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Development and application of tools to characterize the oxidative degradation of AP/HTPB/Al propellants in a propellant reliability study

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Abstract

The oxidative thermal aging of a cross-linked hydroxyl-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) polyurethane rubber was studied at temperatures between 25 and 125 °C. Changes in tensile elongation, mechanical hardening, polymer network properties, density, O_2 permeation and molecular chain dynamics were investigated as a function of age. The techniques used include solvent swelling, detailed modulus profiling, and NMR relaxation measurements. The Arrhenius methodology, which normally assumes a linear extrapolation of high temperature aging data, is critically evaluated by using extensive data superposition and highly sensitive oxygen consumption measurements. Significant curvature in the Arrhenius diagram of these oxidation rates is observed to be similar to previous results found for other rubber materials that have been evaluated by this technique. Preliminary gel/network properties suggest that cross-linking is the dominant process at higher temperatures. The effect on the oxidation rate of the binder when other constituents found in propellants are present, such as ammonium perchlorate (AP), plasticizer and aluminum powder, is presented. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

A collaborative Memorandum of Understanding (MOU) program between the DoD and Sandia National Laboratories (SNL) of the DOE was established in 1998 to support investigations to improve the fundamental understanding and modeling and simulation efforts of the aging behavior of ammonium perchlorate (AP)/hydroxyl-terminated polybutadiene (HTPB)/aluminized (Al) propellants. The first goal of the collaboration is to identify critical aging processes that occur on a micro-scale and affect propellant safety and performance. The second goal is to provide meaningful data and mathematical descriptions of the processes for use in constitutive models that are to be used in codes that predict reliability. To obtain these goals requires an understanding of the aging processes that takes us beyond the identification of mere empirical trends.

Three critical aging processes are currently the focus of this program. For each of these processes, first-generation models already exist or are being developed that can use and apply the results from this study into the final codes that predict the performance and safety of a propellant with age (Fig. 1). Two areas of study that have been identified as critical aging

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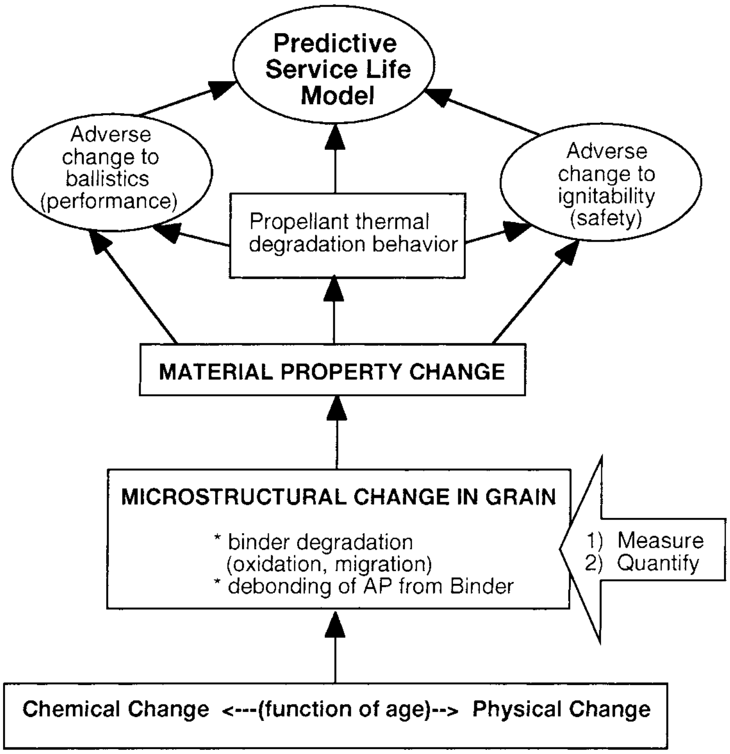

Fig. 1. Project approach involves the development of an understanding of the critical aging processes and the correlation of the processes to the safety and performance characteristics of a composite propellant.

processes are the degradation and oxidation characteristics of the binder and the characteristics of the binder–AP interface. These processes can lead to an increased surface area of the propellant during performance via cracking and dilatation, respectively. The third area of study addresses our concerns with safety performance and reliability of a propellant that has undergone changes in mechanical properties. Thermal decomposition studies are being used to evaluate how physiochemical changes affect the thermal decomposition behavior. These studies will be used to link the physiochemical changes that occur in the binder and at the binder–AP interface to the mechanical changes and then to performance and safety.

In this paper, we will limit the discussion to the findings we have obtained regarding the oxidative degradation of the binder. Detailed studies to characterize the oxidation processes have been conducted on neat samples of the cured binder. Our results show that the binder is highly sensitive to oxidation and that total oxidation levels govern the degradation of the mechanical properties. Similar studies that are conducted on the neat binder samples are currently being conducted on actual propellant samples. Those results will be presented in the future.

The oxidation sensitivity of cured binder samples has been studied between 25 and 125 °C using a unique technique developed at Sandia National Labs. This ultra-sensitive technique measures the rate at which the binder consumes O_2 (chemical oxidation rate). Measurements can be obtained with confidence at low temperatures so that extrapolation from high-temperature oxidation data is unnecessary. The property changes due to oxidation in tensile elongation, polymer network properties and chain dynamics, mechanical hardening and density of the binder are determined with multiple techniques including modulus profiling, solvent swelling, and NMR relaxation measurements. The sensitivity of the instrumentation to measure many of these physical properties is not adequate to detect changes at lower temperatures (<~60 °C) within reasonable experimental timeframes. This is directly related to the much lower oxidation levels under those conditions due to considerably slower oxidation rates. Establishing a correlation between the level of oxidation, which is proportional to the amount of O_2 consumed, and the physical properties allows for the use of O_2 consumption measurements in guiding low-temperature extrapolations from the high-temperature data that cannot be measured with confidence at low temperatures. This is relevant for properties such as tensile elongation and modulus. Mathematical models to describe the rate and effects of oxidation are being developed in this program.

2. Experimental

2.1. Materials

The polyurethane rubber evaluated in this study is made by curing a HTPB prepolymer, obtained from Elf Atochem with an isophorone diisocyanate (IPDI). Cross-linking 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. Methods

2.2.1. Aging and material characterization

Thermal aging of binder 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 [1,2]. Oxygen permeation experiments were performed using a custom-modified commercial Oxtran-100 coulometric permeation apparatus (Modern Controls, Inc., Minneapolis, MN, USA) [3]. Tensile tests utilized an Instron Table Model Testing Machine (Model 1000). Our modulus profiler apparatus, which monitors the penetration of a parabolic-shaped tip into a polymer sample, has been described in detail elsewhere [4,5], with the exception that the current version is now completely automated [6]. Density measurements rely on the Archimedes approach, utilizing the weight difference of a sample (~50 mg) weighed in air and then in isopropanol [7,8]. Solvent swelling experiments [8–10] were carried out using refluxing *p*-xylene for a minimum of 24 h. ^1H and ^{13}C NMR relaxation times were measured at 399.9 and 100.6 MHz, respectively, on a Bruker DRX spectrometer.

3. Discussion

3.1. Assessment of heterogeneous degradation

Diffusion-limited oxidation (DLO)-effects can be predicted via modeling [11] 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 for 2 mm samples suggest 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. Changes in mechanical properties

The measurement of ultimate tensile elongation appears to be highly sensitive to the degradation. A time–temperature superposition [1,2] of the elongation data reveals a rapid decrease as shown in Fig. 2a 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, shown in Fig. 2b, yields ~120 kJ/mol for the high temperature range (linear dependence of $\log(a_T)$

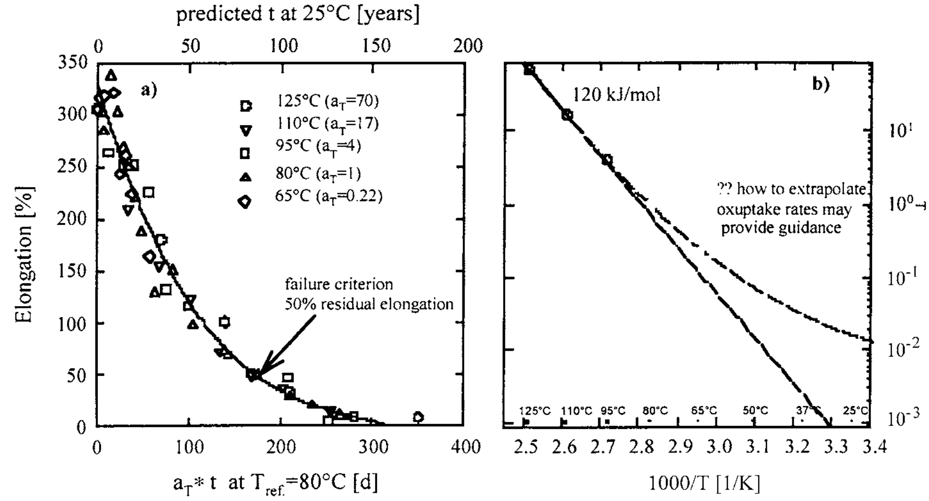

Fig. 2. Empirical time–temperature superposition (a_T factors) of the decrease in tensile elongation are shown in panel a. The corresponding Arrhenius plot is shown in panel b.

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 [6,11,13]. 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. 3. The empirically derived shift factors for both interior and surface modulus values are similar and yield Arrhenius behavior over their temperature range (80–125 °C) with an activation energy of ~100 kJ/mol for this process.

3.3. Changes in the density and polymer network

The thermal degradation of polymers is often accompanied by significant changes in the material

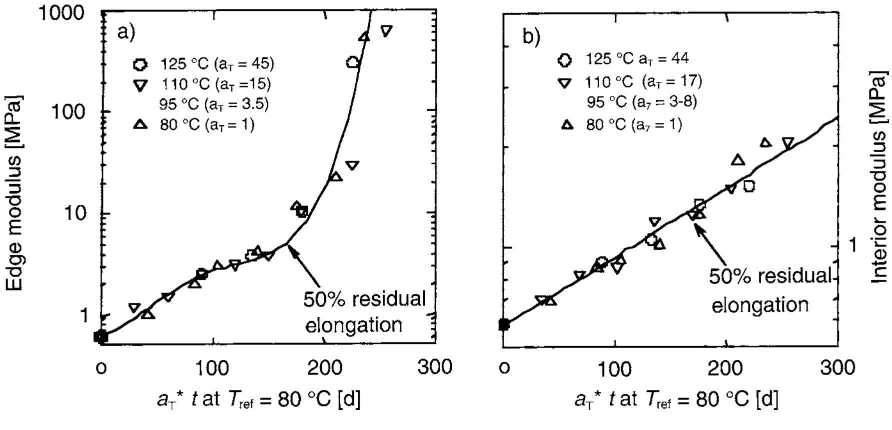

Fig. 3. Empirical time–temperature superposition of the modulus changes: (a) at the surface, and (b) in the interior.

density due to oxidation (incorporation of O_2 as a heavier element) and cross-linking of the polymer network [14,15]. 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). Cross-linking 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 cross-linking 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, at times quantitatively, to polymer mobility [16–18]. A correlation between the polymer chain mobility and the mechanical properties is expected. As a polymer undergoes oxidation, the polymer network will change due to the resulting cross-linking and chain scission reactions. Such reactions will change the polymer network and alter the mobility of the polymer chains, and thus, affect the NMR relaxation parameters. The ^1H spin–spin (T_2) relaxation time is measured as a function of aging for the binder at temperatures between 50 and 125 °C. The results, along with the decrease in elongation and other properties under the same conditions, are shown in Fig. 4. A strong correlation exists between the (T_2) measurements, elongation, and the oxygen uptake results.

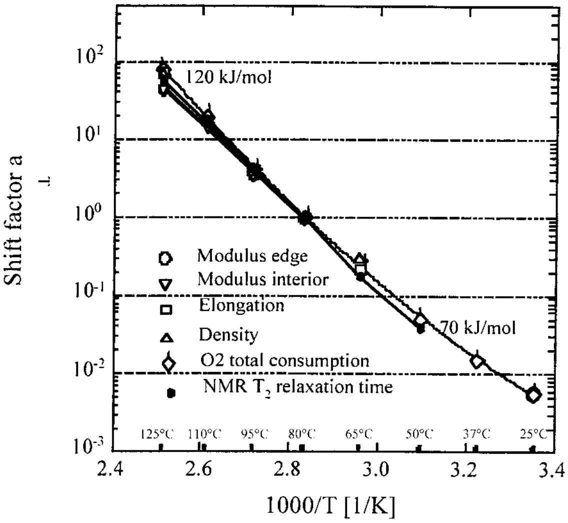

Fig. 4. Shift factors for all property changes and NMR relaxation (T_2) times.

3.5. Influence of other propellant constituents

We have repeatedly shown that oxygen consumption measurements are sensitive enough to probe low temperature regions [1,2,13] and may also be suitable to investigate the influence of fillers or other substances in polymers [6,13]. Shown in Fig. 5 are the averaged O_2 consumption rates (represented as per

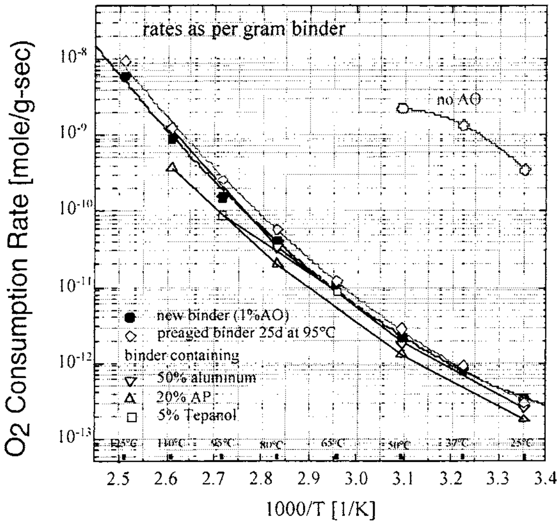

Fig. 5. Oxidation rates of the binder and influence of pre-aging and other constituents typically found in composite propellants.

weight of polymer) for the unaged binder, a pre-aged binder (25 days at 95 °C), and binder samples filled with 50% aluminum powder, 20% AP, or 5% tepanol (amine-based bonding agent). The measured oxidation rates are essentially constant over the useful lifetime of the material at each temperature, in agreement with previous results for other rubber materials [1,2,11,13]. 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 pre-oxidation 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. Predicting service life and Arrhenius methodology

In the Arrhenius diagram of Fig. 6, 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 [1,2,13]. We use integrated oxygen consumption (total oxidation, see Fig. 6a) and 25 °C as a reference temperature. The shifted superposed data are shown in Fig. 6b and the Arrhenius plot of the corresponding empirical shift factors (a_T) are shown in Fig. 6c. 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 [2,13]. 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.

The identical activation energies at high temperatures for oxygen consumption (Fig. 6c) and for the ultimate tensile elongation (Fig. 2b) suggest that the process responsible for mechanical failure be 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. 2b). 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 to 25 °C, we predict that the mechanical failure times

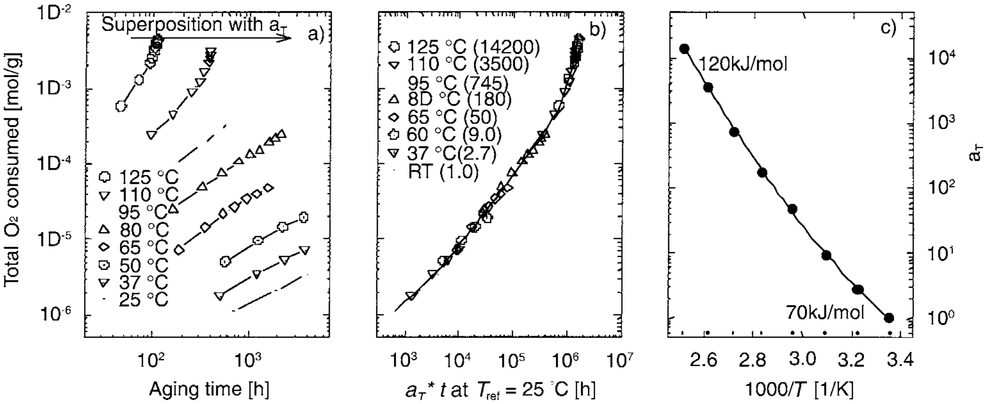

Fig. 6. (a) Total oxidation as a function of time; (b) time–temperature superposition; and (c) Arrhenius plot of empirical a_T shift factors.

will be ~80 years. This is shown in Fig. 3a as the upper *x*-axis. A more limited loss in elongation will occur much earlier.

4. Summary

The thermal oxidative aging characteristics of a cross-linked HTPB/IPDI-based polyurethane rubber has been investigated at temperatures between 25 and 125 °C. From an assessment of DLO conditions using O_2 permeability and consumption data, we conclude that DLO-effects were not important for the samples investigated in the temperature regime of this study. 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 the T_2 relaxation time measurements (chain dynamics) measured by NMR spectroscopy correlate with a decrease in tensile elongation and oxygen consumption. Using solvent swelling measurements to study the polymer network properties, we conclude that additional cross-linking (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.

The chemical nature of the oxidation reaction is being further investigated using Fourier-transform mass spectrometry (FT-MS) and NMR on binder samples that have been aged in $^{17}O_2$ environments. The positioning and functional forms of the labeled oxygen atoms within the polymer will be studied. Furthermore, the correlation of the results of the oxidation studies of the neat binder to the results of the binder when it is formulated into a propellant is currently underway.

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