Thermal degradation studies of a polyurethane propellant binder

M. Celina, A. C. Graham, K.T. Gillen, R. A. Assink, L. M. Minier

Sandia National Laboratories, Albuquerque, NM 87185-1407, USA

Abstract
The thermal oxidative aging of a crosslinked hydroxy-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) based polyurethane rubber, used as a polymeric binder in solid propellant grain, was investigated at temperatures from 25°C to 125°C. The changes in tensile elongation, polymer network properties and chain dynamics, mechanical hardening and density were determined with a range of techniques including modulus profiling, solvent swelling, NMR relaxation and O₂ permeability measurements. We critically evaluated the Arrhenius methodology that is commonly used with a linear extrapolation of high temperature aging data using extensive data superposition and highly sensitive oxygen consumption experiments. The effects of other constituents in the propellant formulation on aging were also investigated. We conclude that crosslinking is the dominant process at higher temperatures and that the degradation involves only limited hardening in the bulk of the material. Significant curvature in the Arrhenius diagram of the oxidation rates was observed. This is similar to results for other rubber materials.

Keywords: HTPB/IPDI, thermal polymer degradation, rubber aging, propellant binder aging, heterogeneous degradation, degradation profiles, modulus profiling, oxygen diffusion effects, oxygen consumption
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1 Introduction

The degradation of polymers often occurs as a non-uniform or heterogeneous process due to diffusion-limited oxidation (DLO), migration of antioxidants, morphological variations or restricted mobility of reactive intermediates in a free radical oxidation process. It is important to consider the development of such heterogeneities to better understand the underlying aging mechanism. The measurement of degradation profiles has been attempted with a variety of methods [1]. Some of the techniques that we have applied in the past to study heterogeneous or diffusion-limited oxidation of polymers are modulus profiling [2,3,4], density profiling [5,6] and more recently fourier transform infrared (FTIR) microscopy [7,8].

We are currently involved in an extensive program to study the thermal degradation of various elastomers, commonly used as propellant binders or seal and o-ring materials. In earlier studies of DLO-effects in thermal environments we showed that modulus increases caused by oxidation could govern mechanical property lifetimes [3,4]. The time-development of degradation profiles could be predicted using a model [4,6] based on the free radical autoxidation process [9], oxygen permeability and consumption rates [10]. The highly sensitive measurement of oxidation rates also allowed for lifetime extrapolation attempts [10,11,12]. At the surface of samples, (important for thin material studies) additional edge effects can occur where considerable hardening (evidence of secondary degradation mechanisms) may not correspond to the same magnitude of chemical oxidation [7,8].

Despite the importance of hydroxy terminated polybutadiene (HTPB) based binders for the manufacture of solid rocket propellants and the obvious concern about property changes due to aging, very few comprehensive investigations on binder degradation appear to be available in the open literature. The binders are highly susceptible to oxidation due to considerable unsaturation in the polymer structure and easy access of atmospheric oxygen (open core configuration of rocket motors). The lifetimes of some propellants may in fact be relatively short. For a HTPB/DDI (dimethyl diisocyanate) binder system incorporating copper based burn rate modifiers a linear extrapolation of high temperature aging data (O₂ consumption based on weight increase, and surface hardening) was correlated with actual data from propellants stored at ambient conditions. For the copper chromite containing
material relative lifetimes of only 7.5 years at 20°C were predicted [13]. The degradation was also noted as being subject to surface initiation. In two studies, different HTPB based propellants were investigated using primarily uniaxial tensile measurements (tensile and relaxation modulus data) and gel analysis (crosslinking) to assess aging at relatively low temperatures (ambient to 65°C) [14,15]. Mechanical properties were found to change linearly with logarithmic aging time [14,15]. Unfortunately, no failure criterion for the propellant was presented. A misleading activation energy of only ~21 kJ/mol was determined for the temperature dependence of the relative degradation rates [14]. An Arrhenius analysis based on the determination of relative rate constants using Δlog(time) is not appropriate for determining the activation energy of the degradation process, since the different slopes of these plots do not permit a time-temperature superposition. It was suggested that the bonding agent in the propellant may influence the rate of degradation and that there was a chemical reaction between the ammonium perchlorate and the polymeric binder [15]. In another investigation of mechanical properties for a similar propellant aged between 25°C and 65°C, identical time dependence was chosen, despite tremendous scatter in the data [16]. A further study compared HTPB based propellants via tensile mechanical (TMA) and dynamic mechanical analysis (DMA) and it was noted that the degradation proceeded faster at the surface of the material [17]. Of interest has also been to investigate the oxidation sensitivity of the HTPB or CTPB (carboxyl terminated) prepolymer during storage [18,19] and the high temperature decomposition of polybutadiene [20] or cured resins [21,22]. In general, the mathematical description of the degradation of energetic materials, by kinetic models can be highly complex, due to the competition of various reactions with differing kinetic order and autocatalysis [23].

The objective of the current work is to characterize the chemical and physical processes associated with the aging of the propellant binder and to provide a basis for predicting and measuring its performance as a function of age. In addition, we sought to determine whether other constituents in the propellant, such as oxidizer (ammonium perchlorate (AP)) or aluminum powder, affect the degradation.
2 Experimental

2.1 Material
The polyurethane (PU) rubber investigated is a cured hydroxy-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) polymer. Samples of the uncured resins were provided by industry (Elf Atochem and Hüls America Inc.). The HTPB resin has a relatively low concentration of reactive hydroxyl groups (~0.74 meq-g⁻¹) that corresponds to an equivalent weight (EW) of ~1350 grams. With an approximate functionality of 2.1 this corresponds to an average molecular weight of M ~2835 g-mol⁻¹. These values are very similar to those reported in other studies for the HTPB type R45M with M ~2800 g-mol⁻¹ and EW ~1370 g [21], or EW ~1300 g [22]. The IPDI has a published isocyanate (NCO) concentration of ~37.65%, which equates to a relative functionality of ~1.992 (M_NCO = 42.017 g-mol⁻¹, M_{IPDI} = 222.287 g-mol⁻¹) and to an equivalent weight of 111.59 grams [24]. Due to the rather low concentration of reactive hydroxyl groups in the HTPB resin, a high ratio of HTPB to IPDI (~12.1 to 1) per weight is required to achieve molar conversion with the IPDI. Both components were mixed in a 1.0 molar reactivity ratio and include 1% Vanox MBPC antioxidant (2,2’-methylene-bis (4-methyl-6-ℓ-t-butylphenol) in the HTPB. The resulting resin was thermally cured for 1 week at 65°C to obtain sheets of 2 mm thickness using teflon coated molds to allow for removal after curing.

2.2 Thermal aging
Thermal aging of rubber strips (approximately 6 mm wide and 150 mm long) cut from the sheets (~2 mm thickness) was carried out in temperature-controlled (±1°C stability), commercial, air-circulating aging ovens under ambient atmospheric conditions (~630 mmHg in Albuquerque).

2.3 Oxygen consumption (uptake)
The consumption of oxygen as well as the formation of CO and CO₂ during thermal aging was determined using a gas chromatography (GC) apparatus. Details of this approach have been described before, and the technique has been established as a simple routine analysis [10]. Known amounts of the PU-rubber were sealed in ampoules of known volume with an initial O₂ pressure calculated to give 150 mmHg at the relevant aging temperature. The containers were then aged for times that led to consumption of approximately 30% of the O₂. This resulted in an average partial pressure of O₂ during each aging exposure of ~13
cmHg which is roughly equal to ambient air conditions in Albuquerque. At each aging temperature, the same sample was used sequentially to obtain time-dependent results. By varying aging times and the ratio of sample to gas volume in sealed ampoules, a large sensitivity range ($\phi \sim 10^{-13} - 10^{-8}$ mol·g·s·l) is easily obtainable [10,11]. This sensitivity allows for measurements to be made down to ambient temperature within a reasonable experimental time frame (a few months for the current binder material).

2.4 Permeability measurements
Oxygen permeation experiments were performed on a disk sample of approximately 64 mm diameter and 2 mm thickness using a custom-modified commercial Oxtran-100 coulometric permeation apparatus (Modern Controls, Inc., Minneapolis, MN, USA), which is based on an ASTM standard [25]. To allow for high temperature analysis a modified sample holder was positioned in a common laboratory oven. More details on this instrumentation and its application to various materials will be published separately.

2.5 Tensile testing
Tensile tests were performed with an Instron Table Model Testing Machine (Model 1000) equipped with pneumatic grips and an extensometer. The strain rate was 12.7 cm/min for an initial crosshead separation of 5.1 cm and the stress/strain data up to failure were determined.

2.6 Modulus profiling
Our modulus profiler apparatus, which monitors the penetration of a paraboloidally-shaped tip into a polymer sample, has been described in detail elsewhere [2,3], with the exception that the current version is now completely automated [7]. Penetration data are converted to inverse tensile compliance values, which approximate the modulus. The instrument allows for convenient scanning across a sample with a resolution of approximately 50 μm. The rubber specimens were cut in cross-section, three identical samples were positioned side-by-side [2] and encapsulated in epoxy resin to improve sample handling, and mounted in a custom-made clamp. The surface was metallographically polished, and the modulus profile obtained by measuring individual modulus data across the sectioned surface of the sample.
2.8 Density determination
The density was determined using the Archimedes approach [26,27], where the sample (~50 mg) is weighed in air and then in isopropanol on a balance with a reproducibility of better than 10 μg. The density is calculated from the weight difference between the two measurements [27].

2.9 Solvent swelling analysis
Solvent swelling experiments [27,28,29] were carried out by first exposing a known weight of sample (w₀) 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 (wₔ) determined. The ratio of wₔ/w₀ was defined as the solvent-swelling factor. The amount of insoluble material (gel content) was obtained by comparing the final weight with the initial weight after drying the swollen samples under vacuum (wₕₐₙₐl) (i.e. % gel = 100 wₕₐₙₐl/w₀).

2.10 NMR
The ¹H relaxation times were measured on a Bruker DRX spectrometer at 399.9 MHz using a 5-mm broadband probe for liquid samples. The T₁ relaxation times were measured using an inversion recovery pulse sequence while the T₂ relaxation times were measured using a spin-echo pulse sequence. The ¹³C cross-polarization spectra were recorded on a Bruker AMX spectrometer at 100.6 MHz equipped with a 7-mm MAS probe. The total spectra intensities of non-spinning samples were measured for 10 to 12 contact times and fitted with the standard cross-polarization relaxation function.

3 Oxidative degradation of HTPB/IPDI rubber

3.1 Oxygen consumption and permeation measurements
We determine O₂ consumption rates (ϕ) and permeability coefficients (Pₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐportion of the material at each temperature, in agreement with previous results for other rubber materials [4,8,10,11]. We expect the observed
increase in the oxidation rates beyond the lifetime of the material to be related to a complete consumption of the antioxidant. At this point the mechanical properties such as tensile elongation or modulus have been severely affected (as discussed later).

The $O_2$ permeability coefficient ($P_{\infty}$) was determined at temperatures up to 115°C. We determine the permeability by correcting the measured permeation data for the fraction of oxygen that is consumed in the material due to oxidation during the permeation process itself. This is particularly important at elevated temperatures and for thick samples, and is achieved via an iterative process. Further discussion of this approach will be published separately. This iterative data analysis requires knowledge of the oxygen consumption rate at all temperatures and a value for $\beta$, a factor that combines rate constants, solubility and $O_2$ partial pressure, and which essentially describes the sensitivity of oxidation rates on $O_2$ pressure [4]. For our permeability calculations we used $\beta = 10$, a value that was obtained from preliminary pressure-dependent oxygen consumption rate measurements, and is larger than $\beta$ values on the order of 1 observed for other rubber materials [4]. The measured permeability data (corrected for $O_2$ consumption) for the PU-rubber versus temperature are shown in Fig. 2. At the higher temperatures (>95°C) the permeation coefficient is highly time dependent. Oxidation leads to a reduction in the permeability coefficient. Since the experiments require at least a few hours to reach equilibrium, we extrapolated time-dependent permeability data to zero time (data included as triangles in Fig. 2). For a filled material (binder loaded with other propellant constituents) we would expect the permeability to be proportionally lower.

### 3.2 Diffusion-limited oxidation and predicted degradation profiles

The competition between oxygen consumption (chemical oxidation) and supply of oxygen through diffusion (physical process of $O_2$ permeation) in the material determines the magnitude of DLO-effects. For thick samples and relatively high values of $\phi$ or equally, low values of $P_{\infty}$, the resulting degradation may be a highly heterogeneous process. A first degree estimation of the importance of DLO-effects at various temperatures is obtained by calculating the critical sample thickness ($L_{90\%}$) below which DLO-effects are insignificant (90% of homogeneous oxidation). We use equation 1, where $\alpha_c$ is a factor related to sample geometry ($\alpha_c \sim 70$ for $\beta=10$, see Figure 10 in ref. [6]), and $p$ is the partial pressure of $O_2$ at the sample surface (13.2 cmHg in Albuquerque) [3,4,6]. A plot of the critical sample thickness ($L_{90\%}$) versus temperature is shown in Fig. 3a. We note that the oxidation of the
binder for thick samples will be diffusion limited at elevated temperatures (i.e. \( L_{90\%} = -3 \) mm at 110°C), and even at ambient temperatures the oxidation is expected to proceed heterogeneously for samples of more than ~ 50 mm thickness.

\[
L_{90\%} = \sqrt{\frac{\alpha_c \beta \beta_0}{\beta + 1}}
\]  

(1)

Knowing the most important parameters describing the oxidation of the material (\( \phi, P_{ox}, \beta, L \) (thickness)) allows for modeling (data in Table 1) of expected oxidation profiles [4]. Some examples of predicted profiles for different samples are shown in Fig. 3b. At 95°C a sample of 0.5 cm thickness ages homogeneously, whereas a 2 cm sample will develop a strong diffusion-limited profile. At 50°C there is generally less oxidation but for thicker samples (i.e. 10 cm) heterogeneity can still occur. For the latter two samples, these predictions imply that the oxidative degradation will be confined to the exterior parts and will proceed essentially without the contribution of atmospheric \( O_2 \) in the interior. Similar profile formation is expected for filled materials, since lower permeability coefficients should be counterbalanced by a reduction in oxidizable polymer (lower \( O_2 \) consumption rates per gram of material).

<table>
<thead>
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<th>Table 1: Modeling parameters</th>
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<tr>
<td>Temperature</td>
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<td>( \phi ) [mol/g-s]</td>
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<tr>
<td>( P_{ox} ) [ccSTP/cm-s-cmHg]</td>
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It should be noted that the above discussion utilizes the initial values for consumption and permeability at each temperature. In the final stages of the degradation, the oxidation rate can increase substantially, as seen for the 125°C and 110°C data in Fig. 1. Simultaneously, the extensive oxidation corresponding to these increases can lead to reductions in the oxygen permeability coefficient [4] as observed for the permeation measurements at the high temperatures. This combination will result in a significant lowering of the \( L_{90\%} \) values. Assuming that the permeability remains unchanged at 110°C, for instance, we can
use the changing oxygen consumption results in Fig. 1 to predict that $L_{90\%}$ is ~3.3 mm initially, but that it drops to ~2 mm after 8 days, ~1.5 mm after 12 days and ~0.7 mm after 15 days. These drops will even be more significant, since the permeability coefficient decreases by a factor of ~3 within a day and then levels off (equivalent in a further reduction of $L_{90\%}$ by a factor of ~0.6). It is clear that aging of a 2 mm thick sample at 110°C will initially be predicted to be homogeneous, but important DLO effects should appear after approximately a week of aging.

### 3.3 Modulus and tensile elongation changes

While the measurement of oxidation rates follows a chemical change, it is important to measure properties that reflect mechanical aging in the material. We have chosen modulus profiling and tensile elongation, which are related to material hardening. The modulus data obtained for three different temperatures and aging times are shown in Fig. 4. The modeling discussed above predicted the absence of important DLO effects initially at all three temperatures. This is consistent with the relatively uniform increase in modulus observed over most of the early-time samples at each temperature. The degradation of the relatively soft material (~0.7 MPa for unaged material) surprisingly does not involve the extensive hardening in the bulk of the sample normally observed for other rubbers [4,7,8]. Later in the aging (close to complete tensile failure), enhanced hardening clearly occurs near the surface of the samples at all three temperatures. Increasingly important DLO effects are caused by increases in the consumption rate coupled with decreases in permeability, especially at the highest temperature. Other surface-related mechanisms also appear to participate for longer aging times at the lower temperature (80°C), perhaps involving preferential loss of antioxidants or other unknown mechanism. In particular, we note a dramatic increase in the surface modulus during the final stages of degradation at 80°C.

The best approach to determine the temperature dependence (activation energy) of the modulus changes or any degradation parameter is achieved by a time-temperature superposition. The advantage of this approach is that it utilizes the complete data set and does not require explicit knowledge of an underlying kinetic model (i.e. 1st or 2nd order kinetics) [10,11]. We first select the lowest temperature (80°C) as the reference temperature ($T_{\text{ref}}$). If increasing the temperature to $T$ equally accelerates all of the reactions underlying the oxidation, than the time behavior of the moduli changes will be accelerated by a constant multiplicative shift factor, $a_T$. For each higher temperature, we empirically
determine the value of $a_T$ that results in the best superposition with the data at $T_{ref}$. Figure 5 shows the superposed results for the moduli increase, both at the surface (Fig. 5a) and in the interior (Fig. 5b) of the binder material with the empirically derived $a_T$ values indicated on the Figure. Since the $a_T$ values are similar for the surface and interior modulus values it is likely that the same kinetic scheme underlies both properties. The corresponding Arrhenius plot of the empirical $a_T$ values used for shifting is shown in Fig. 6 (the $a_T$ values for other parameters are included and will be discussed later). The two modulus results give approximately Arrhenius behavior (linear dependence of log $a_T$ versus inverse absolute temperature) over their temperature range (80°C-125°C); with an activation energy of ~100 kJ/mol for this process. The activation energy ($E_a$) between two temperatures can be easily calculated using equation (2) and the corresponding shift factors.

$$E_a = \frac{R \ln \frac{a_{T_1}}{a_{T_2}}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$  (2)

The measurement of ultimate tensile elongation appears to be considerably more sensitive to the degradation than the modulus growth. A time-temperature superposition of the elongation data reveals a rapid decrease as shown in Fig. 7 and a temperature of 65°C is the lowest condition at which this property can be monitored within a reasonable experimental timeframe. The shift factors for this superposition are included in Fig. 6 and yield ~120 kJ/mol for the high temperature range. However, evidence of curvature (deviation to lower activation energy) is observed for the 80 and 65°C data. A failure criterion of 50% residual absolute elongation was chosen to obtain time values that would indicate a constant level of degradation and allow comparison with modulus changes or other properties. The resulting failure time (relative lifetime) of ~170 days at 80°C is noted on the modulus plots in Fig. 5. Despite some edge hardening, this corresponds to only limited hardening throughout most of the sample (see bulk modulus changes in Figs. 4 and 5), which is also apparent for other temperatures in the superposition analysis. Considerably larger changes in modulus are normally observed for other rubbers [4,7,8].
3.4 Density changes and polymer network analysis

The thermal degradation of polymers is often accompanied by significant changes in the material density, a simple property that is easily measured but often ignored in polymer aging studies. We have recently demonstrated that density measurements can be a suitable approach to identify mechanistic differences during aging [27] and to determine induction periods [30]. Density increases are due to elimination of organic volatiles (increasing the weight of higher density fillers in filled materials), oxidation (incorporation of O₂ as a heavier element) and crosslinking of the polymer network (shrinkage [31]). The degradation of the binder over the material lifetime is accompanied by an increase of more than 2% in density. A superposition of the density data, shown in Fig. 8a yields an activation energy of ~117 kJ/mol; the corresponding plot of the αT shift factors is included in Fig. 6. Important is the fact that density changes may be associated with volumetric shrinkage. We measured this effect at two temperatures and observed that the density increase is accompanied by shrinkage (see Fig. 8b). Contraction of the binder in a filled polymer may lead to tension in the material, initiate phase separation and thus may be involved in heterogeneous degradation aspects (i.e. micro crack and void formation).

Crosslinking of rubbers during degradation normally leads to a stronger polymer network resulting in a reduction of the average molecular weight between crosslinks. When the degradation is dominated by scission reactions, the opposite occurs leading to a more flexible overall polymer network and the formation of some soluble polymer (i.e. not a totally crosslinked material). The determination of solvent swelling and gel content is a very sensitive technique to follow changes in the polymer network related to crosslinking and scission reactions either in purely thermal [28] or in combined radiation-thermal environments [27,29]. For the binder material investigated here, we would expect that the curing process will result in a relatively ‘weak’ polymer network with the average molecular weight of an -(HTPB-IPDI)₁₀- chain between crosslinks of ~3*10⁴ g-mol⁻¹. This is due to the fact that on average ten HTPB prepolymer molecules are required for one additional functionality (reactive hydroxyl group) to participate in the formation of a three dimensional network. The reaction of the bifunctional IPDI with an HTPB of functionality 2 would only result in a linear polymer chain. The weak nature of the cured resin network is confirmed by the relatively low gel content of ~60% (Fig. 9a) and corresponding large solvent swelling factor (Fig. 9b) for the unaged material. However, the oxidative degradation of the binder at higher temperatures involves considerable crosslinking,
presumably due to free radical reactions involving the high concentration of unsaturation in the polymer. This is evident as an increase in the gel content (from ~60 to 90%, see Fig. 9a) and a reduction in the solvent swelling factor (see Fig. 9b) for aging at 95°C. Initially the gel can absorb ~50 times the amount of solvent (p-xylene) with a reduction to only ~5 times over the relative lifetime at 95°C. Preliminary measurements confirm that crosslinking is the dominant mechanism at temperatures of 80-100°C. We are currently investigating whether this process is equally important at lower temperatures (requires long aging times).

3.5 NMR molecular dynamic measurements
For actual propellant samples, it is more difficult to study changes in mechanical or polymer network properties, since the highly dispersed binder may only represent 10% of the material. A non-destructive spectroscopic technique may be a better approach. We have chosen to evaluate NMR spectroscopic measurements, since NMR relaxation parameters have been shown to be coupled to the physical properties of organic materials [32] and network formation via crosslinking [33]. For preliminary studies, we measured the 1H spin-lattice, T1, and spin-spin, T2, relaxation times as a function of aging for the binder at 95°C. The results, along with the decrease in elongation under the same conditions, are shown in Fig. 10a. After 40 days the elongation decreased to less than 20% of its initial value (mechanical failure criterion). During the same period, the 1H relaxation times show almost no change. Obviously, 1H relaxation times are not a good probe for the binder deterioration. However, it was also shown that the 13C cross-polarization time constant, T_{cp}, can be a sensitive probe of mechanical properties for a wide range of polymers [34]. Marinko et al. used the Maxwell model for viscoelastic materials and a common expression between T_{cp} and the molecular correlation time to derive a relationship between Young’s modulus and T_{cp} [34]. They predicted that the mechanical properties of a material are related to the square of T_{cp}. We confirmed this relationship for a butadiene/natural rubber and silica filled siloxane material. The behavior of T_{cp} for the aged binder is included in Fig. 10a. A plot of the normalized elongation versus normalized (T_{cp})^2 is shown in Fig. 10b. The correlation between the two quantities is encouraging. We are currently continuing to exploit the potential of NMR to probe the changes in molecular chain dynamics that occur with binder aging.
3.6 Influence of other components

A temperature of 65°C is the lowest condition at which mechanical properties (i.e. tensile elongation) can be monitored within a reasonable experimental timeframe; below this temperature any quantification of mechanical aging would necessitate predictive extrapolation. We have repeatedly shown that oxygen consumption measurements are sensitive enough to probe low temperature regions [8,10,11] and may also be suitable to investigate the influence of fillers or other substances in the polymer [7,8]. Fig. 11 shows averaged O₂ consumption rates (represented as per weight of polymer) for the unaged binder (compare with Fig. 1), a preaged binder (25 days at 95°C), and binder samples filled with 50% aluminum powder, 20% ammonium perchlorate (AP) or 5% tepanol (amine based compatibilizer). A sample containing no antioxidant oxidizes ~3 orders of magnitude faster than the stabilized material confirming the action of the antioxidant. We note that the oxidation is dominated by the behavior of the binder, since other constituents or preoxidation of the binder seem to show little or no effect on the relative oxidation rate. Interestingly, the oxidation rates determined for the AP filled sample tend to be somewhat lower than those observed for the pure binder. This suggests that AP may act as a limited oxidation inhibitor, rather than a pro-oxidant or initiator as would be expected from such a strong oxidizer. Thermally induced free radical decomposition of AP in propellants has been observed down to a temperature of 110°C using mass spectroscopy [35,36]. However, chlorine-containing organic compounds are also well known to interfere during free radical polymerization via enhanced radical transfer and termination reactions (radical scavenging) leading to shorter molecular weights [37]. A similar effect may be the reason for the slightly lower oxidation rates. It is obvious that O₂ consumption studies are an excellent approach to investigate the influence of other components in the binder and would allow us to study the effects of other catalytically active substances or burn rate modifiers on the binder degradation. Additional studies on the importance of AP in the binder are continuing.

3.7 Life-time prediction and Arrhenius methodology

In Fig. 11 we also notice that all materials exhibit the same curvature in the Arrhenius diagram emphasizing the underlying dominance of the binder oxidation rates. The oxidation rates at the lower temperatures are clearly larger than would be predicted from a linear high temperature extrapolation. Again, the best approach to determine the temperature dependence of the oxygen consumption data is achieved by using the time-
temperature superposition approach for the complete data set \([10, 11]\). We use integrated oxygen consumption (Fig. 12a) which is proportional to total oxidation and use 25°C as a reference temperature. The shifted superposed data are shown in Fig. 12b and the Arrhenius plot of the corresponding empirical shift factors \((a_T)\) is shown in Fig. 12c. These values result in non-Arrhenius behavior (non-linear dependence of \(\log a_T\) versus inverse absolute temperature) over the complete temperature range. The activation energy at the lower temperatures is approximately 70 kJ/mol and at the higher temperature \(~120\) kJ/mol.

The similarity of the latter activation energy to that found for the decrease in ultimate tensile elongation over the same temperature range suggests that the process responsible for mechanical failure is closely related to total oxidation. Additionally, evidence of curvature in the Arrhenius plot is also observed for the tensile data at 65°C (see Fig. 6). Thus it should be valid to use the temperature dependence of the integrated oxidation \((a_T\) shift factors) to predict the time development of tensile elongation at temperatures below 65°C. This, of course, depends on the assumption that a constant amount of oxidation is required to reach mechanical failure. To demonstrate the potential of oxygen consumption measurements in guiding low temperature extrapolations, their relative shift factors (normalized to a reference temperature of 80°C) have been included in Fig. 6. Using these shift factors to extrapolate from 80°C to 25°C, we predict that the mechanical failure times will be on the order of 80 years. This is shown in Fig. 7 as the upper x-axis. Obviously, more limited loss in elongation will occur much earlier.

The observed curvature in the Arrhenius plots (Fig. 6 and 12c) shows that the oxidation at the lower temperature range proceeds much faster than would be predicted from high temperature extrapolations. This may be related to a change in the predominant oxidation mechanism. We do, in fact, expect different reactions to have varying importance with regard to temperature \([11]\). Some reactions may only be important in one temperature regime. Similar curvatures in Arrhenius diagrams have now been determined for a range of materials \([8, 11]\), as observed for an EPDM (Fig. 13a) and neoprene rubber material (Fig. 13b). It demonstrates the importance of evaluating the widest temperature range possible to more confidently predict and extrapolate degradation behavior. Clearly, the one technique with the highest sensitivity and available temperature range is oxygen consumption.
4 Conclusions
The thermal oxidative aging of a crosslinked hydroxy-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) based polyurethane rubber has been investigated at temperatures of RT to 125°C. This material is commonly used as a polymeric binder in solid rocket propellant grain. From an assessment of diffusion-limited oxidation (DLO) conditions using O₂ permeability and consumption data, we concluded that DLO-effects were not important for the samples investigated. The degradation is easily monitored using tensile elongation, solvent swelling and density measurements. Interestingly, mechanical hardening, measured by modulus profiling, is limited and occurs predominantly at the edges (possible loss of antioxidant) and at the end of the relative lifetime of the material. A change in density is also accompanied by volume contraction. This may be important for filled propellants where phase separation and mechanical integrity are of concern. Changes in ¹³C cross-polarization relaxation times (chain dynamics) measured by NMR spectroscopy correlate with a decrease in tensile elongation. This technique may be applied to a highly filled binder. Using solvent swelling measurements to study the polymer network properties, we conclude that additional crosslinking (increased gel content and reduced solvent swelling) accompanies the degradation at the higher temperatures.

We critically evaluate the Arrhenius methodology that is commonly used with a linear extrapolation of high temperature aging data using extensive data superposition and highly sensitive oxygen consumption experiments. Significant curvature in the Arrhenius plot of cumulative oxidation was observed similar to results for other rubber materials. The activation energy found for O₂ consumption at the higher temperatures is similar to those observed for tensile elongation and density changes, suggesting that oxidation is primarily responsible as a degradation mechanism and that the oxidation behavior at the lower temperatures could be used for predictive purposes. O₂ consumption analysis also shows that other constituents used in propellants do not have a significant influence on oxidation rates. It is an excellent method to characterize the oxidation sensitivity of the binder and is readily extended to ambient conditions to provide increased confidence in predicting the behavior of the binder at low temperatures and long aging times.
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References


Figures

Fig. 1  Oxygen consumption rate data for the polyurethane rubber.

Fig. 2  Oxygen permeability measurements.

Fig. 3  Diffusion-limited-oxidation predictions, a) critical thickness for >90% homogeneous oxidation versus temperature and b) theoretical oxidation profiles for samples at 95°C and 50°C.

Fig. 4  Development of modulus profiles at different temperatures.

Fig. 5  Time-temperature superposition of the modulus changes for both the sample edge and interior (empirical shift factors noted for each temperature).

Fig. 6  Arrhenius plot of the time-temperature superposition shift factors for various degradation parameters.

Fig. 7  Time-temperature superposition of tensile elongation results (empirical shift factors noted for each temperature).

Fig. 8  a) Time-temperature superposition of the changes in bulk density (empirical shift factors noted for each temperature) and b) associated material shrinkage at 110°C and 95°C.

Fig. 9  Changes in the network properties at 95°C, a) gel content and b) swelling data.

Fig. 10  NMR relaxation measurements for samples aged at 95°C. a) 1H relaxation times (1/T1, T2) and 13C cross polarization relaxation time (Tm), and b) normalized elongation versus the normalized square of the 13C cross polarization time.

Fig. 11  Oxygen consumption rates of the binder and influence of other components.

Fig. 12  Superposition of O2 consumption data. a) integrated consumption, b) time-temperature superposition and c) Arrhenius plot of the corresponding shift factors (αf).

Fig. 13  Consumption rates for other rubber materials showing non-linear Arrhenius behavior a) EPDM and b) neoprene.
![Graphs showing edge and interior modulus as a function of time at different temperatures.](image)

- **Graph (a):**
  - circles: 125°C ($a_T = 45$)
  - inverted triangles: 110°C ($a_T = 15$)
  - squares: 95°C ($a_T = 3.5$)
  - triangles: 80°C ($a_T = 1$)
  - 50% residual elongation

- **Graph (b):**
  - circles: 125°C ($a_T = 44$)
  - inverted triangles: 110°C ($a_T = 17$)
  - squares: 95°C ($a_T = 3.6$)
  - triangles: 80°C ($a_T = 1$)
  - 50% residual elongation

Time [d] at $T_{ref.} = 80°C$
a) 125°C ($a_T=67$)  
   110°C ($a_T=16.5$)  
   95°C ($a_T=3.9$)  
   80°C ($a_T=1$)  
   65°C ($a_T=0.29$)

b) 110°C  
   95°C

Density [g/cm³] vs. Time [d] at $T_{ref.}=80°C$

Volume change [%] vs. Time [d]
rates as per gram binder

\[ O_2 \text{ uptake rate [mol/g-s]} \]

- new binder (1%AO)
- preaged binder 25d at 95°C
- binder containing
  - 50% aluminum
  - 20% AP
  - 5% Tepanol

Temperature:
- 125°C
- 110°C
- 95°C
- 80°C
- 65°C
- 50°C
- 37°C
- 25°C

\[ 1000/T \text{ [1/K]} \]