Polymer aging techniques applied to degradation of a polyurethane propellant binder

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Abstract

The oxidative thermal aging of a crosslinked hydroxy-terminated polybutadiene (HTPB)/ isophorone diisocyanate (IPDI) polyurethane rubber, commonly used as the polymeric binder matrix in solid rocket propellants, was studied at temperatures of RT to 125°C. We investigate changes in tensile elongation, mechanical hardening, polymer network properties, density, O_2 permeation and molecular chain dynamics using a range of techniques including solvent swelling, detailed modulus profiling and NMR relaxation measurements. Using extensive data superposition and highly sensitive oxygen consumption measurements, we critically evaluate the Arrhenius methodology, which normally assumes a linear extrapolation of high temperature aging data. Significant curvature in the Arrhenius diagram of these oxidation rates was observed similar to previous results found for other rubber materials. Preliminary gel/network properties suggest that crosslinking is the dominant process at higher temperatures. We also assess the importance of other constituents such as ammonium perchlorate or aluminum powder in the propellant formulation.

1 Introduction

We are currently involved in an extensive program to study the thermal degradation of various polymers, such as propellant binders, seal and o-ring materials, and cable insulation. The often heterogeneous degradation of such materials, particularly at elevated temperatures, has been investigated in the past using modulus profiling [1,2,3,4], density profiling [5,6], and more recently fourier transform infrared (FTIR) microscopy [7,8]. Highly sensitive measurements of oxidation rates allow for lifetime extrapolation attempts [9,10,11]. 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.

In this paper we will show that the binder is highly sensitive to oxidation and thus total oxidation levels govern mechanical degradation. Oxidation of the binder is associated with a loss of mechanical properties (tensile elasticity), hardening (modulus increase), densification, shrinkage, crosslinking, and changes in molecular chain dynamics. We discuss the use of oxygen consumption measurements to characterize the aging process. By measuring the oxidation rates as a function of temperature, we are able to predict the overall aging behavior at room temperature. In addition, we determine how other constituents in the propellant, such as oxidizer (AP) or aluminum powder affect the degradation. A more detailed discussion of these studies has recently been submitted for publication [12].

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2 Experimental

2.1 Material
The polyurethane rubber that is commonly used as a binder in solid rocket propellants is based on a hydroxy-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) system. Crosslinking is achieved via an isocyanate/hydroxyl addition reaction yielding a simple polyurethane linkage. Both components were mixed in a 1.0 molar ratio and include 1% Vanox MBPC antioxidant (2,2'-methylene-bis (4-methyl-6-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 Aging and material characterization
Thermal aging of rubber strips (~6-mm wide and 150-mm long) cut from the sheets was carried out in commercial air-circulating aging ovens. Oxygen consumption measurements were carried out using gas chromatography, an established routine analysis [9,10]. Oxygen permeation experiments were performed using a custom-modified commercial Oxtran-100 coulometric permeation apparatus (Modern Controls, Inc., Mineapolis, MN, USA) [13]. Tensile tests utilized an Instron Table Model Testing Machine (Model 1000). Our modulus profiler apparatus, which monitors the penetration of a paraboloidally-shaped tip into a polymer sample, has been described in detail elsewhere [1,2], with the exception that the current version is now completely automated [7]. Density measurements rely on the Archimedes approach, utilizing the weight difference of a sample (~50 mg) weighed in air and then in isopropanol [14,15]. Solvent swelling experiments [15,16,17] were carried out using refluxing p-xylene for a minimum of 24 hours. ^{1}H and ^{13}C NMR relaxation times were measured at 399.9 MHz and 100.6 MHz respectively on a Bruker DRX spectrometer.

3 Oxidative degradation of HTPB/IPDI rubber

3.1 Assessment of heterogeneous degradation
Diffusion–limited oxidation (DLO) effects can be predicted via modeling [4] and require the measurement of O_2 consumption rates (ϕ) and permeability coefficients (P_{ox}). 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. Predictions suggests that DLO-effects will initially be unimportant for temperatures up to 110°C. A slight increase in oxidation rates and a decrease in permeability will lead to more important DLO-effects throughout the aging, and may be the reasons for some of the edge hardening observed for the degradation of the material [12].

3.2 Mechanical property changes
The measurement of ultimate tensile elongation appears to be highly sensitive to the degradation. A time-temperature superposition [9,10] of the elongation data reveals a rapid decrease as shown in Fig. 1a and a temperature of 65°C is the lowest condition at which this property can be monitored within a reasonable experimental timeframe. Below this temperature any quantification of mechanical aging would necessitate predictive extrapolation. The temperature dependence of the empirically derived shift factors (Fig. 1b) yields ~120 kJ/mol for the high temperature range (linear dependence of log(a_T) versus inverse absolute temperature). Some 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 (i.e. ~170 days at 80°C) was chosen to allow 'failure' comparisons with other properties such as modulus. The degradation of the relatively soft binder material (~0.7 MPa for unaged material) surprisingly does not involve the extensive hardening (modulus increase) in the bulk of the sample normally observed for other rubbers [4,7,8]. Despite some edge hardening, the aging induces only limited hardening throughout most of the sample. A time-temperature superposition of the modulus changes at the surface and in the interior of the material is shown in Fig. 2. The empirically derived shift factors for both interior and

surface modulus values are similar and yield Arrhenius behavior over their temperature range (80°C-125°C) with an activation energy of ~100 kJ/mol for this process.
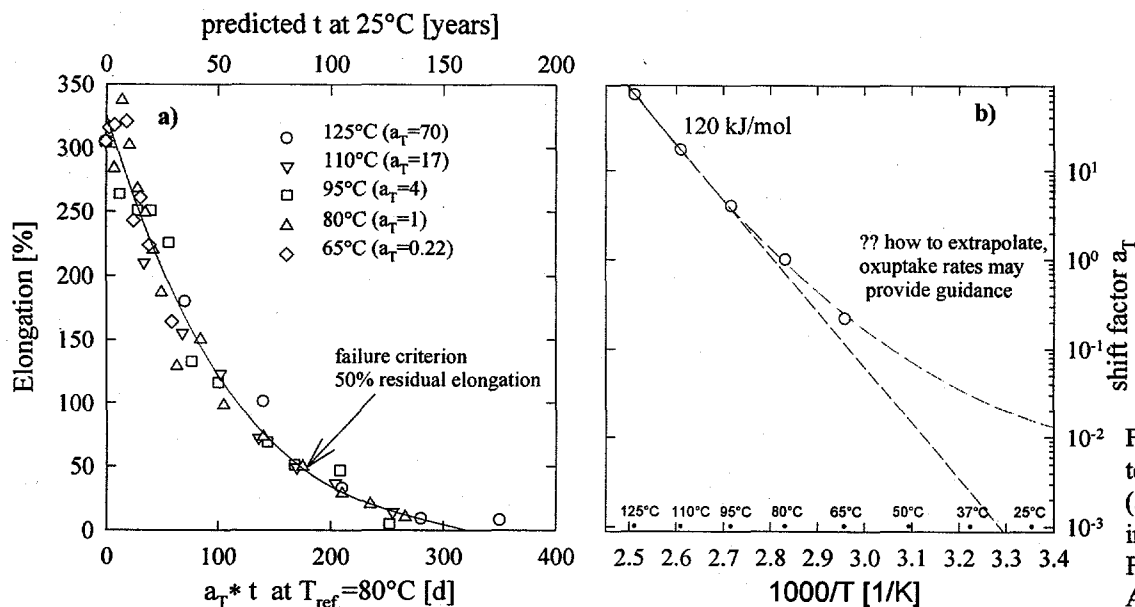

Fig. 1a Empirical time-temperature superposition (a_T factors) of the decrease in tensile elongation.
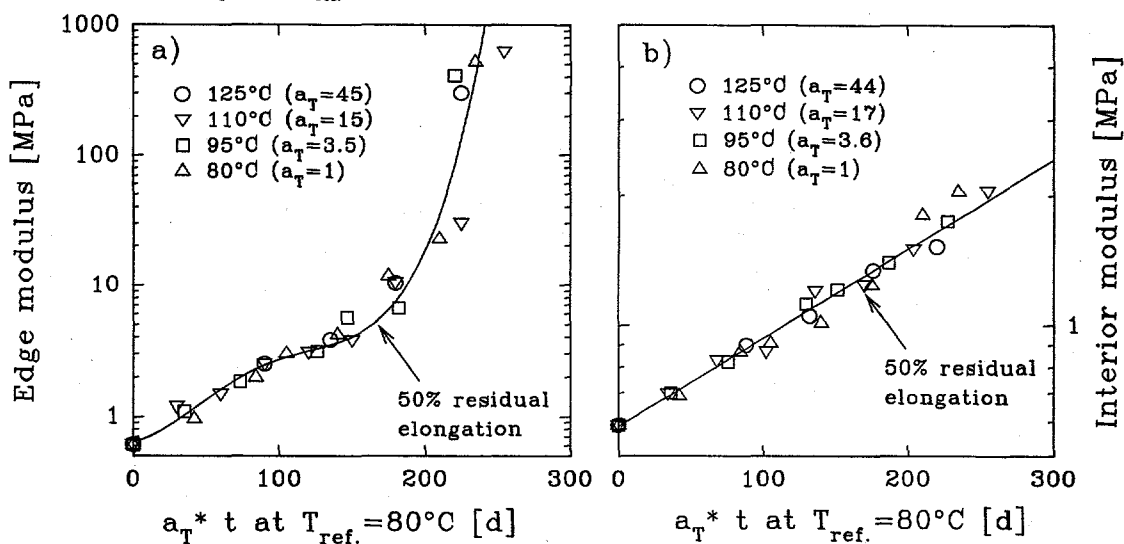Fig. 1b corresponding Arrhenius plot

Fig. 2 Empirical time-temperature superposition of the modulus changes a) at the surface and b) in the interior.

3.3 Density and polymer network changes

The thermal degradation of polymers is often accompanied by significant changes in the material density due to oxidation (incorporation of O_2 as a heavier element) and crosslinking of the polymer network [18,19]. For the binder we find a density increase of ~2% during the material 'lifetime' and similar shrinkage. 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 is normally more important than scission during the degradation of rubbers, 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%) and a reduction in the associated solvent swelling factor. At 95°C the gel can initially absorb ~50 times the amount of solvent (p-xylene) with a reduction to only ~5 times during aging. 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 (long aging times required).

3.4 NMR molecular dynamic measurements

To measure mechanical or polymer network changes in actual propellant samples is more difficult, since the highly dispersed binder may only represent 10% of the material. A non-destructive spectroscopic technique may be a better approach. For that reason, we have chosen to evaluate NMR, since NMR relaxation parameters are coupled to polymer mobility [20,21,22]. For preliminary studies, we measured the ^{1}H spin-lattice (T_1), the ^{1}H spin-spin (T_2) and the ^{13}C crosspolarization (T_{cp}) 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. 3. The correlation between $(T_{cp})^2$ and normalized elongation 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.
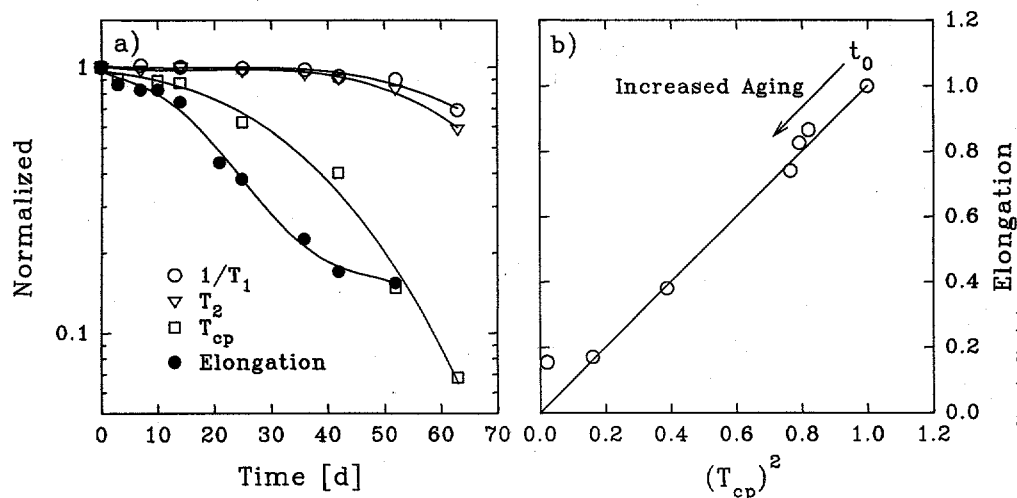

Fig. 3 NMR relaxation and crosspolarization times measurements for aging at 95°C.

3.5 Influence of other components

We have repeatedly shown that oxygen consumption measurements are sensitive enough to probe low temperature regions [8,9,10] and may also be suitable to investigate the influence of fillers or other substances in polymers [7,8]. Fig. 4 shows averaged O_2 consumption rates (represented as per weight of polymer) for the unaged binder, a preaged binder (25d at 95°C), and binder samples filled with 50% aluminum powder, 20% ammonium perchlorate (AP), or 5% tepanol (amine based compatibilizer). The measured oxidation rates are essentially constant over the useful lifetime of the material at each
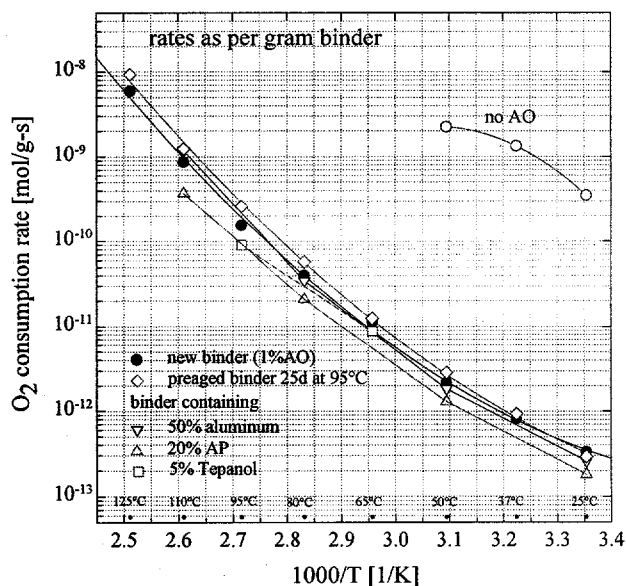

Fig. 4 Oxidation rates of the binder and influence of preaging and other constituents.

temperature, in agreement with previous results for other rubber materials [4,8,9,10]. 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. Additional studies on the importance of AP in the binder are continuing.

3.6 Life-time prediction and Arrhenius methodology

In the Arrhenius diagram of Fig. 4 we notice that all materials exhibit similar curvature which emphasizes the underlying dominance of the binder oxidation rates. As usual, a time-temperature superposition is the best approach to determine the temperature dependence of the oxygen consumption data [9,10,12]. We use integrated oxygen consumption (total oxidation, see Fig. 5a) and 25°C as a reference temperature. The shifted superposed data are shown in Fig. 5b and the Arrhenius plot of the corresponding empirical shift factors (a_T) is shown in Fig. 5c. 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 observed curvature in the Arrhenius plot shows that the oxidation at the lower temperature range proceeds much faster than would be predicted from high temperature extrapolations. Similar curvatures have now been determined for a range of materials [8,10]. 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 greatest available temperature range is oxygen consumption.
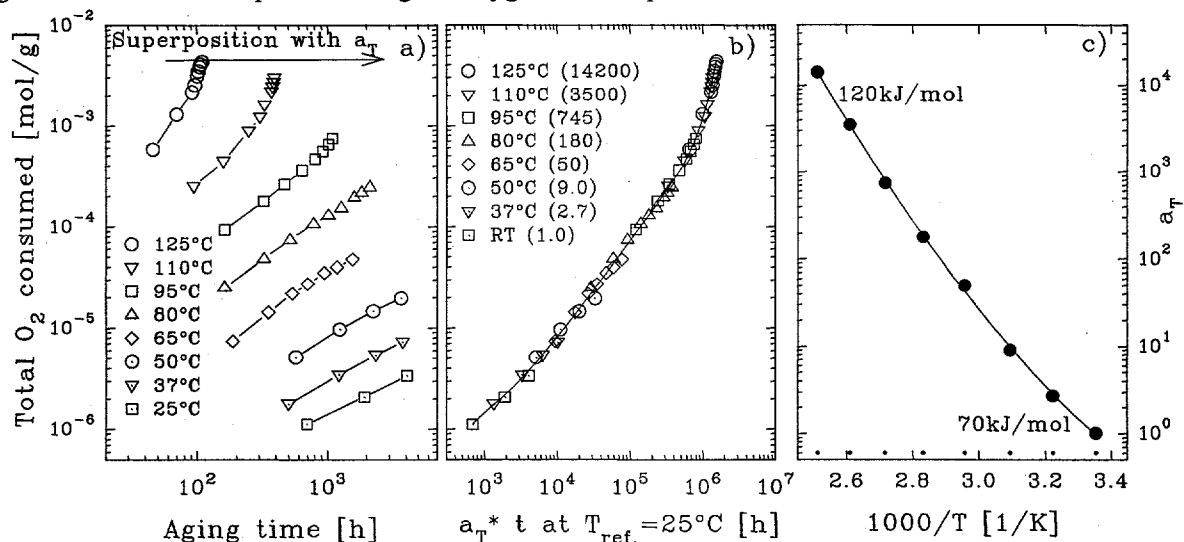

Fig. 5 a) Total oxidation versus time, b) time-temperature superposition and c) Arrhenius plot of empirical a_T shift factors.

The identical activation energies at high temperatures for oxygen consumption (Fig. 5c) and for the ultimate tensile elongation (Fig. 1b) suggests that the process responsible for mechanical failure is closely related to total oxidation. Additionally, some evidence of curvature in the Arrhenius plot is also observed for the lowest temperature tensile data (see 65°C in Fig. 1b). Thus we 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 reasonable assumption that a constant amount of oxidation is required to reach mechanical failure. Using these shift factors to extrapolate from 80°C to 25°C, we predict that the mechanical failure times will be ~80 years. This is shown in Fig. 1a as the upper x-axis. A more limited loss in elongation will occur much earlier.

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. From an assessment of diffusion-limited oxidation (DLO) conditions using O_2 permeability and consumption data, we conclude that DLO-effects were not important for the samples investigated. 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 is density is also accompanied by volume contraction. Changes in ^{13}C cross-polarization relaxation times (chain dynamics) measured by NMR spectroscopy correlate with a decrease in tensile elongation. This technique may be applied to binders from which the AP component has been extracted. 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.

Significant curvature in the Arrhenius plot of cumulative oxidation was observed to be similar to results for other rubber materials. The activation energy found for O_2 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. O_2 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.

Acknowledgments

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