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PREDICTION OF PACKAGING SEAL LIFE USING THERMOANALYTICAL TECHNIQUES

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SUMMARY

In this study, Thermogravimetric Analysis (TGA) has been used to study silicone, Viton and Ethylene Propylene (EPDM) rubber. The studies have shown that TGA accurately predicts the relative order of thermo-oxidative stability of these three materials from the calculated activation energies. As expected, the greatest thermal stability was found in silicone rubber followed by Viton and EPDM rubber. The calculated lifetimes for these materials were in relatively close agreement with published values. The preliminary results also accurately reflect decreased thermal stability and lifetime for EPDM rubber exposed to radiation and chemicals. These results suggest TGA provides a rapid method to evaluate material stability.

INTRODUCTION

The primary purpose of radioactive materials (RAM) packaging is to permit RAM to be transported without posing a threat to the health or property of the general public. The containment system for a Type A package is defined in the United States by regulations promulgated by the Department of Transportation and published in the Code of Federal Regulations (DOT, 49 CFR 171.403). For a Type B package, the definition of the containment system is promulgated by the Nuclear Regulatory Commission and is published in the Code of Federal Regulations (NRC, 10 CFR 71.4). As published in both 49 CFR 171.403 and 10 CFR 71.4, the containment system is an assembly of components of the packaging intended to retain the RAM during transport. It typically consists of a packaging body, a closure (lid), any fasteners used to secure the closure onto the packaging body, one or more penetrations into the closure, and one or more seals at each interface where RAM could otherwise escape. The requirements of 10 CFR 71 specify a wide range of environments in which the seals and closures of RAM packages must function for the useful life of the packaging under both normal and accident conditions. A review of the seal or gasket materials used in transport packages in the U.S. indicates that metals and elastomers are very important. Since seals play such an important role in providing containment for RAM in transportation packaging, the ability to readily determine the reliability of elastomer seals is very useful. A method which enables prediction of the service life of an elastomer can provide quantitative data to demonstrate seal reliability.

Numerous methods exist for estimating component lifetimes. Typically a series of tests, performed at different temperatures, enable the creation of a semi-logarithmic plot of lifetime versus the reciprocal of failure temperature. The methods generally assume first-order kinetics and use extrapolation to estimate the long lifetimes encountered during normal use temperature. The application of first-order kinetics to estimate elastomer lifetime is particularly fortuitous. Many elastomers are known to decompose by first-order kinetics

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(Sen et al. 1992). For those that do not, the earliest stages of decomposition can be approximated well with first-order kinetics. These traditional procedures, while useful, are very time consuming, often taking many months, especially for temperature resistant elastomers. The time required for a full series of tests becomes excessive and costly. A thermoanalytical technique known as thermogravimetric analysis (TGA), which monitors weight changes in a material as the temperature is changed, offers a viable, quick alternative to lengthy oven aging experiments. TGA is a well established thermoanalytical technique that has been used extensively to provide kinetic information that can be used to characterize materials (Papazian 1972). With computer controlled instruments, modern thermogravimetric analyzers are capable of heating materials at controlled rates, measuring temperatures close to the specimen and of automatically recording the mass or percentage mass change continuously to the required sensitivity and precision. Through the use of proprietary software, the parameters of interest for the material can be calculated by the computer from the thermograms.

In this paper, a preliminary evaluation of TGA methods for the determination of seal life in silicone, Viton, and EPDM rubber will be discussed. From a determination of the kinetic parameters for these materials, the estimated seal life for these materials was calculated. For EPDM rubber, the effect of gamma radiation dose and exposure to harsh chemical environments on the seal life were also evaluated.

EXPERIMENTAL

Materials

The elastomers used in this study were ethylene-propylene (EPDM), silicone rubber, and Viton™ rubber. These materials were obtained from the Parker Seal Group, Lexington, Kentucky in the form of square test platens (10 cm x 10 cm, and ~ 3 mm thick sheets). The respective Parker Compound designations were E0540-80, S0604-70, and V0884-75. Small rectangular (~4 x 3 x 1mm) samples weighing approximately 10-30 mg were cut from the center of these test platens. The first of these materials was chosen because of its known resistance to various chemical compounds and radiation (Nigrey et al. 1997) while the later materials were selected because of their relative high temperature resistance.

Instrumentation

A thermoanalytical system manufactured by TA Instruments, Inc., New Castle, Delaware was used in this study. The TGA system consisted of a Model 2050 TGA equipped with an automatic sample loader, a gas switching accessory, and a computer controller. The systems software developed by TA Instruments was *Thermal Solutions* and is based on the OS/2™ operating environment. Temperature calibration of the instrument was performed at the start of the experiments with Curie Point Standards using standardized practices (ASTM E1582). After developing a test method within the software, samples were analyzed at heating rates of 1, 2.5, 5, and 10°C/min. The ~10-30 mg samples were heated from room temperature to 800° C in ultra-high-purity air. The resulting computer generated data output thermogravimetry curves of mass-loss versus temperature.

Decomposition Kinetics Analysis

The percent weight loss versus temperature data contained in a thermogravimetry curve was used in the *TGA Kinetics Analysis* software developed by TA Instruments. This computer program analyzes thermogravimetry curves in accordance with a standard decomposition kinetics test method developed by the American Society of Testing and Materials (ASTM E1641). Using at least two TGA files that contained the thermogravimetry curves of the material at two different heating rates 10°C/min or less, the program calculated the temperature at constant conversion (decomposition) levels. The thermogravimetry curves at the different heating rates should have the same general shape and exhibit a weight loss increasing monotonically with increasing temperature. The program selects certain default conversion levels such as 1%, 2.5%, 5%, and 10%. However, the user can select up to ten conversion levels provided that the upper limit of 20% is not exceeded. During the early stages of decomposition, i.e., below 10% weigh loss, the decomposition reaction obeys first-order kinetics. Using these calculated temperatures (T) at constant conversion and the heating rates (β), the program is able to generate a plot of log β versus 1/T. By repeating these calculations for each set of conversion values, a series of straight lines should be obtained. Assuming first-order kinetics, a least-square best fit straight line to these data and determination of slope enables the calculation of an Arrhenius activation energy (kJ/mole) for the material at each conversion level. From the activation energy, the program can further calculate other kinetic parameters such as rate constants, half-life, and material lifetime. If sufficient quality thermogravimetric data have been used in these calculations, uncertainty in the determination of these kinetic parameters can be minimized.

DISCUSSION AND RESULTS

TGA measures the weight loss that a material experiences as the temperature is increased at an experimentally chosen heating rate. In elastomeric materials that are used in sealing applications such as o-ring seals in transportation packagings, the manufacturer of Viton and silicone rubber suggests that these materials can be used at temperatures as high 230°C (Parker Seal Group 1991). All the information published by o-ring manufacturers is intended to provide the users with general guidance for usage. Furthermore, users are specifically cautioned that information on seal life at certain temperatures should be used as a guide and that precise predictions for seal life should not be made. The purpose of this study was to ascertain whether TGA could be used to provide an independent method to quickly provide data that could be used to evaluate elastomer lifetimes. Since o-ring performance at elevated temperatures in transport packagings is valuable for packaging designers, this methodology could be used to confirm and extend prediction of lifetimes in elastomeric materials.

An example of a computer-generated thermograms of Viton rubber heated in air is shown below in Figure 1. Shown are four TGA curves for Viton rubber at heating rates from 1 to 10°C/min.

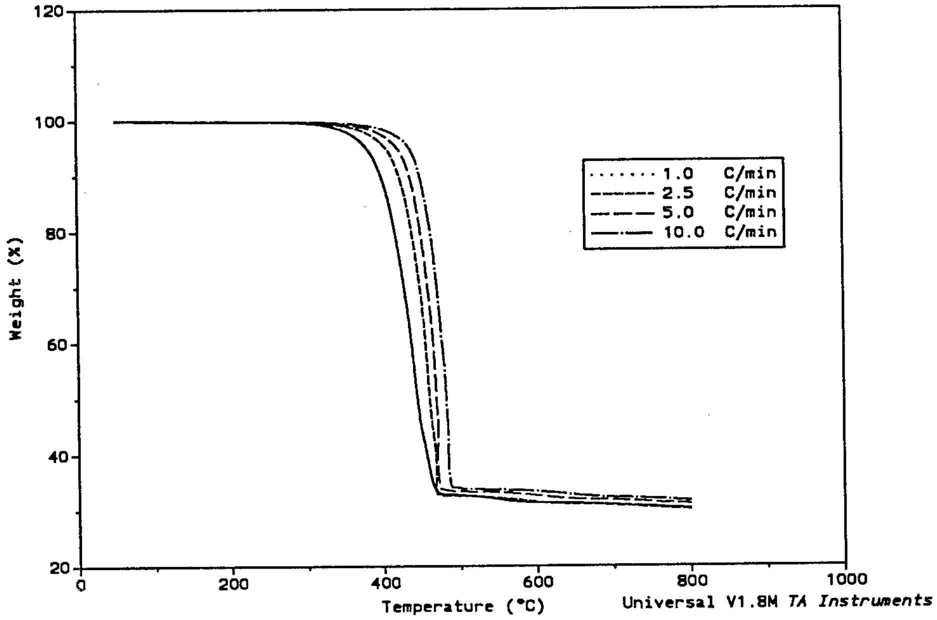

Figure 1. TGA curves for Viton rubber heated in flowing air (50 mL/min) from ambient to 800°C at four different heating rates.

The curves shift to higher temperatures as the heating rates are increased. What should also be noted from the curves is that the material experiences mass loss starting at ~250°C. The identities of components evolved at these temperatures are not determined in simple TGA experiments. However, through the use of companion analytical techniques such as mass spectrometry and infrared analyses, these evolved volatile species could be identified. What is also evident from the TGA curves is a residue (~ 30%) between 500 and 800°C. The general curve shapes also indicate that Viton thermally decomposes by a single decomposition process under these conditions in air. The selection of air as a purge gas was made since it represents conditions that an o-ring material might experience during normal and accidental transport scenarios. From these curves, the data analysis process requires the selection of different levels of decomposition. The values for these decomposition levels are referred to as conversion levels by the kinetics analysis software. Typically, a value early in the decomposition profile is desired since the decomposition mechanism here is more likely to be that of the actual product failure. On the other hand, selecting such a value too early on the curve may result in the measurement of some volatilization of the elastomers components (e.g., moisture or oils) which are not involved in the failure mechanisms. A 5% value for conversion levels is commonly chosen, but other values may be selected to provide correlation with other types of lifetime testing methods. However, a correlation between conversion levels in seals and leaktightness has not been established.

Using conversion values of 1, 2.5, 5, and 10%, the temperatures (in Kelvin) at those conversion levels were calculated for each TGA curve. A plot of the logarithm of the heating rates versus the corresponding reciprocal temperature at constant conversion is generated by the software. At each conversion value these plots should produce a straight line. Figure 2 shows a series of such lines created from the four curves shown in Figure 1. If the particular specimen decomposition mechanism is the same at all conversion levels, the lines should all have the same slope. This is the case for Viton rubber tested under these conditions. In instances where the slopes of the lines are quite different, justifications exist for the selection of other conversion values as "best" points of constant conversion.

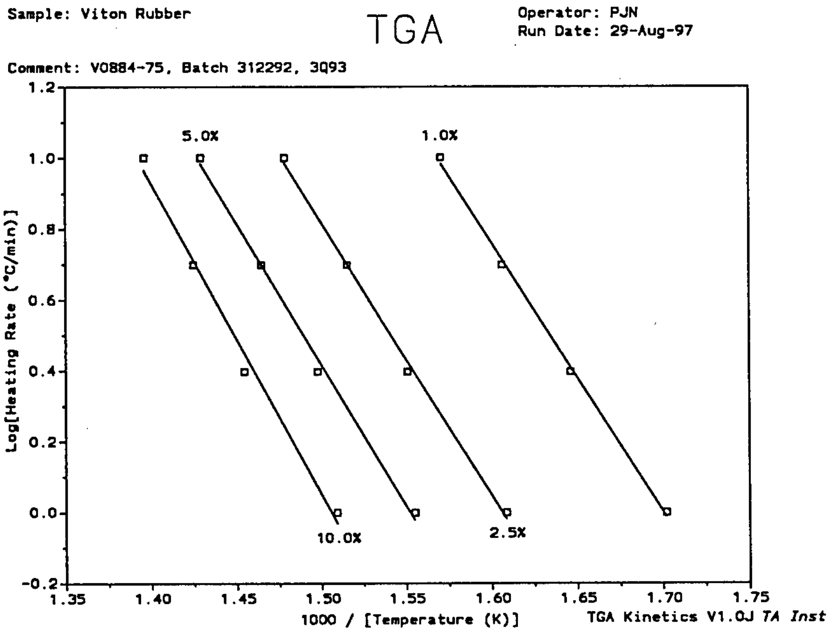

Figure 2. Arrhenius plot of heating rate and temperature at constant conversion rates of 1, 2.5, 5, and 10% for Viton rubber heated in air.

The next step in the computation process performed by the software is the calculation of activation energy (E_a) from the slope of the line for each conversion level in Figure 2. The calculation uses a method developed at the National Bureau of Standards (Flynn and Wall 1966). The basis for this calculation is given in Equation 1 below:

$$E_a = -R/b\ [\ d\ \mathrm{Log}\beta/\ d\ (1/T)] \qquad (1)$$

where E_a is the activation energy (J/mole), R is the gas constant (8.314 J/mole K), T is the temperature (Kelvin) at constant conversion, and b is a constant (0.457). The value of the derivative term [d Logβ/ d (1/T)] is the slope of the lines in Figure 2. The value for the constant b (given in tabular form by Flynn and Wall) varies depending upon the value of E/RT during the first iteration of the computational process. An iterative process must be used where E_a is first estimated, a corresponding value of b chosen, then a new value for E_a is calculated by the software. This computational process is continued until E_a no longer changes with successive iterations.

A relationship has been postulated (Toop 1971) between activation energy and the estimated lifetime of wire insulation. This relationship is given in Equation 2,

$$\ln t_f = E_a/RT_f + \ln\ [E_a/\beta R \bullet P(X_f)] \qquad (2)$$

where t_f is the estimated time to failure (min); T_f is the failure temperature (K); and $P(X_f)$ is a function whose value depends on E_a at the failure temperature. To calculate the estimated time to failure, the value for the temperature at the constant conversion point is first selected for a slow heating rate. This value, along with the activation energy is used to calculate the quantity E_a/RT. This value is then used to select a value for log $P(X_f)$ from the numerical integration table given by Toop. Selection of a value for the failure temperature (T_f) permits the calculation of t_f from Equation 2 above.

Rearrangement of Equation 2 yields a form which may be used to calculate the maximum use temperature (T_f) for a given lifetime (t_f).

$$T_f = (E_a/R)/\{\ln t_f - \ln[E_a/\beta R \bullet P(X_f)]\} \qquad (3)$$

Equations 2 and 3 are used by the software to create a plot in which the estimated lifetime is plotted versus the failure temperature. Such a plot obtained for Viton rubber at 1% conversion levels in air is shown in Figure 3. In addition to providing an estimate of the lifetime, the plot gives activation energies, pre-exponential factors, and 60-minute half-life values for the materials. For the Viton rubber analyzed by the previously mentioned instrumental software, an activation energy of ~ 147 kJ/mole was calculated at 1% decomposition. With increasing levels of decomposition, the activation level also increased. Since the plot in Figure 3 displays the material's lifetime (i.e., time intervals spanning minutes to centuries) versus failure temperature, selected values for lifetime allow an extrapolation of the failure temperature. For example in the Viton rubber samples, a 1000 hour lifetime was estimated to occur at a temperature of ~192°C. Corresponding lifetimes at 1, 10, and 100 hours were ~ 291, 259, and 220°C, respectively at 1% decomposition levels. Additional material lifetime values are easily calculated by the software at the higher conversion levels. At these higher levels of decomposition, correspondingly higher values for failure temperature were computed. The calculated failure temperatures for Viton rubber at these higher decomposition levels were ~40 to 60°C greater than those found for the 1% levels. These results suggest that thermal failure lifetimes, as determined by this methodology, are very dependent on decomposition levels. When conservative values for thermal failure lifetimes are required for the material, the lower decomposition levels should be chosen. Additionally, the temperatures that were calculated for the material to exhibit a 1000 hour lifetime could be used to represent a conservative value.

In order to test the reasonability of the failure temperatures obtained by TGA, a comparison with readily available literature data for elastomer lifetime such as the Parker O-ring Handbook (Parker Seal Group 1991) and SNL reports (Bronowski 1995) was made. These sources reported that a 10 hour service life for Viton rubber can be expected at a temperature of ~240°C. From the above discussion, thermoanalytical testing predicted a 19°C higher failure temperature (259 vs. 240°C) for a 10 hour service life. Since the experimentally determined activation energies are sensitive to experimental parameters such as sample morphology, sample size, and instrumental variables, the relatively close agreement of predicted lifetime and failure temperatures for these preliminary experiments is encouraging.

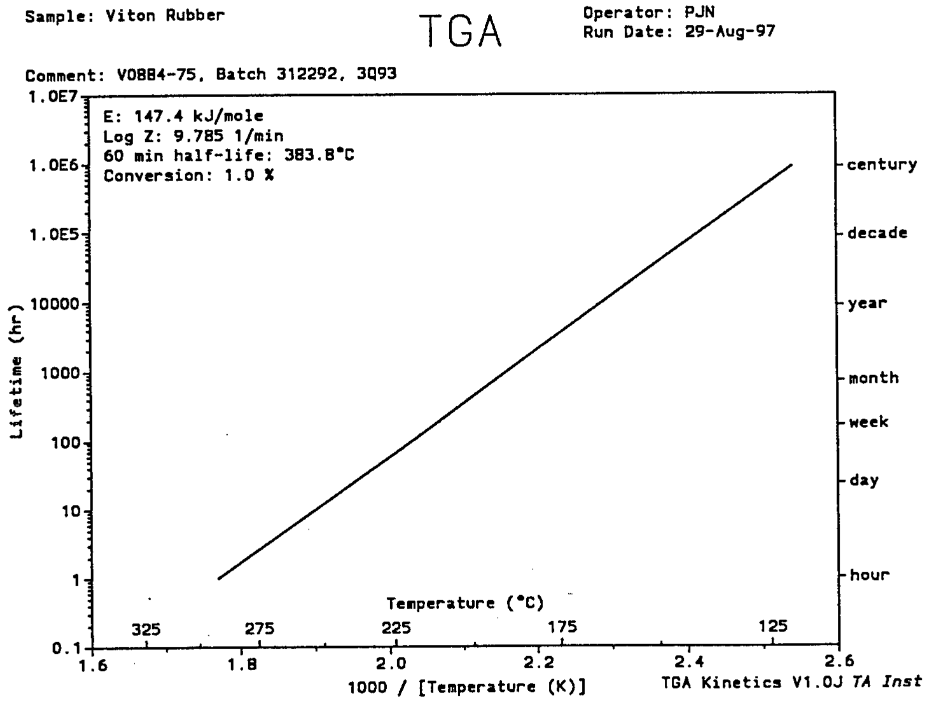

Figure 3. Predicted lifetime plot for Viton rubber at 1% conversion in air.

The previous discussions have concentrated on Viton rubber; subsequent discussions will describe the results obtained for silicone and EPDM rubber. A tabulation of the activation energies and the predicted lifetimes for the other two elastomeric materials, silicone and EPDM rubber, is given below in Table 1. The approximate temperature values appearing in the parentheses are those listed in the Parker O-ring Handbook (Parker Seal Group 1991). Since the methods by which these temperature values were developed are not known, it is assumed that some conservatism is applied by the o-ring manufacturer's to the published seal-life data.

Table 1. Activation Energies and Predicted Lifetimes for Elastomers

Materials (Conversion)	**E_a (kJ/mole)**	**Lifetime at Temperature (°C)**			
		1 h	**10 h**	**100 h**	**1000 h**
Silicone Rubber (5 %)	207	340 (320*)	308 (270)	276 (250)	251(230)
Viton Rubber (1%)	147	291 (290)	259 (240)	220 (230)	192(200)
EPDM (5 %)	129	258 (250)	218 (200)	184 (170)	154(150)
EPDM - 3.6 Mrad (5 %)	119	250 (250)	209 (200)	175 (170)	144(150)
EPDM - radiation and chemical exposure (5 %)	101	250 (250)	201 (200)	164 (170)	130(150)

*Numbers in parentheses are the reported lifetimes of the material at these approximate temperatures given in the Parker O-ring Handbook (Parker Seal Group 1991).

For silicone rubber, the higher activation energy reflects a greater high temperature stability for this material. The computed lifetimes for this material ranged from 1000 hours at 251°C to 1 hour at 340°C in air. However, note that the predicted temperatures are significantly higher than the recommended service life of this material reported by the manufacturer. As can be seen from the data in Table 1, the computed temperatures from TGA were up to 40°C higher than the manufacturer's recommendations for silicone rubber. In the case of EPDM rubber, the lower activation energy calculated for this material indicates a lower thermo-oxidative resistance. The resulting predicted lifetimes were at correspondingly lower temperatures. They ranged from 1000 hours at 154°C to 1 hour at 258°C in air. Also note the closer agreement between the computed lifetimes and those reported by the manufacturer of the material.

The effects of exposure to radiation and chemicals on EPDM were evaluate at relatively high radiation doses, long exposure time, and relatively high temperatures. To evaluate the effect of radiation on the predicted lifetime of an elastomer, an EPDM rubber sample that had received a dose of 3.6 Mrad (36 kGy) of gamma radiation and then held at 60°C for 180 days was studied first. Another EPDM rubber sample, exposed to 36 kGy of gamma radiation followed by exposure to a caustic chemical at 60°C for 180 days, was used to see what effect these environmental conditions would have on predicted lifetime of the elastomer. The rational for the use of these specific environmental conditions is given in greater detail in a companion paper at this conference (Nigrey and Dickens 1998).

For the irradiated EPDM samples, Table 1 shows that a lower activation energy was calculated. The lower activation energy results in a predicted material lifetime at lower temperatures. These results point to a lower thermal stability in the irradiated EPDM material. The EPDM that received radiation and chemical exposure showed even lower activation energies and material lifetimes than EPDM which had only been irradiated. Correspondingly lower temperatures were observed for this material for 1, 10, 100, and 1000 hour lifetimes. While the temperatures for a 1 hour lifetime were the same between the irradiated EPDM and EPDM irradiated and chemically exposed samples, the temperatures were significantly lower between these samples at longer lifetimes. The greatest difference in values were at the 1000 hour lifetime. For example, EPDM exposed to radiation and chemicals had a 14°C lower 1000 hour lifetime than samples exposed to only radiation. Both of these materials had significantly lower temperatures at lifetimes greater than 10 hours. These results are consistent with increased material degradation at increasingly aggressive environmental exposure.

CONCLUSIONS

Since seals play such an important role in providing containment for RAM in transportation packaging, the ability to readily determine the reliability of elastomer seals is very useful. Specifically, the ability to quickly determine kinetic data that would enable the prediction of elastomer lifetimes is important. Various thermoanalytical methods have been used in the rubber industry to predict the service life of elastomers. In this study, TGA has been applied to silicone, Viton and EPDM rubber. The studies have shown that TGA accurately predicts the relative order of thermo-oxidative stability of these three materials from the calculated activation energies. The greatest thermal stability was found in silicone rubber followed by Viton and EPDM rubber. The calculated lifetimes for these materials were in acceptably close agreement with published values. The preliminary results also accurately reflect decreased thermal stability and lifetime for EPDM rubber exposed to radiation and chemicals. These results suggest TGA provides a rapid method to evaluate material stability. Additional studies are indicated to determine whether the TGA results correlate with leak-rates determinations under similar conditions.

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