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Use of a respirometer to measure oxidation rates of polymeric materials at ambient temperatures

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Abstract

The use of a respirometer is introduced as a novel technique for measuring the oxidation rates of thermally degrading polymers. A dual channel respirometer with fuel cell detectors demonstrates sufficient sensitivity to measure the oxidation rates of low-density polymeric samples at ambient temperatures in a relatively short period of time. Samples of low-density polyurethane foam were aged for various lengths of time in sealed chambers at temperatures ranging from 23 to 110 °C. The extent of oxygen depletion was measured by flushing the chamber with air and comparing the oxygen concentration in the chamber flow to that of a reference flow. Oxidation rates of the 0.1 g/cm^3 polyurethane foam could be measured in less than 600 h of aging time at 23 °C. This corresponds to approximately 2 ppm oxidation by weight. Oxidation rates of the foam were used to calculate acceleration factors over a wide temperature range, including ambient conditions. Acceleration factors for the compressive force of the polyurethane foam were determined at elevated temperatures. Assuming that the aging behavior of compressive force of the foam is correlated to its oxidation rate, it is possible to calculate acceleration factors for the compressive force and predict the performance of the foam at ambient temperatures.

Keywords: Oxidation rate; Thermal degradation; Respirometer

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1. Introduction

We are investigating the chemical changes associated with polymer aging [1,2]. In addition to providing insight into the aging mechanism, it is often possible to measure chemical changes associated with aging more precisely than mechanical changes associated with aging. This increased sensitivity can be used to measure the very low rate of degradation at ambient conditions, so that extrapolation from high temperature behavior to low temperature behavior can be made in a scientific manner. The goal of measuring chemical processes is to provide improved methods to predict the service life of polymers.

Oxidative processes are the primary degradation mechanisms for many polymers exposed to ambient environmental conditions. The report by Scheirs et al. [3] provides an excellent review of the various methods of oxygen uptake for measuring polymer oxidation rates. A majority of the more than 100 studies summarized in the review calculate the oxidation rate from the time dependence of the head gas pressure, which is measured by either a manometer or pressure transducer [4]. Pressure measurements can be complicated by contributions from gaseous oxidation products, such as water and CO_2, which are often removed by molecular sieves and adsorbents. Other investigators have used gravimetric methods [5] and electrode sensors [6,7] to measure oxidation rates. Gas chromatographic (GC) techniques have been employed to measure oxygen partial pressures [8] and notably can independently measure the contributions from both the oxygen and oxidative products. Wise et al. further developed the GC approach into the ultrasensitive oxygen consumption (UOC) method which provides a powerful tool for predicting acceleration factors over a wide temperature range including ambient temperature and for understanding fundamental phenomena of oxidative polymer degradation [9,10]. This method enables degradation rates for mechanical properties measured at elevated temperatures to be more accurately extrapolated to ambient temperatures [11]. In the UOC experiment, a polymer sample is placed into an ampoule

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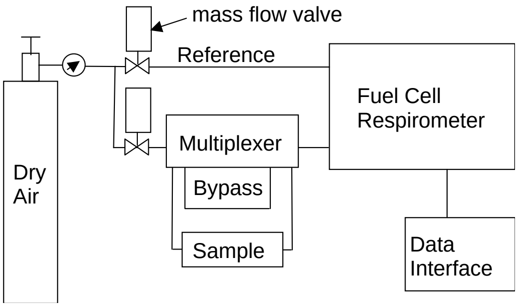

Scheme 1.

containing a known pressure and volume of oxygen. After an aging period at a fixed temperature, the gas composition in the free volume is analyzed by a GC technique and the total amount of oxygen consumed is determined. The UOC method has been used extensively to predict the lifetime of polymers undergoing thermo-oxidative aging [11–15].

In this paper we describe the use of a commercial differential fuel cell respirometer to measure oxidation rates of polymeric materials. This instrument has been successfully employed for measuring the respiratory cycles of small animals and insects in real time [16,17]. We have adapted the operation of the instrument for measuring the extremely low oxidation rates of polymers. Polymer samples were placed in a sealed chamber, filled with air and allowed to oxidize at a fixed temperature for an extended period of time. At the end of the oxidation period the sample chamber was flushed with a flow of air and the oxygen depletion measured by the respirometer. Experiments on bulk natural rubber were used to confirm that these measurements were in agreement with UOC measurements. In order to test the limits of the respirometer, the oxidation rates of a 0.1 g/cm^3 polyurethane foam were measured from 23 to 110 °C and acceleration factors over this temperature range calculated. The oxidation acceleration factors measured by the respirometer were compared to those measured for the compressive strength of the foam at elevated temperatures and then used to predict acceleration factors and service life for the compressive strength of the foam under ambient conditions.

2. Experimental

2.1. Instrumentation

The respirometer, an Oxzilla II Dual Absolute and Differential Oxygen Analyzer from Sable Systems International (Las Vegas, NV), is based on sensitive fuel cell detectors. The output of each fuel cell detector depends on the concentration of oxygen in the air stream directed to that fuel cell. The output of the fuel cell connected to the sample chamber is subtracted from the output of the fuel cell connected to the reference flow and the difference is used to calculate the amount of oxygen that was consumed by the polymer sample during aging. A simplified outline of the arrangement is shown in Scheme 1. The respirometer and a gas multiplexer (also purchased from Sable Systems International) are controlled by a laboratory PC, which was also used to record the data. Ultrapure air was supplied by Matheson Inc. A source of compressed air with consistent composition was necessary because the instrument was in a laboratory with cryogenic equipment and carbon dioxide storage, which perturbed the ambient oxygen levels. The same cylinder of air was used to fill and analyze a sample, since oxygen levels fluctuated somewhat from cylinder to cylinder. The cylinder air was passed through a column of Dririte and then split into two flows, each regulated by a mass flow valve. One flow went directly to the respirometer, while the second flow was directed by the multiplexer through either a short bypass loop or through the sample chamber. After passing over the sample, this flow was directed through Dririte and Ascarite to remove water and CO_2 produced during the degradation process and then to the respirometer. These lines were made as short as possible in order to minimize the time required to flush the chamber. A pressure-vacuum manifold with a pressure transducer was used to monitor the operation of the system and to remove the ambient air from short sections of the gas pathway that were exposed during connection of a sample chamber to the system. The sample chamber consisted of a stainless steel tube 7.5 cm long by 1.5 cm inside diameter fitted to a Conflat flange at each end. The chamber was fastened to stainless steel Swagelok valves, outfitted with Conflat flanges, by means of gold plated copper seals. The total sealed volume of the chamber was 19.1 cm^3.

2.2. Materials

A carbon-black filled natural rubber was used to test the respirometer and compare the results obtained by the respirometer with the UOC method. The polyurethane foam is a flexible, open celled foam with a density of approximately 0.1 g/cm^3.

2.3. Procedure

A known amount of polymer was placed in a sample chamber. The sample was typically 0.2 cm or less in thickness for the bulk natural rubber and 0.4 cm or less for the polyurethane foam in order to reduce diffusion limited oxidation effects [10,18]. The vessel was evacuated; cylinder air at 40 cm^3/min was passed over the sample for several minutes and the chamber sealed. After an interval of at least 1 h, air was again passed over the sample in order to completely eliminate any contribution originating from ambient air dissolved in the sample. The chamber was removed from the manifold and placed in an air-circulating oven. After 20 min, one of the chamber valves was momentarily opened to equilibrate the pressure at elevated temperature so that the oxidative aging and compressive force aging were both conducted at the atmospheric pressure of Albuquerque (630 Torr). After aging, the sample chamber was reconnected to the manifold and the short sections of the connecting gas pathways that had been exposed to atmosphere were evacuated and refilled with cylinder air. The respirometer was stabilized by passing air through the bypass loop and setting each of the outputs of the respirometer to a nominal value of 20.95% oxygen.

At time '0', the multiplexer was instructed to switch the air flow from the bypass loop to the sample chamber. The difference between the oxygen concentration of its air flow and the reference air flow was recorded as a function of time. The difference reached a maximum after 60 s, and recovered after approximately 3 min, although the flow was usually continued for at least 5 min in order to obtain a stable baseline. There was some concern that there would be 'dead' spaces in the chamber that would not readily exchange with the air flow. After the initial air flow, samples were allowed to equilibrate from 2 to 16 h and then flushed again. The second experiment showed levels of depletion ranging from 1 to 5% of the initial experiment. These levels, which were a combination of additional aging at ambient temperature, incomplete exchange during the first flush, and a dissolved oxygen effect, were not considered significant. The dissolved oxygen effect originates from the diminished concentration of oxygen in the polymer at the end of the aging experiment due to the reduced partial pressure of oxygen in the headspace. A third experiment showed no contribution from incomplete exchange or dissolved oxygen.

2.4. Calculation

The volume of oxygen at STP was calculated by multiplying the integral of the oxygen concentration versus flow time (units of percent oxygen × minute) by the flow rate (40 cc STP/min) and dividing the result by 100%. The volume of oxygen at STP was then converted to moles of oxygen and divided by the sample weight in grams and the aging time in seconds to provide an oxidation rate in units of mole O_2 STP/g sample/s.

2.5. Calibration

Samples with a known excess of oxygen were prepared by adding 20–40 Torr of oxygen to an empty sample chamber and then completing the fill with cylinder air. The oxygen excess in cm^3 STP could be calculated from the partial pressure and volume of oxygen. The calculated excess agreed with that measured by the respirometer to within 10%. The flow of the mass flow meters (which is a crucial parameter in all oxygen depletion calculations) was ensured by monitoring the flows with Matheson gas flow meters and occasionally performing water displacement experiments with an inverted volumetric flask. Comparisons of the respirometer and UOC methods on actual samples are presented in the following section.

2.6. Compressive strength

Compressive strength of the foam was measured on an Instron 5500R instrument using foam cubes with dimensions of $2.5 \times 2.5 \times 2.5\ cm^3$. The foam was twice compressed to 40% of its initial height and then compressed to 50% of its initial height and the force recorded. Foams are often compressed multiple times for improved reproducibility and this procedure had been adopted early in the mechanical testing program for these foams.

3. Results and discussion

Fig. 1 shows the oxygen deficit trace from a sample chamber containing 0.207 g of carbon filled natural rubber that had been aged for 16 h at 80 °C. The dual detectors were first balanced with identical air streams flowing through both channels. At $t = 0$, one of the air streams was redirected to the sample chamber by the multiplexer unit. After approximately 40 s the oxygen deficit became apparent, reached a maximum at 60 s and then began to decrease. The hatched area represents the total oxygen deficit, which was calculated to be 0.0819 cm^3 O_2 at STP or 117 μg O_2. This amount of oxygen corresponds to an oxidation rate of 3.06×10^{-10} mol O_2 STP/g sample/s.

There was some concern that the air in the chamber would not be fully displaced in a reasonable period of time. Note that with an air flow of 40 cm^3/min, the volume of air flowing over the sample would be more than twice the volume of the sample chamber (19.1 cm^3) during each minute of flow. Thus, it seems reasonable that the deficit appears to be fully recovered approximately 2 min after the maximum deficit. The completeness of the exchange was also confirmed by allowing the chamber to equilibrate for times ranging from 2 to 16 h. After equilibration, the experiment was repeated with the detector set for increased sensitivity. The second traces were always less than 5% of the first trace and were typically in the range of 1–2% of the first trace. Much of the contribution to the second trace could be attributed to the oxygen deficit of the air that was dissolved in the sample. This air would not exchange with the gas flow during the several minutes of the experiment, but would exchange during the equilibration period and then be detected during the second experiment.

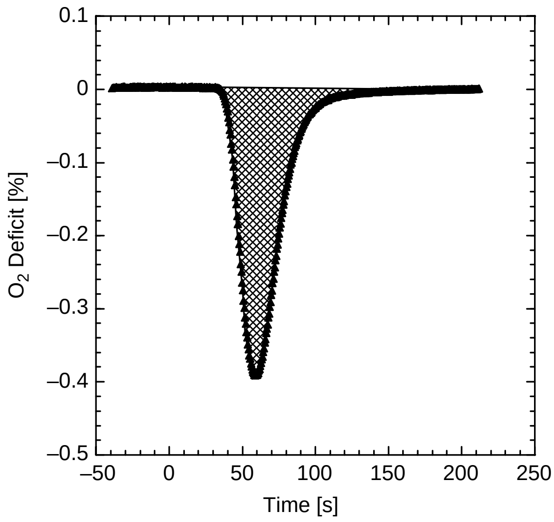

Fig. 1. The respirometer recording of the oxygen deficit trace of 0.207 g carbon filled natural rubber that has been aged for 16 h at 80 °C.

Table 1
A comparison of the oxidation rates of a carbon filled natural rubber at 95 °C as measured by a respirometer and the UOC method

Respirometer (mol/g/s × 10^{-10})	UOC (mol/g/s × 10^{-10})
12.6	14.8
12.4	11.5
12.3	19.0
11.8	15.4
11.5	
Average	
12.1 ± 0.5	15.2 ± 3.1

Table 1 shows a comparison between oxygen consumption experiments on natural rubber performed by the respirometer and by the UOC methods at an aging temperature of 95 °C. The agreement between the two methods is reasonable and demonstrates the validity of the respirometer experiment. Note that the experimental scatter is significantly less for the respirometer experiments. We attribute this to the greater sensitivity of the respirometer and its stability over time. The sensitivity can be appreciated by the lack of noise in the oxygen deficit trace in Fig. 1. The calibrations of the respirometer and the air flows were checked several times over the 6 month operation of the instrument. Other than balancing the response of the two detectors to a nominal value of 20.95%, adjustment of the instrument was not required during this time.

The oxygen deficit trace of a 10% polyurethane foam sample aged at 23 °C for 555 h is shown in Fig. 2. The low density of the foam limited the amount of sample that could be easily placed into the chamber to 1.07 g. Additional material would have lead to compression of the foam and obstruction of the free flow of air through the chamber. Aging at room temperature represents the lowest oxidation rate that needs to be measured for normal aging conditions. The oxygen deficit range of the respirometer was set to maximum sensitivity. Although the trace exhibits considerable fluctuation (the response was not time-filtered), the integral represented by the crosshatched area could be measured reliably. Later in the paper, we will discuss the reproducibility of repeat measurements. The total deficit equals 0.00149 cm^3 O_2 STP or 2.1 μg for the 1.07 g sample and predicts an oxidation rate of 3.12×10^{-14} mol O_2 STP/g sample/s.

The goal of this study is to determine acceleration factors for the oxidation rate of the foam over a wide temperature range, including room temperature, so that high temperature aging behavior can be reliably extrapolated to room temperature. We have demonstrated that the respirometer can be used to measure these oxidation rates in a relatively short period of time. One complication that needs to be considered is the possibility that the oxidation rate of the foam changes during the aging process. This factor is typically handled by performing a time–temperature superposition of all of the temperature measurements. The high temperature measurements are conducted for a sufficiently long period of time so that the entire degradation process is mapped out on the time–temperature superposition plot. Changes in the oxidation rate with time are then identified by a change of slope in the oxidation rate. A considerable effort was expended measuring the oxidation rate of the foam by UOC methods in order to validate the respirometer. The results of the UOC method will be presented next and will also be used to determine if the oxidation rate depends on the extent of aging.

Fig. 3 shows the oxygen consumption of the polyurethane foam as a function of aging time for temperatures ranging from 50 to 125 °C. The lines represent power law fits to the data sets for each temperature. The R values for the fits range from 0.982 to 1.000 and average 0.995. The power law exponents (slopes in Fig. 3) are 0.98, 0.83, 0.97, 0.90 and 1.10 for the 65–125 °C data sets, with an average exponent of 0.96 ± 0.10. The exponents exhibit no strong trend with respect to temperature and their average values do not differ in a statistically significant way from the value of 1.0. Thus, we conclude that the oxidation rate does not depend on the extent of degradation.

The acceleration factor, a_T, for an aging process at a particular temperature is defined as the multiplicative factor that needs to be applied to the time axis in order for the data at

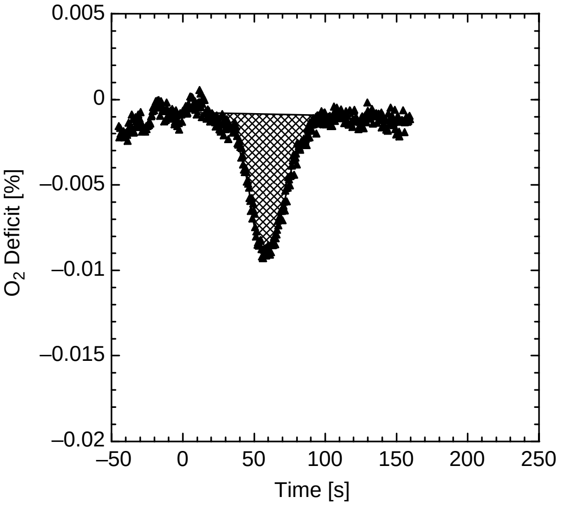

Fig. 2. The respirometer recording of the oxygen deficit trace of 1.07 g polyurethane foam that has been aged for 555 h at 23 °C.

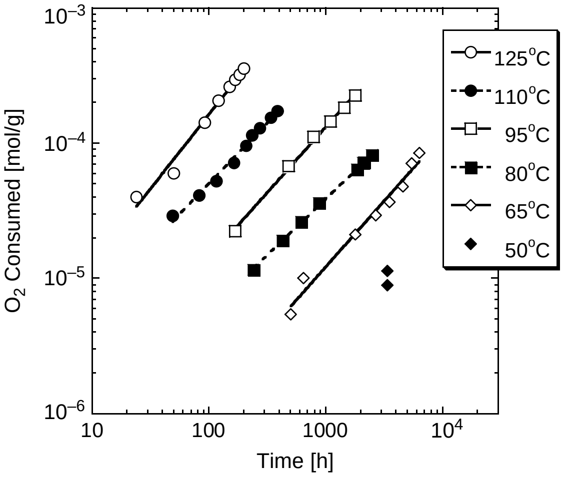

Fig. 3. The oxygen consumption of a polyurethane foam measured by the UOC method as a function of aging time for various temperatures.

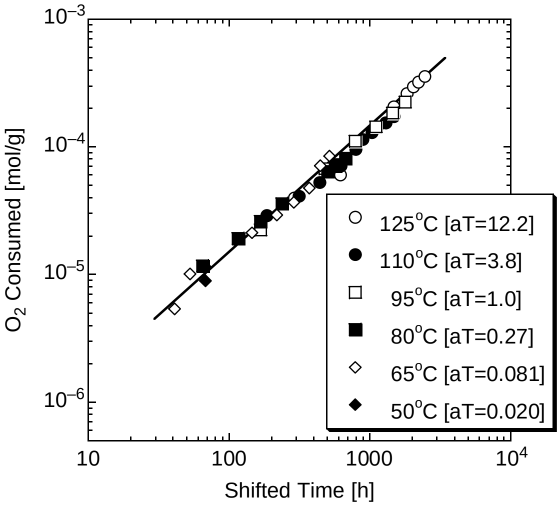

Fig. 4. The time–temperature superposition of oxygen consumption of a polyurethane foam measured by the UOC method.

that temperature to superimpose with the data at a chosen reference temperature. For the oxygen consumption of the polyurethane foam, we chose 95 °C as the reference temperature. Fig. 4 shows the time–temperature superposition plot for oxygen consumption of the polyurethane foam measured by the UOC method. The data superimpose reasonably well and are fit by a straight line that was forced to have a slope of 1.0. The acceleration factors for the time–temperature superposition are shown in the legend of Fig. 4 and are plotted versus inverse temperature in Fig. 5. The acceleration factors exhibit a moderate amount of curvature. Curvature in the lower temperature regime of an acceleration factor plot is seen for many polymers [19]. Although curvature is often attributed to a change in aging mechanisms, the effect may be somewhat more subtle. The aging process for a real polymer normally consists of multiple chemical reactions both in series and in parallel. Curvature is then expected if the various reactions have unique activation energies so that different reactions are rate limiting at high and low temperatures, although the overall reaction scheme may remain constant. Note that the curvature in this plot is not as pronounced as is sometimes observed because we do not have oxidation rate data for temperatures approaching ambient. Exposure times at room temperature are quite lengthy because the total weight of foam that can be placed in the sample chamber is limited. Attempts to increase the sample mass by cutting the material into small pieces and compressing the sample resulted in significantly faster oxidation rates than observed for intact uncompressed samples.

Because the UOC experiments demonstrated that the oxidation rate is largely independent of the extent of oxidation, we measured the oxidation rates with the respirometer for only limited periods of time at various temperatures. The oxidation rates as a function of inverse temperature are shown in Fig. 6. The experiment was repeated seven times at 23 °C using exposure times ranging from 236 to 555 h in order to determine the reproducibility of the measurement under the most stringent requirements. The average oxidation rate at 23 °C was 3.4×10^{-14} mol O_2 STP/g sample/s with a standard deviation of $\pm0.6\times10^{-14}$ O_2 STP/g sample/s. Four separate samples were used for the seven measurements with no observable variation of oxidation rate from sample to sample. These results demonstrate that the respirometer can reproducibly measure very slow oxidation rates of less dense materials at room temperature in a relatively short period of time.

The oxidation rates at each temperature were averaged and used to calculate acceleration factors that were normalized to 1.0 at 95 °C. The results versus inverse temperature are shown in Fig. 7. The acceleration factor plot exhibits some curvature in the lower temperature region of the curve. The activation energy of the relatively linear region between 50 and 110 °C is 92 kJ/mol.

The purpose of measuring acceleration factors for oxidation is to apply these same acceleration factors in the low temperature region to a mechanical property of interest. The foam is used as a packaging material to protect items

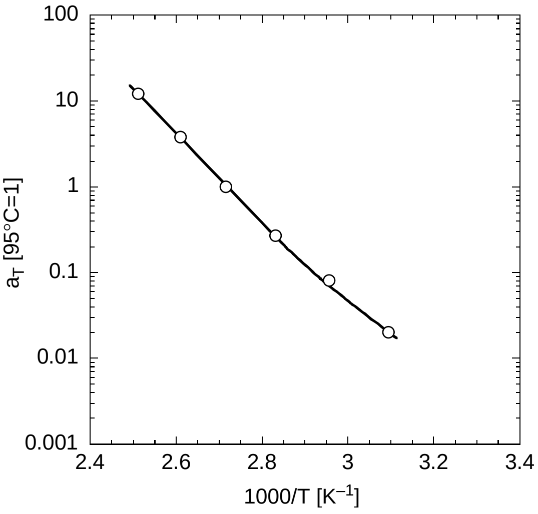

Fig. 5. The acceleration factors versus inverse temperature for the oxygen consumption of a polyurethane foam measured by the UOC method.

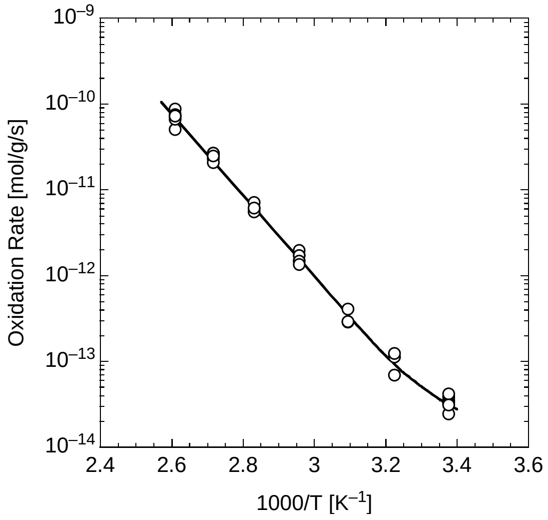

Fig. 6. The oxidation rates of a polyurethane foam measured by the respirometer versus inverse temperature.

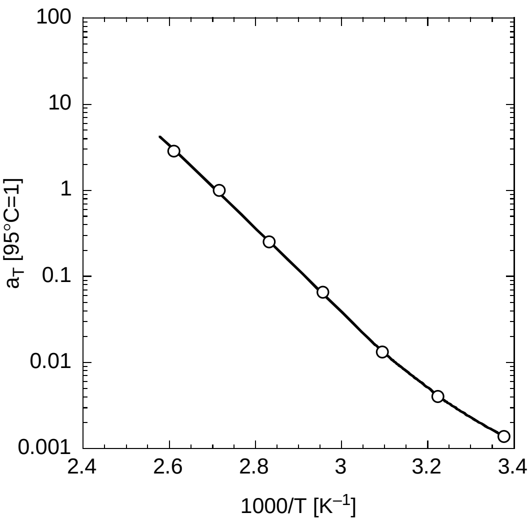

Fig. 7. The acceleration factors versus inverse temperature for the oxidation of a polyurethane foam measured by the respirometer.

from shock and vibration. An important property for the performance of this task is the compressive strength of the foam. As described in the experimental section, the foam is compressed twice to 40% of its initial height and during the third cycle compressed to 50% of its initial height and the force measured. The compressive forces of foam samples as a function of aging time and temperature are shown in Fig. 8. The shape of the compressive strength curves for samples aged from 95 to 140 °C are reasonably similar and suggest that a time–temperature superposition is possible. Note that the very limited data available at 80 °C means the results for this temperature are very uncertain. The time–temperature superposition plot is shown in Fig. 9. The data points for the various temperatures fall reasonably well on the smooth curve. The acceleration factors shown in the legend of Fig. 9 are plotted versus inverse temperature in Fig. 10 along with the acceleration factors determined by UOC and respirometer experiments.

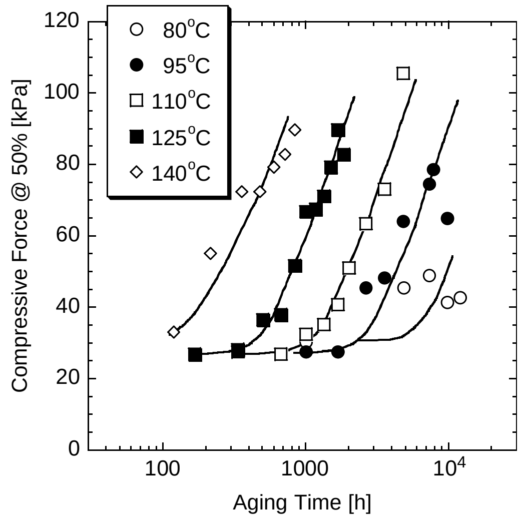

Fig. 8. The compressive force of a polyurethane foam as a function of aging time for various temperatures.

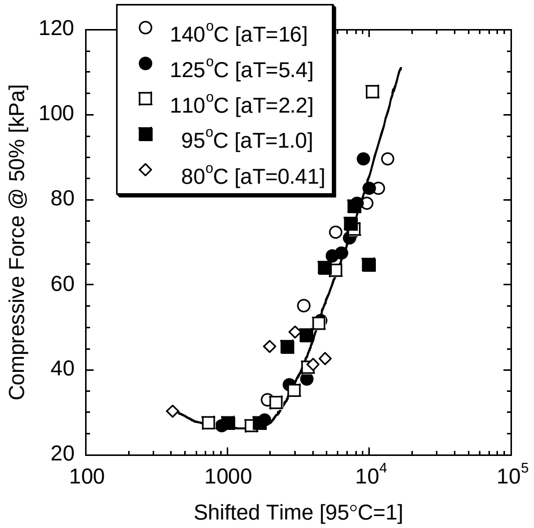

Fig. 9. The time–temperature superposition of the compressive force for a polyurethane foam. The shift factors for the various temperatures are shown in the legend.

The acceleration factors in Fig. 10 determined by the various techniques correlate reasonable well as a function of temperature. The line fit exhibits curvature similar to that shown in Fig. 7 for the oxidation rates measured by the respirometer because the low temperature region, 25 and 37 °C, is defined solely by the respirometer data. The least squares fit of all the acceleration factors for temperatures ranging from 50 to 140 °C yields an activation energy of 87 kJ/mol with an *R* value of 0.95. We believe that this is reasonably good correlation for three techniques that measure both mechanical and chemical properties over nearly three orders of magnitude.

The oxidation rate acceleration factors at room temperature can now be used to predict the behavior of the compressive strength as a function of time at room temperature. Suppose we arbitrarily define ‘failure’ of the foam to occur when its

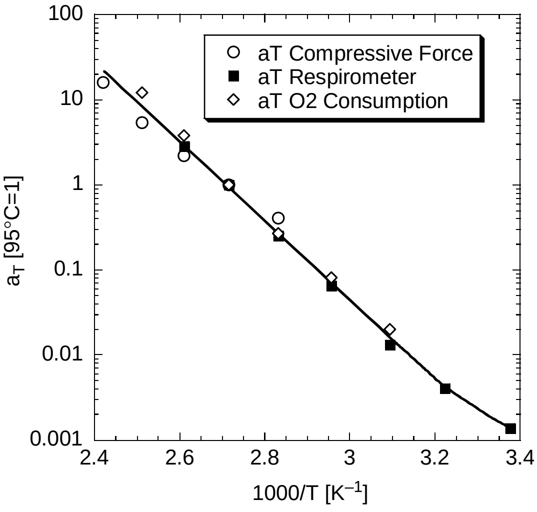

Fig. 10. The acceleration factors for the compressive force, the oxidation rate measured by the respirometer and the oxidation rate measured by UOC for a polyurethane foam.

compressive strength has increased to 60 kPa. At 95 °C, the time required to reach this state is approximately 5000 h. Using the ratio of acceleration factors at 95 and 23 °C from Fig. 10 (1.0 and 0.002), we predict that at 23 °C, the compressive strength of the foam will reach 60 kPa after 2,500,000 h or approximately 280 years of service. Similar calculations estimate service lifetimes of 110 and 40 years of service for temperatures of 37 and 50° °C, respectively. These predictions assume that the compressive strength is related to the oxidation rate at these lower temperatures in quantitatively the same fashion as they are related at 95 °C. Similar assumptions coupling oxidation rates to mechanical properties of polymers have proven quite useful for a variety of polymers and clearly the relationship could depart significantly from ideality before oxidative aging became an issue at room temperature.

The obvious manner to increase confidence in these predictions is to continue to measure compressive forces of these materials for longer period of times at lower temperatures in order to determine if the acceleration factors for compressive force and oxidation rate continued to correlate. The aging time required for obtaining reproducible changes in compressive strength at even 80 °C makes it difficult, however, to test the relationship in this time and temperature regime. On the other hand, the lengthy time required to observe significant changes at this temperature attests to the long life of the foam.

4. Conclusions

We have adapted a respirometer for measuring the extremely low oxidation rates of polymers and found that it offers several advantages compared to the UOC method. Most importantly, it is sensitive to lower amounts of oxidation. The exact sensitivity advantage is difficult to quantify because sensitivity is always a tradeoff between speed and accuracy. The sensitivity of each of the methods can be increased by filling the sample chamber with additional sample. The accuracy is then compromised, however, as the dissolved gas becomes an increasingly large faction of the total gas in the chamber and uncertainty is introduced unless the solubility and efficiency of gas transfer are known. A reasonable comparison between the two methods can be made by observing the actual times used to perform measurements at 37 °C (the lowest temperature completed by the UOC method). The UOC method required nearly 6 months of aging while the respirometer required 1 week of aging. Along with this factor of 25 in decreased experimental time, the standard deviation of the respirometer data was typically 3 or 4 times less than that of the UOC method, implying an additional decrease in experimental time for comparable accuracy. Sensitivity is essential when measuring oxidation rates at low temperatures and is especially important when investigating materials such as low density foams where the total oxygen depletion is reduced compared to an experiment with bulk materials. We take advantage of the increased sensitivity by reducing the aging time and also placing less material in a chamber, thereby minimizing the effects related to oxygen solubility and gas transfer. By using only 1 g of foam in a chamber volume of approximately 20 cc, the gas dissolved in the foam represents 0.5% of the total gas assuming a typical solubility constant for oxygen of 10%. This small fraction of dissolved oxygen eliminates the need for a solubility correction. Finally, the improved sensitivity and reduced experimental time implies that the partial pressure of oxygen is reduced to a lesser extent during an experiment. This decreases the uncertainty introduced by the possible dependency of the oxidation rate on the partial pressure of oxygen. The respirometer extends our capabilities to lower temperatures and less dense samples, shortens the aging time and improves the accuracy of oxidation experiments.

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