Bulk Modulus Determination of Solid Propellant Void Content

S. W. Beckwith* and H. B. Carroll†
Hercules Aerospace Division, Magna, Utah

Nitrate ester decomposition in propellant systems leads to a slow buildup of internal gas pressure which potentially can create internal porosity, void formation, and fracture. While related experimental techniques currently available can provide information on ultimate propellant fracture by monitoring gross property changes, few procedures were available to monitor prefracture changes. This study used bulk compressibility measurements to define changes in internal void content (porosity) in solid propellants due to gas evolution. The rate of internal void formation was determined in three propellant families: composite modified double-base (CMDB), crosslinked double-base (XLDB), and nitrate ester polyether (NEPE) systems. Good correlation was found between void content and location in a 16-in. cube and bulk compressibility measurements as well as X-ray examination. Elevated temperature storage at 158 and 176 °F was used to accelerate the void formation in the three propellant systems. The CMDB propellant exhibited the highest void formation rate of the three propellants. The utility of recent developments in fracture mechanics applied to gas generation induced voids was also explored in this study.

Introduction

Gas Evolution

MANY high energy solid propellant systems containing nitroglycerin (NG) and nitrocellulose (NC), undergo a very slow chemical decomposition which generates gases.[1-4] These gases generally dissolve in the propellant or diffuse toward free surfaces in the rocket motor. At elevated temperatures the rate of gas formation may exceed the transport capability, resulting in pressure buildup. Consequently, the service life may be limited by the ability of the propellant or case bond system to withstand fracture or void formation.

Most operational motor systems are designed to function at moderate temperatures (60-100°F), and the service life may actually extend to periods well past the original design goal. In some cases, the time periods of interest are 15-25 years. Long-term or cyclic pressure buildup at operational temperatures can, at least potentially, lead to eventual propellant fraction. Generally speaking, the solid propellant industry has relied on the use of thermally accelerated aging and "cracking cubes" to establish estimates of gas generation crack life. Research by Arhart et al.,[1] Martin,[2,3,6] and Stenson[4-5] has suggested several other techniques. Some of the suggestions put forth in these references indicate that the cracking cube experiments would be more meaningful if the void formation and rate of formation were monitored in the period prior to ultimate cracking.[6] This study was aimed primarily at evaluating bulk compressibility measurements as a means of following void content growth.

Bulk Compressibility Technique

The bulk compressibility relationship is given by

$$P = -K\left(\frac{\Delta V}{V_o}\right) \tag{1}$$

where

P = superimposed pressure

K = bulk modulus

$\frac{\Delta V}{V_o}$ = volumetric strain

The bulk modulus K is often used in solid propellant grain analysis and several techniques are discussed in the literature for measuring it.[7-9] With any amount of porosity or internal voids created by gas evolution, the measurement of the "effective bulk modulus" becomes important. It is desirable in this instance that a curve of $\Delta V/V_o$ vs P be available.[9] Ultrasonic techniques have been used to provide some measurement of the bulk modulus and assess porosity,[10] but with only limited success.

At this point, it may be worthwhile to show how the initial void content and propellant shear modulus affect the bulk modulus. The overall pressure-volume behavior relating these variables has been given by Murnagham[11] as

$$\frac{V}{V_o} = \frac{e^{-P/K}}{[(1-\delta e^{-3P/4G})/(1-\delta)]^{(4G/3K)+1}} \tag{2}$$

where

V = instantaneous volume, V_o = unstrained volume, P = superimposed pressure, K = bulk modulus, G = shear modulus, and δ = initial void content or porosity.

Figures 1-3 were selected to demonstrate how the values of K, G, and δ can affect the general curve shape of the pressure-volume relationship. The value of the elastic bulk modulus was varied from 750,000 to 1,250,000 psi in order to cover the range observed in actual tests. These values are represented by the slope of the line for $\delta = 0$. The most dominant effect observed in Figs. 1 and 2 is that of the initial void content, δ, which tends to increase the volumetric response significantly. The change in δ creates a linear vertical shift along the volume change axis. The response is highly nonlinear at pressures below about 200 psig because most of the energy is going into collapsing the internal voids. Once a level of 200 psig is reached, the curves become parallel with a slope of $1/K$, and the effect of δ is not significant. The curve shape suggests that one can extrapolate the linear region back

Presented as Paper 83-1119 at the AIAA/ASME/SAE 19th Joint Propulsion Conference, Seattle, Wash, June 27-29, 1983; received Aug 5, 1983; revision received Feb 22, 1984.

*Superintendent, Materials Technology Department. Associate Fellow AIAA.

†Technical Specialist, Product Engineering Department. Member AIAA.

to $P=0$ and determine the initial void content effectively. This was the primary approach taken in this study, with the intent of following the gas-evolution-created void content.

Figure 3 demonstrates the effect of changing the propellant shear modulus G from 75 to 150 psi. Neither the bulk modulus nor the initial void content change as a result. However, the transition from the open voids to the collapsed voids is reflected in the shape of the curves in the region below 200 psig. The lower shear modulus increases the volumetric change at low pressures and allows the voids to collapse at much lower pressures. It does not appear that the differences in response are sensitive enough to allow one to estimate the effective shear modulus from this test.

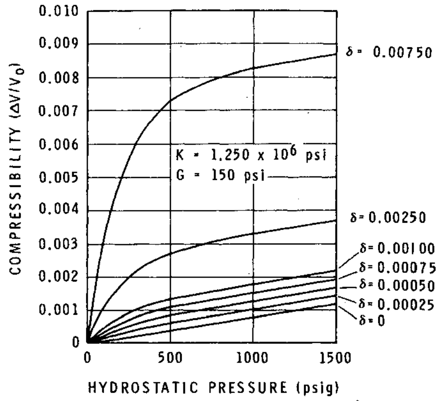

Fig. 1 Effect of initial void content δ on theoretical compressibility of solid propellant.

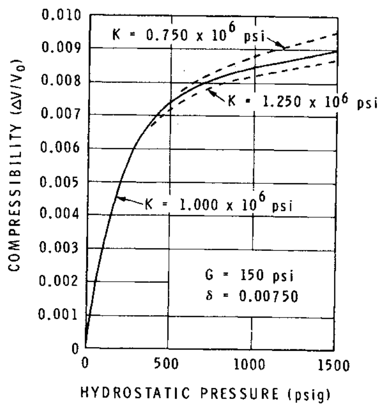

Fig. 2 Effect of bulk modulus K on theoretical compressibility of solid propellant.

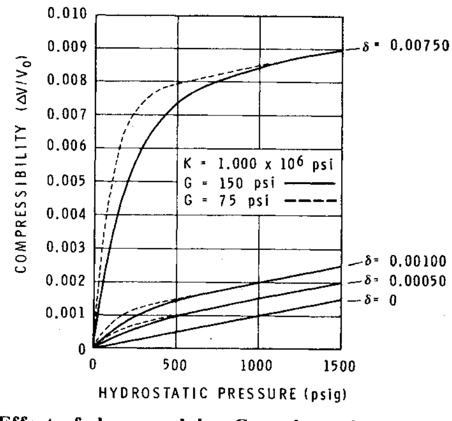

Fig. 3 Effect of shear modulus G on theoretical compressibility of solid propellant.

Experimental Program

Test Fixture

The test fixture consists of a pressure vessel, piston arrangement, and pressurization fluid, as shown in Fig. 4. The bulk modulus pressure vessel is a heavy-walled steel chamber capable of withstanding pressures as high as 2500 psig, although tests were conducted only to 1000-1500 psig. Generally speaking, the results shown in Figs. 1 and 2 indicate that lower pressure levels are sufficient to determine K and δ.

Perhaps the most critical parameters in the system are the piston seal and the pressurization or confining fluid. The seal consists of a polyurethane lip, which is cast onto the piston and then machined to a slight oversize so that a good seal is made with the piston bore. The confining fluid is a white mineral oil with a nominal bulk modulus around 280,000 psi. Extreme care is taken to ensure that all air bubbles are removed prior to testing, since their presence is the greatest source of error. All internal surfaces are sloped slightly or vertically to allow air bubbles to move freely to the tip of the pressure vessel.

Figure 5 shows the general behavior of the bulk modulus as a function of the solids level. The initial void content is close to zero for propellants cast under a vacuum or with pressure cure. Measured void contents typically average 0.002% ($\delta = 0.00002$ in.^{3}/in.^{3}); however, this value most likely represents a zero void content and the inability to completely remove all the entrapped air from the confining fluid. Results in this range are assumed to represent a value of $\delta = 0$ for analytical purposes.

Tests were also conducted to assess the effect of NG absorption in the fluid. During a normal test duration of 15-30 min, the amount of NG which is absorbed from a 4-in. cube (96-in.^{2} surface area) is less than 10 ppm. This does not change the confining oil bulk modulus effectively, nor is the quantity significant in terms of propellant behavior.

Propellant Selection

The test program was conducted on propellants from three widely different families. A CMDB formulation with a nominal solids loading around 60% and a demonstrated service life in excess of 15 years was selected as a control. Figure 5 suggests the bulk modulus for this propellant to be near 750,000 psi on the basis of solids level. Tests on propellant cubes removed from previously dissected full-scale motors confirmed these values and defined the void contents to be in a range from 0.002 and 0.006%. Typical propellant strain capability at room temperature is in the 45-50% range.

The other two propellants were chosen to be lower modulus, high-elongation formations in order to provide some contrasting behavior. The first of these was a state-of-the-art XLDB propellant with a 70% solids level, a strain capability of 180-200%, and a demonstrated service life (to date) of five years. This formation has already undergone extensive moisture and thermal aging characterization over the past eight years and is well understood. A NEPE propellant was the final formulation chosen. This propellant has a solids level of 73% and a strain capability in the 200-250% range. This formulation has been characterized over conditions similar to the XLDB for the past five years.

Sample Configuration

The bulk modulus apparatus (Fig. 4) works best with a nominal 4-in. cube of propellant, or more directly, with roughly 60-70 in.^{3} volume of propellant. Small cubes lead to a lower signal-to-noise ratio and a higher contribution of the confining fluid such that the bulk modulus and void content results become sensitive to these factors. In cases where a 4-in. cube is not available, the samples are cut so that the resultant quantity satisfies the volume requirement at the expense of shape considerations. All samples, which were stored at aging

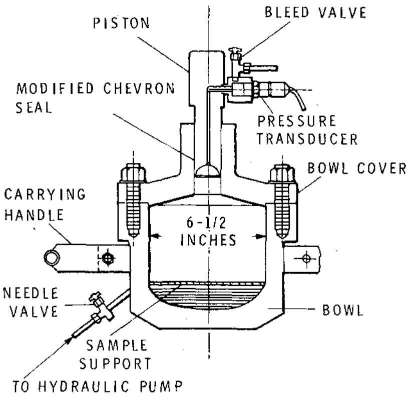

Fig. 4 Bulk modulus test fixture.

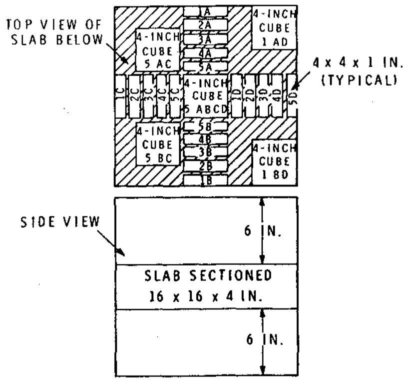

Fig. 6 Sectioning plan for 16-in. CMDB propellant cube stored at 120°F.

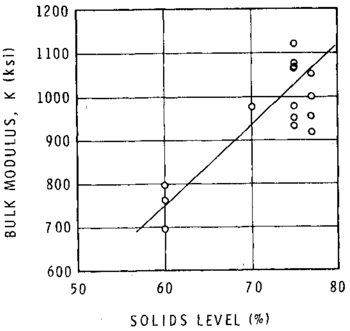

Fig. 5 Effect of solids level on high-energy solid propellant bulk modulus.

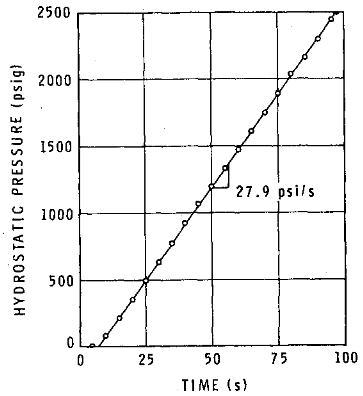

Fig. 7 Typical pressure-time history for bulk modulus test.

conditions and then tested in the bulk modulus fixture, were prepared as 4-in. cubes with one exception. Figure 6 represents a 16-in. cube of the CMDB propellant which was available from a previous program. This cube has been stored at 120°F and had cracked (as determined by X-ray examination) in a 200-290 day period. The cube was sectioned as shown in Fig. 6 to obtain 4-in. cubes or four segments of $4 \times 4 \times 1$ in. blocks at various locations from the cube center.

Preliminary Tests

Several preliminary tests were conducted to establish baseline conditions. The pressurization rate is generally established by driving the piston at a controlled speed. Figure 7 demonstrates the good linearity achieved in the pressure-time trace at the condition selected for these studies.

We were concerned about possible pressurization rate effects on the bulk modules, since it could be somewhat viscoelastic. However, pressurization rate tests conducted over three decades showed no viscoelastic effect on either bulk modulus or initial void content.

The white mineral oil is well characterized and has been used for all of our tests to date. A typical bulk compressibility curve is shown in Fig. 8. The oil is used as a calibration medium for each daily set of tests. Two test runs are performed using the oil as the confining fluid and as the test sample by completely filling the reservoir with oil. Since the computer output traces depend on a value of bulk modulus for the oil in the analytical calculations, three theoretical values are input to the computer to provide three output experimental curves for the oil. The theoretical input and experimental output bulk modulus values are then cross-plotted to obtain the daily calibration value of K_{oil} for all the propellant tests.

As a further check, the piston was pulled out of the reservoir to a predetermined distance in order to achieve an air void close to 0.2%. The pressure lines were then closed and

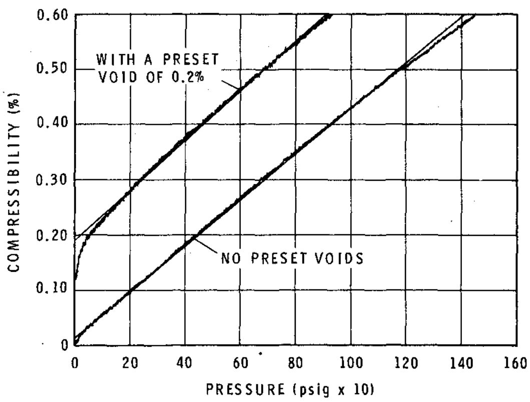

Fig. 8 Effect of preset void content on white mineral oil compressibility.

the oil tested to obtain the compressibility response shown in Fig. 8. The asymptotic bulk modulus value remained the same, and we were able to detect the initial void content which was preset in the oil reservoir. The initial void content in this test was determined to be about 0.190-0.195%.

Storage and Test Conditions

Except for the 16-in. CMDB cube, all other cubes were stored as precut 4-in. cubes. The cubes were double-wrapped in aluminum foil and placed in storage. Storage periods were a maximum of 56 days at 158°F and seven days at 176°F. Cubes were placed in storage at staggered intervals so that bulk modulus tests could be conducted on one to three sets near the end of the conditioning program. Upon removal from storage, the cubes were tested within 2-3 hours.

All of the tests were conducted with the oil at 70-80°F at a pressure rate of 30 psi/s to a maximum pressure of 1500 psig for at least two pressurization-depressurization cycles. The latter was done to see if the collapsed voids tend to reopen between cycles and, if so, to what extent it affects the effective initial void content. Roughly half the oil volume (about 50 $in.^3$) was changed after each test to maintain temperature and minimize contamination effects. Samples were X-rayed prior to testing so that some correlation might be made with the void content measurements.

Results and Discussion

Low-Temperature 16-in. Cube

The low temperature (120°F) cracking cube tests were performed well in advance of the other tests. The results are shown in Fig. 9 for the center cube, taken where the most cracking occurred in the cube. Both cycles are shown to indicate the degree of initial void content recovery and change in bulk modulus. The void content is much higher than observed from control (zero-time motor propellant) samples and is typically about 0.55%. It should be remembered that this value is averaged over a 2-in. distance from the center of the 16-in. cube, since the current test is restricted to using 4-in. cubes. Consequently, it might be expected that the value of the void content at the exact center of the cube is much higher.

Neither the asymptotic bulk modulus nor the initial void content change appreciably between loading cycles. Since the bulk modulus is determined after the voids collapse, the difference of 3.6% was considered to be test variability, rather than material response differences. The initial void content does not change much when there is a high degree of porosity (>0.05%), and it appears that the voids essentially pop out into their original volume between cycles. However, at lower levels the voids may remain closed between cycles, possibly due to intersurface attractions.

The initial void contents determined from all the samples are shown in Fig. 10 as a function of the distance from the center of the cube. There are not sufficient data to fully define the curve shape. However, gas transport calculations were performed that suggest a "bell-shaped" curve of internal gas pressure. If the assumption can be made that internal gas pressure and void content are directly related, then one might expect Fig. 10 to be bell-shaped as well. Results of rough X-ray analysis are shown in Fig. 11. The crack surface area was estimated from the X-ray film and plotted against the distance from the cube's center. There is fairly good agreement between the X-ray analysis and the bulk modulus measurements. It should be remembered that X-ray examination is not sensitive to porosity as is the bulk modulus. Therefore, the bulk modulus provides a better measure of the internal void content over all possible void sizes, whereas X-ray can only quantify those that have separated into distinct cracks.

High-Temperature Aging Tests

The results of the accelerated aging tests were encourgaging as far as the utility of the bulk modulus test was concerned. The results of the 158 and 176°F Aging tests are shown in Figs. 12 (CMDB), 13 (XLDB), and 14 (NEPE). A quick look at the three figures shows that the CMDB propellant behaves in a manner quite different from that of the XLDB and NEPE propellants.

The CMDB data are plotted against logarithmic time in order to expand the time scale. At 158°F, the voids begin to grow slowly over the first 30-40 days and then rapidly increase at about 50 days of exposure. The maximum values are around 0.72%, somewhat higher than that seen at 120°F in the 16-in. cube. The data at 176°F show almost continuous void growth starting at 3-4 days. Earlier data are needed in the 0.5-3 day period to define the initial behavior. The maximum void content values observed were in the range of 0.87-1.17%.

Except for a very slight increase toward the end of the 158°F storage period, the void content remains unchanged in both the XLDB and NEPE propellants. One explanation of the difference may be the aging behavior of the different families. Although one must consider mechanical property changes with age as well as gas generation rates (pressure buildup rates, essentially), we shall look primarily at modulus and strain changes based on mechanical property aging data.

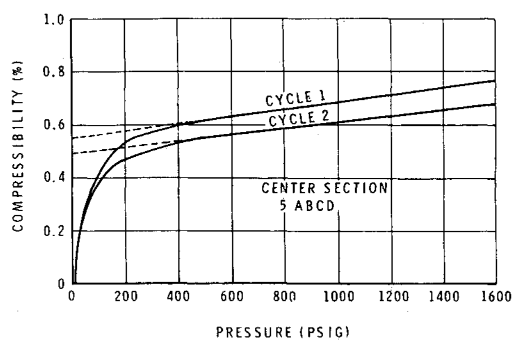

Fig. 9 Typical bulk modulus response for CMDB propellant block.

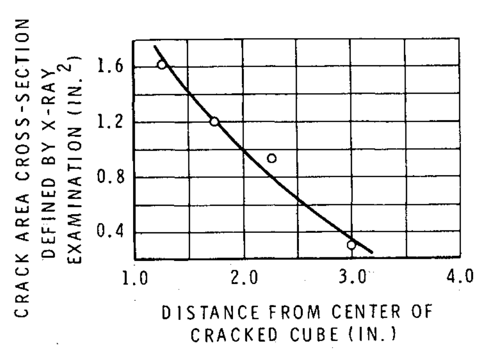

Fig. 11 Nominal crack cross-section area defined by X-ray.

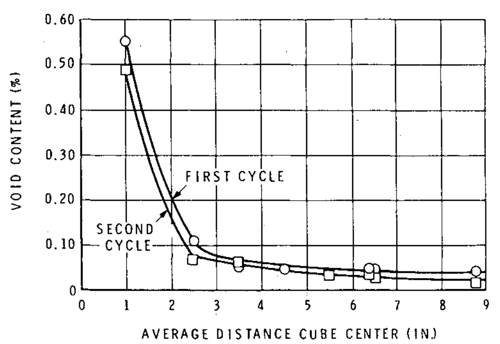

Fig. 10 Void content measurements as a function of location in cube.

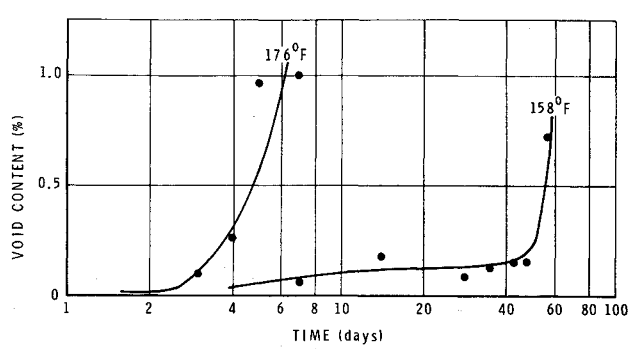

Fig. 12 Void content response in CMDB propellant with aging.

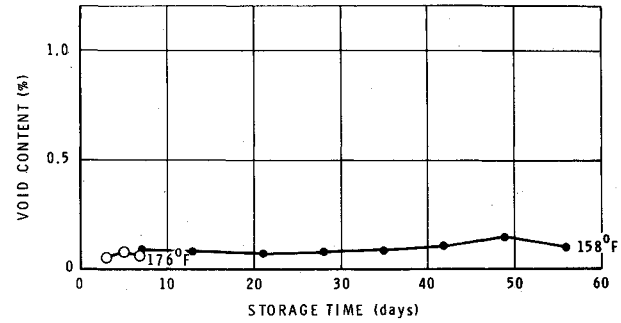

Fig. 13 **Void content response in XLDB propellant with aging.**

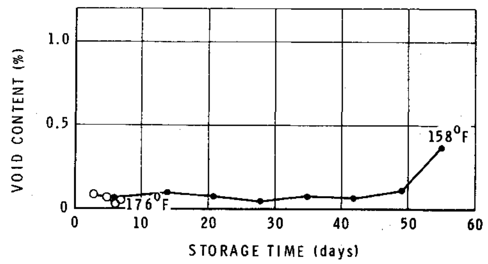

Fig. 14 **Void content response in NEPE propellant with aging.**

The CMDB, XLDB, and NEPE propellant systems all tend to follow psuedo-first-order aging response in terms of mechanical property changes. The CMDB prepellant tends to increase in modulus very slightly, whereas the strain capability tends to decrease at a rate about 2-5 times faster than the modulus increases. The rate difference is also dependent upon temperature. The XLDB and NEPE propellant behave in the opposite manner.[12] The modulus decreases and the strain capability increases. Because of this "softening" effect, the XLDB and NEPE propellants may not be as prone to void formation and cracking as the CMDB propellants. Further work needs to be done in this area to determine the actual mechanisms.

Fracture Mechanics Approach

The approach by Martin[2,3,6] to predict and quantify gas evolution-related propellant failure has recently focused on fracture mechanics as a potential tool. Using the spherical flaw model developed by Williams and Schapery[13,14] coupled with uniaxial tensile constant rate data, he defined the critical pressure for cracking to occur as

$$P_{cr} = \sigma_m (1 + \epsilon_m) \left[\frac{\alpha - 1}{\alpha} \right] \tag{3}$$

where

$$\alpha = 1 + \frac{\Delta V_{cr}}{V_o} \tag{4}$$

and

$$\frac{\Delta V_{cr}}{V_o} = \epsilon_m \phi_f \left[\frac{\ln(E/F)}{1 + \ln(E/F)} \right] \tag{5}$$

such that P_{cr} = critical pressure, σ_m = maximum tensile strength, ϵ_m = strain at maximum tensile stress, ΔV_{cr} = critical volume change or void content, V_o = unstrained volume, ϕ_f = volume fraction of solids, E = initial tangent modulus, and $F = \sigma_m / \epsilon_m$; secant modulus at maximum tensile stress.

Martin[6] has used this approach with uniaxial data and found that the results are quite different from predictions made using the other aging models.[4,5] The bulk modulus technique discussed in this paper could be used to determine the void content (δ) and the void growth rate ($d\delta/dt$) directly at various times and temperatures such that the critical pressure (P_{cr}) may be estimated.

Conclusions

The results of this study showed that the bulk compressibility test could be used to measure internal void content changes in solid propellants which result from gas generation. In fact, the magnitude and rate of void growth could be determined as well as the time of maximum void growth rate initiation. It is proposed that compressibility data can be useful in the fracture mechanics approach formulated by Martin[6], since they are a direct measure of critical parameters rather than extrapolations of uniaxial tensile data.

Void content profiles within a large cube were found to match X-ray film analysis closely and are believed to be more accurate because of the increased sensitivity with the bulk compressibility technique. Multiple pressurization cycles on bulk modulus cubes obtained from the accelerated aging tests showed no effect on asymptotic bulk modulus or initial void content measurements. The large voids and/or porosity remain open between loading cycles, whereas the smallest porosity can remain closed to a large extent.

Although the CMDB propellant exhibited a high void formation rate and content, neither the XLDB nor NEPE propellants showed any increase in void content over the zero time values. Part of this behavior could be explained by the differences in aging mechanisms previously demonstrated by these families.

Acknowledgment

The assistance of D. B. Gunn and C. D. Wahlin in preparing the bulk modulus cubes for testing is appreciated. Aging storage and monitoring was carried out by L. R. Beck and H. D. Dixon. Final data reduction of the bulk modulus tests was performed by C. D. Wahlin.

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