. Any reductions in oxidation in interior regions will lead to reductions in degradation and therefore compression set. The results of the set measurements are summarized in Table I.

Table I. Average compression set values after aging on 14.7-mm CSR samples

Temperature, °C	Compression set- center of disk	Compression set- surface of disk
80	55%	55%
95	41%	57%
110	46%	79%
125	56%	90%

The data show that as the aging temperature increases, substantially more degradation occurs near the outer, air-exposed regions of the disk, clearly consistent with DLO effects. Since the amount of force decay at 80°C, 110°C and 125°C is comparable (Fig. 3), the results in Table I indicate how DLO effects can artificially slow down the apparent rate of oxidative degradation. The results also underscore an interesting danger in utilizing compression set measurements to monitor degradation, since these measurements typically probe the thickest part of the sample. When DLO effects are present, the thickest part (the central region) will be aging under oxygen-depleted or oxygen-starved conditions, implying that the measurements may have little relevance to oxidative degradation.

Modeling DLO effects involves the coupling of diffusion equations with kinetic expressions for the oxygen consumption rate [1,3-5,24]. A particularly useful and general kinetic rate expression is based on a variant of the basic autoxidation scheme (BAS), which has been utilized for more than 50 years [25,26] to describe the oxidation of organic materials. For stabilized materials, such as the present butyl elastomer, the simplified kinetics is given by Scheme 1 [1].

Scheme 1. Classical oxidation scheme.

Analysis of this scheme under steady state conditions for the two radical species and the ROOH concentration leads to the following expression for the oxygen consumption rate, ϕ :

$$\phi = \frac{d[\text{O}_2]}{dt} = \frac{C_1[\text{O}_2]}{1 + C_2[\text{O}_2]} \quad (2)$$

where

$$C_1 = \frac{k_1 k_2}{k_5} \quad (3)$$

$$C_2 = \frac{k_2(k_4 - 2k_3)}{k_5(k_3 + k_4)} \quad (4)$$

Equation (2), the expression for the oxygen consumption rate, has been combined with standard diffusion expressions [27] to model diffusion-limited oxidation (DLO) effects for samples with planar geometry [3]. The resulting theoretical expressions have been shown to give quantitative agreement with experimental results for both thermoxidative aging of nitrile and neoprene rubbers [5] and radiation-oxidative aging of EPDM [4] and viton [28] materials. For the current work, a solution analogous to that derived for planar geometry [3], but relevant to a cylindrical specimen, was necessary [24]. The CSR sample was modeled as a cylindrical disk having unit thickness and radius a . The axis-symmetric geometry used is shown in Fig. 5. For the modeling, the oxygen concentration is given by $[\text{O}_2]$ and the planar surfaces of the disk are taken to be impermeable. Using the diffusion-reaction equation appropriate to radial coordinates [27] together with

standard finite element methods, we obtained solutions for the integrated relative oxidation (IRO) versus two parameters α' and β , given by

$$\alpha' = \frac{C_1 a^2}{D} \quad (5)$$

$$\beta = C_2 S p = C_2 [O_2]_e \quad (6)$$

where p is the oxygen partial pressure surrounding the sample and S is the oxygen solubility coefficient for the polymer (the permeability coefficient, P_{O_2} is the product of D and S). The parameter α' is used here to distinguish the disk theory from the theory for sheet material of thickness L that utilizes the parameter α , given by [3]

$$\alpha = \frac{C_1 L^2}{D} \quad (7)$$

and the same parameter β , defined in Eq. (6). The following simple relationship exists between α' and β

$$\alpha' = \frac{(1 + \beta)\phi\alpha^2}{pP_{O_2}} \quad (8)$$

similar to the expression relating α and β for sheet material [3]

$$\alpha = \frac{(1 + \beta)\phi L^2}{pP_{O_2}} \quad (9)$$

It is clear from Eqs. (5) – (7) that β can be changed by changing the oxygen partial pressure surrounding the sample and that α and α' are geometry-sensitive parameters that can be changed by changing the sample thickness and diameter, respectively.

Figure 6 plots selected IRO (integrated relative oxidation) values (percentage of the sample oxidized versus a homogeneously oxidized sample) for disk geometry versus the parameters α' and β . As expected, the results show that DLO effects become more significant as α' increases (disk radius increases) and as β decreases (oxygen partial pressure surrounding the sample decreases).

We can now use the modeling to estimate the importance of DLO effects for the experiments conducted on the standard 14.7-mm diameter CSR disks if we can estimate values for ϕ , P_{O_2} and β versus aging temperature. Figure 7 summarizes time-dependent oxygen consumption rate measurements made on the currently studied butyl material at six temperatures ranging from 110°C to 25°C. At the higher temperatures, the rate slowly decreases with time. In order to obtain rough estimates of the ϕ values at the

temperatures of interest to the DLO estimates, we note that over the first 1000 h, ϕ at 110°C averages $\sim 9 \times 10^{-11}$. Since we will show below that the activation energy E_a for ϕ equals ~ 82 kJ/mol, we use this E_a together with the estimated ϕ at 110°C in order to estimate ϕ values at the other temperatures, with the results summarized in Table II.

Table II. Estimates of ϕ and P_{Ox} at the temperatures of interest.

$T, ^\circ\text{C}$	140	125	110	95	80	70
$\phi, \text{mol/g/s}$	5.8e-10	2.4e-10	9e-11	3.1e-11	1e-11	4.4e-12
$P_{Ox}, \text{ccSTP/cm/s/cmHg}$	7.0e-9	5.5e-9	3.75e-9	2.3e-9	1.25e-9	8.4e-10

The oxygen permeability coefficient P_{Ox} was measured at several temperatures ranging from 30°C to 95°C, with the data shown in Fig. 8. The P_{Ox} results tabulated for 70°C, 80°C and 95°C in Table II come from a smooth curve through these data; the table entries at 110°C through 140°C are based on a rough extrapolation of the results of Fig. 8 to higher temperatures, as indicated by the dashed curve in the figure.

Knowing ϕ , P_{Ox} , p (13.2 cmHg in Albuquerque) and the butyl density (1.152 g/cc), Eq. (8) can now be used to estimate values for α' if values of β can be estimated. The available evidence indicates that β values for thermoxidative aging of elastomers are typically close to unity [5] and that IRO values are relatively insensitive to values of β [4,5,24]. We therefore assume a β value of unity for the current calculations. Equation (8) now allows us to estimate values of α' versus disk diameter, which then leads to IRO estimates from the theory (see Fig. 6 for example). A summary of IRO results versus disk diameter at the temperatures of interest to the current CSR experiments are plotted in Fig. 9. These results show immediately the importance of DLO effects for the standard 14.7-mm diameter CSR disks. At 125°C, the integrated oxidation across the material is only about 30% of the oxidation that would occur for a homogeneously oxidized sample. As the temperature drops to 70°C, the oxidation grows progressively, but even at 70°C, represents only $\sim 70\%$ of fully oxidized. The estimated IRO values, which are plotted above the CSR data points on Fig. 4, confirm our earlier concerns about the likelihood that DLO effects cause the non-Arrhenius behavior and the low effective activation energies found for the 14.7-mm samples.

Parallel mini-disk CSR experiments

An easy method for eliminating anomalous DLO effects involves reducing the size of the CSR disk diameter. For instance, Fig. 9 indicates that a disk diameter of ~ 6 mm will give IRO values greater than $\sim 90\%$ at 70°C and 80°C, so we ran experiments with 6-mm diameter disks at these temperatures. Because the amount of force generated in the CSR jig from the compression of a 6-mm disk is approximately one quarter of the force generated by the standard 12.7-mm unstrained (14.7-mm strained) disk, we placed four of the 6-mm disks between the metal plates. We allowed sufficient spacing between the four disks so that they would not touch when strained in parallel. Above 80°C, even

smaller disks are needed to minimize DLO effects. At 125°C, Fig. 9 indicates that disks on the order of 2-mm diameter are required. Therefore, for experiments at 95°C, 110°C and 125°C, a special procedure was used to cut 2-mm disks from the 1-mm thick sheet (a single disk therefore has the same diameter to height ratio as the 12-mm and 6-mm samples). Again, because of the substantial loss in force that occurs when compressing such small disks, fifty of the 2-mm disks were strained in parallel for the three high temperature runs.

The results of these parallel, mini-disk experiments are shown in Fig. 10. As might be anticipated, the force decays are faster than the earlier results for the 14.7-mm diameter samples (Fig. 3). For comparison at 125°C, the 2-mm results are plotted as the dashed curve on Fig. 2 (the triangles represent the standard 14.7-mm CSR results). It is now evident from Fig. 2 that the magnitudes of the "synergistic" and "oxidation" effects are even larger than shown on the figure when DLO effects are eliminated from the CSR experiment.

Similar to the earlier "Arrhenius" analysis of Fig. 4, we determine the times required for the force values of Fig. 10 to decrease by 50% and 75% and plot the log of these times versus inverse absolute temperature on Fig. 11. Also shown on Fig. 11 are the results from Fig. 4. The first observation from Fig. 11 is that the mini-disk results for both 50% and 75% loss of force give linear behavior with identical slope, consistent with the Arrhenius assumption. In addition, the activation energy derived from the slope is ~80 kJ/mol, a reasonable value for oxidation. Comparing the 75% loss of force results for the 14.7-mm diameter samples and the mini-disk samples shows that DLO effects have a large effect at the highest temperature (125°C), but are becoming minor at 80°C. Since we estimated earlier that the IRO for the 80°C standard sample was ~62%, these results imply that DLO effects may become unimportant when the IRO is greater than ~70-80%, at least for the current butyl material.

It should be noted that the Arrhenius analyses used in Figs. 4 and 11 only used one or two processed data points from each time-dependent data set in Figs. 3 and 10, eliminating most of the experimental points from the analysis. Since the Arrhenius model assumes that an increase in temperature will increase the underlying degradation reactions by a constant multiplicative factor, a consequence of this assumption is that the degradation curves at two temperatures will be related by a constant multiplicative factor. This implies that when degradation curves are plotted versus log of the aging time, they should have the same shape; the results in Fig. 10 appear to be consistent with this idea. The concept can be quantitatively tested using the principal of time-temperature superposition [1,8,12]. To test this approach, the lowest temperature is usually selected as the reference temperature (70°C for the data of Fig. 10). Then, for each set of data at a higher temperature T , we multiply the experimental times at this temperature by a constant shift factor, a_T , chosen empirically to give the best overall superposition with the reference temperature data ($a_T = 1$ at the reference temperature). Figure 12 shows the results of using this procedure on the CSR results of Fig. 10, where the bottom x-axis gives the superposed results at the reference temperature of 70°C. The excellent superposition that occurs is not surprising, given the earlier observation that the raw experimental results at

the various temperatures had similar degradation shapes when plotted versus log of the aging times. The next step is to determine whether a simple model can be used to explain the relationship between the empirically determined shift factors and the temperature. For example, the Arrhenius model would predict that

$$a_T = \exp \frac{E_a}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \quad (10)$$

If Arrhenius is valid, a plot of the log of a_T versus the inverse absolute temperature should give linear behavior. Figure 13 shows that the CSR results for a_T are consistent with the Arrhenius assumption, with $E_a \sim 80$ kJ/mol, determined from the slope of the line through the results. To make predictions below the lowest experimental temperature of 70°C ($a_T = 1$), the normal procedure would then be to extrapolate the result (the dashed line extension). For instance, at around 25°C, the extrapolated a_T would be ~ 0.0145 , which would imply that this material would last ~ 69 times longer at this temperature compared to its lifetime at 70°C.

It is important to reiterate that, unlike the normal Arrhenius testing procedure that may use as few as one processed point from each curve, the time-temperature superposition procedure illustrated in Fig. 12 uses all of the raw data generated in the study. In addition, if time-temperature superposition is not found for a given set of data, the functional relationship between time and temperature must depend on the amount of degradation (non-constant acceleration). This situation makes modeling much more difficult and extrapolation of results extremely tenuous.

Ultrasensitive oxygen consumption measurements to test extrapolation

In the previous section, we found reasonable Arrhenius behavior for the parallel mini-disk CSR results and showed how shift factors can be used to extrapolate this behavior to temperatures lower than those used for the accelerated aging experiments. Unfortunately, such extrapolations can be quite dangerous since the effective activation energy for the degradation mechanism may change over the extrapolation region. As an example, there might be a second degradation mechanism, which is insignificant at higher temperatures, but becomes important at the lower temperatures. This would typically result in a drop in activation energy, resulting in lifetimes that are greatly reduced from the linear, Arrhenius predictions. Work done at Bell Laboratories many years ago [29] confirmed that significant drops in the effective degradation activation energies can occur at low temperatures for oxidation of stabilized polyolefin materials, causing low-temperature predictions, based on linear extrapolations of high temperature results, to be overly optimistic by orders of magnitude. For stabilized low-density polyethylene materials, typical activation energies of 120 kJ/mol and greater at higher temperatures were found to be reduced to around 80 kJ/mol at 80°C [29] and still further to ~ 60 kJ/mol at 45°C [30].

Because of such effects, and the importance of extrapolations to lifetime predictions, it is apparent that better extrapolation methods are required. One approach that we have recently developed [1,8] involves ultrasensitive oxygen consumption measurements. Clearly any method capable of monitoring degradation at low temperatures must be sensitive and must follow a property that can be shown to correlate with the degradation parameter of interest. When oxygen is present during polymer aging, oxidation reactions normally dominate the degradation. Therefore the oxygen consumption rate might be expected to have a reasonable correlation with the degradation rate. Our studies have shown that that oxygen consumption rate measurements can easily be made down to levels of sensitivity better than 1×10^{-13} mol/g/s [8]. For many polymers, this sensitivity allows measurements to be made at temperatures that correspond to 100 or more years of mechanical property lifetime. This is usually sufficient for predictive purposes. Previous studies on nitrile [8], neoprene [8] and EPDM [1] materials have shown that the oxygen consumption measurements correlate with traditional mechanical properties in the accelerated aging region. When the oxygen consumption values were followed to much lower temperatures, the Arrhenius slope remained unchanged for the nitrile and neoprene materials, but dropped substantially for the EPDM.

For the current butyl material, oxidation effects were shown to dominate CSR force decay (Fig. 1). In addition, continuous stress-relaxation is dominated by scission processes [20] and oxidation often leads to scission. Thus, one might expect a reasonable correlation of oxygen consumption and stress-relaxation. Figure 7 shows our oxygen consumption rate measurements on this material. Data were taken at several high temperatures (110°C, 95°C, 80°C) that overlap the region probed with the CSR experiments, as well as at several temperatures in the extrapolation region (65°C, 50°C, 25°C). These data are integrated in order to obtain oxygen consumption values versus time at the six temperatures, with the results shown in Fig. 14. Using a reference temperature of 25°C (as usual, the lowest experimental temperature), these data are then time-temperature superposed. The resulting superposition is excellent, as shown in Fig. 15. The empirical shift factors, which are noted on Fig. 15 and plotted on Figure 13, give excellent linear (Arrhenius) behavior all the way down to 25°C. In addition, the Arrhenius activation energy obtained from the slope is ~ 82 kJ/mol, virtually identical to the E_a determined for the CSR shift factors. This result confirms a correlation between these parameters and the unchanged slope of the oxygen consumption data in the extrapolation region strongly suggests that the accelerated CSR results can be confidently extrapolated to 25°C. Such an extrapolation gives the 25°C predictions shown in Fig. 12 (upper x-axis time scale).

Conventional (unstrained) properties

The results above are consistent with the expected correlation between oxygen consumption and CSR force decay. Our previous applications of oxygen consumption results to test extrapolations of Arrhenius behavior dealt with the degradation of conventional (non-mechanically strained) properties, such as ultimate tensile elongation, modulus and density [1,8]. For the current butyl material, the CSR decay is an order-of-magnitude faster than the decay in conventional properties (an apparent synergism

between thermoxidative environment and mechanical strain). Given the expectation that oxidation also dominates the decay of the butyl material's conventional properties, an examination of these properties and their correlation with the oxygen consumption measurements might be helpful in understanding the mechanisms underlying this apparent synergism.

Oven aging of unstrained butyl samples was done at four temperatures ranging from 140°C to 95°C. In order to avoid DLO effects, aging was done on the ~0.7-mm thick samples. Using the estimates of ϕ and P_{Ox} from Table II together with an L of 0.7 mm and the assumption that $\beta \sim 1$, Eq. (9), the appropriate expression for sheet material, gives α values less than 2 at all temperatures, corresponding to IRO values greater than 99% [3]. For materials dominated by oxidation effects, easily measured density increases are often observed [4,32,33]. Density results for the butyl material are consistent with this expectation; the data at the four aging temperatures are plotted versus log of the aging time in Fig. 16. These data give excellent time-temperature superposition, as seen in Fig. 17. Results for the ultimate tensile elongation are shown in Fig. 18. Although the data scatter is fairly large, reasonable superposition is possible (Fig. 19). The empirical shift factors derived from the density and elongation data (shown on Figs. 17 and 19) are plotted on Fig. 13 for comparison with the oxygen consumption and CSR results. The results are in accord with Arrhenius behavior and indicate an Arrhenius E_a of ~86 kJ/mol. Since this is quite similar to the E_a found for oxygen consumption (~82 kJ/mol), it suggests that indeed the oxygen consumption is intimately related to the degradation of conventional properties.

Another conventional property of possible interest to degradation is the material modulus. We have used our modulus profiling apparatus to follow the thermoxidative degradation of several elastomers, including nitrile [8], neoprene [8], SBR [33] and chlorosulfonated polyethylene (CSPE) materials. In each of these materials, the degradation of the elongation was found to be correlated to an increase in modulus (hardening) of the material, implying that the oxidative hardening caused cracks to initiate leading to tensile failure. Modulus measurements were made with our modulus profiling apparatus [17]. After aging, samples are cross-sectioned and then polished using metallographic polishing techniques. The modulus profiling instrument is then used to measure modulus values across the exposed sample cross-section; it is capable of quantitative measurements (typical scatter of $\pm 5\%$) with ~50 μ m resolution. As a representative example, Fig. 20 shows the correlation of average modulus results with normalized elongation data for a CSPE cable jacketing material aged for various times at five different aging temperatures. For the current butyl material, however, modulus profiling results showed surprisingly little change with aging time, as evidenced by the 125°C results plotted in Fig. 21. For each aging time on this figure, the modulus values are plotted versus position on the sample cross-section from one air-exposed surface (Position = 0%) to the opposite air-exposed surface (P= 100%), a distance of ~0.7 mm. These modulus results would at first seem to imply that an approximate balance between crosslinking and scission exists as the butyl oxidizes. However, solvent uptake and gel measurements, shown in Fig. 22, clearly indicate that scission dominates crosslinking during the oxidation. It is therefore likely that the incorporation of higher density

oxidative species in the polymer during aging causes sufficient hardening to approximately balance the softening caused by the domination of scission processes. This accidentally leads to a relatively constant modulus value, which may partially account for the relatively long lifetimes for the conventional properties. When mechanical strain is added, the force decay (stress-relaxation) is sensitive primarily to scission processes, leading to a much faster rate of degradation.

CONCLUSIONS

In oxygen-containing environments, oxidative scission appears to be the dominant mechanism underlying the degradation of a commercially formulated butyl material, both under mechanically strained and unstrained conditions. When conventional compression stress-relaxation (CSR) experiments are used to predict decays in sealing force, anomalous diffusion-limited oxidation (DLO) effects lead to non-Arrhenius behavior, with a range of effective activation energies that are much smaller than the range expected for oxidation processes. Important DLO effects can also lead to totally wrong results for compression set measurements, which probe the part of the sample most influenced by DLO effects. Modeling of the DLO effects for the disk-shaped geometry appropriate to CSR experiments, in combination with measurements of oxygen consumption rates and oxygen permeability coefficients, allows one to determine the size of disks needed to eliminate DLO effects versus the aging temperature. Parallel mini-disk CSR experiments based on this analysis lead to the recovery of Arrhenius behavior with an activation energy consistent with expectations. To gain confidence in longer-time, low-temperature extrapolations of this Arrhenius behavior beyond the lowest CSR temperature (70°C), we measured oxygen consumption rates from 110°C down to room temperature (25°C). Since these measurements had the same activation energy at high temperatures as the CSR measurements and indicated little change in E_a down to 25°C, confident CSR predictions at room temperature could be made.

ACKNOWLEDGEMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000. The authors gratefully acknowledge G. M. Malone who was involved with many of the experimental measurements.

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FIGURE CAPTIONS

Fig. 1. Compression stress-relaxation modulus versus aging time for standard disk samples.

Fig. 2. Time-dependent aging results at 125°C for normalized force measurements on standard CSR samples run in air and under nitrogen and for normalized ultimate tensile elongation measurements on unstrained, oven-aged samples.

Fig. 3. Normalized force measurements versus log of the aging time for standard CSR disk samples at the four indicated temperatures. At the two highest temperatures, the ~6-mm thick initial disk height was made by stacking six 1-mm disks on top of each other. At the two lower temperatures, three 2-mm disks were stacked together.

Fig. 4. Arrhenius plot of the times required for the normalized force measurements to decay 75% from their initial value using the data from Fig. 3 plus an additional time from data taken at 95°C using a stack of six 1-mm disks.

Fig. 5. Axis-symmetric geometry used to model DLO effects for the CSR geometry.

Fig. 6. Theoretical Integrated Relative Oxidation (IRO) profiles for disk-shaped geometry plotted versus model parameters α' and β .

Fig. 7. Oxygen consumption rates for the butyl material as functions of time at the indicated temperatures.

Fig. 8. Oxygen permeability coefficient measurements as a function of inverse absolute temperature.

Fig. 9. Theoretical plots of the expected IRO values for the butyl material versus CSR disk diameter at the indicated temperatures.

Fig. 10. Normalized force measurements versus log of the aging time for parallel, mini-disk CSR experiments at the five indicated temperatures. The diameters of the mini-disks used at each temperature are indicated.

Fig. 11. Arrhenius plot of the times required for the normalized force measurements to decay 50% and 75% from their initial value using the data from Fig. 10. For comparison of these mini-disk results with results from the standard CSR disks, the data of Fig. 4 are replotted on this figure.

Fig. 12. Empirical time-temperature superposition at a reference temperature of 70°C for the mini-disk CSR results shown in Fig. 10.

Fig. 13. Arrhenius plots of the empirical shift factors found for the mini-disk CSR force measurements, the oxygen consumption measurements and for elongation and density data.

Fig. 14. Integrated oxygen consumption results plotted versus log of the aging time at the indicated temperatures.

Fig. 15. Empirical time-temperature superposition at a reference temperature of 25°C for the oxygen consumption results shown in Fig. 14.

Fig. 16. Density measurements on unstrained butyl material versus aging time at the indicated temperatures.

Fig. 17. Empirical time-temperature superposition at a reference temperature of 95°C for the density results shown in Fig. 16.

Fig. 18. Ultimate tensile elongation measurements on unstrained butyl material versus aging time at the indicated temperatures.

Fig. 19. Empirical time-temperature superposition at a reference temperature of 95°C for the elongation results shown in Fig. 18.

Fig. 20. Normalized elongation results versus modulus measurements on a CSPE material aged at the five indicated temperatures.

Fig. 21. Modulus profiles across cross-sections of the butyl material after aging at 125°C for the indicated times. The x-axis variable denotes the percentage of the distance from one air-exposed surface to the opposite air-exposed surface of the ~0.7-mm thick samples.

Fig. 22. Solvent uptake and percentage gel measurements versus aging time at 110°C.

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