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IN PBX-9404 DURING THERMAL DECOMPOSITION

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IN PBX-9404 DURING THERMAL DECOMPOSITION

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ABSTRACT

Acoustic wave experiments were conducted on the heterogeneous explosive, PBX-9404, at a temperature of 116°C and a frequency of 1 MHz to study the influence of thermal decomposition on the mechanical response of the material. The longitudinal phase velocity was approximately 2.2 km/s and was found to be essentially independent of the extent of decomposition until the stabilizer was depleted. Thereafter, the velocity increased slowly with time as the temperature was maintained. Several possible explanations for this observation will be discussed in light of some information obtained in post-test chemical analysis.

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INTRODUCTION

Recently, Kennedy and Nunziato [1,2] reported some experimental results on the shock initiation of the heterogeneous explosive, PBX-9404. In particular, at low shock amplitudes (< 4 GPa) they found that the chemical reaction was initiated in a region at some distance behind the shock front and that this reaction resulted in the growth of a strong disturbance which subsequently overtook the shock front. The process by which this second disturbance overtakes the front is governed by the acoustical properties of the partially reacted explosive at high stresses and temperatures.

To gain some insight into this process occurring during initiation, acoustic wave experiments were performed on PBX-9404 at elevated temperature and atmospheric pressure. The temperature was maintained at 116°C and the behavior of the longitudinal phase velocity at 1 MHz was observed as a function of time in order to study the influence of thermal decomposition on the mechanical response of the material.[†] This temperature was selected because the anticipated time of the experiment (48 hr.) was not sufficient to cause significant reaction or weight loss in the HMX constituent of the PBX-9404, but was sufficient to cause some reaction of the cellulose nitrate (NC) in the binder phase [4].

It was found that the velocity was essentially constant with time at 2.2 km/s until the stabilizer was depleted. Then the velocity was observed to increase slowly with time up to the termination of the experiment. This latter result was somewhat surprising and some possible explanations will be offered on the basis of information obtained in post-test chemical analysis.

[†]Acoustic data have been obtained on PBX-9404 up to 40°C and were reported by Sutherland and Kennedy [3]. Short-time, thermal decomposition effects are negligible in this temperature range and were not evident in their experiments.

MATERIAL DESCRIPTION

The PBX-9404-03 explosive material used in this investigation was formulated by the Los Alamos Scientific Laboratory. This material is a hot-pressed mixture which is 94 parts by weight HMX (1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazacyclooctane), 3 parts cellulose nitrate (12.0% N), 3 parts tris-(2-chloroethyl)phosphate (CEF), and 0.1 part diphenylamine stabilizer [5]. The HMX crystals, the discrete phase in the mixture, are present in a bimodal particle-size distribution; three-fourths of the HMX has a mass-median particle diameter of 125 μm and the remainder has a mass-median particle size of 25 μm . The average density of our samples was 1.841 Mg/m^3 .

Three cylindrical specimens of the PBX-9404 were machined for this study. Each had a diameter of 50 mm and a length of 12.7 mm, 8.9 mm, or 6.4 mm. To protect these samples from absorbing the acoustic-transducer bonding agent, the specimens were sprayed with a thin coat of lacquer before they were tested. The specimens were stored in a cool place before and after testing.

Acoustic Velocity Measurements

A direct transmission technique was used here to measure the acoustic velocity of the specimens. This technique has been used extensively in the past [6], and the exact experimental apparatus is described in Ref. 3. The essence of the technique is to measure the difference in transit times through two specimens of the same material which have different lengths. The velocity is computed by dividing the difference in lengths by the difference in transit times. For this set of experiments, 1-MHz center-frequency transducers were used. Nonaq stop-cock-grease was used to couple them to the specimens, and spring-loaded fixtures were used to hold the transducers in place. Measurements were recorded on Polaroid film for reduction at a later time.

Testing Procedures

As the specimens had to be raised to a uniform temperature and held at that temperature for an extended period of time, they were tested in a controlled-temperature chamber whose stability was $\pm 1^{\circ}\text{C}$. For safety, the temperature chamber and specimens were placed in a reinforced-concrete detonation chamber, while the ultrasonic equipment was in an adjacent room. This arrangement required rather long electrical leads between the equipment and the specimens (on the order of 8 m). These long leads may have introduced more scatter into the data than one would normally expect with the equipment and the techniques which were used.

Immediately before the test, the specimens were removed from the storage facility, the transducers were bonded to them, and the holding fixtures were attached. The specimens were then placed in the temperature chamber and tested to make sure all connections were correct and the transducer specimen bonds were of good quality. The temperature was then set to 116°C . Approximately 10 minutes were required to bring the chamber to temperature and an hour to bring the specimens to temperature. The chamber temperature was monitored by a thermocouple mounted inside the holding fixture.

At one hour and forty minutes into the test, two bonds failed. At this early point in the test, it was decided to repair the bonds and start the test over. The chamber heat was immediately cut off and the door was opened. Twenty-five minutes later (specimen temperature of 66°C), the transducers were rebonded and the test restarted. The specimens were back to temperature one hour after the faulty bonds were discovered.

Acoustic measurements were made on the samples (each of the three possible combinations of the specimens) at one-hour intervals and the specimens were visually observed through a port to note any color changes. At 28 hours

after the second start, the bond on specimen 3 became unstable, and by 31 hours, the bonds on specimens 2 and 3 had failed. As it was not totally clear that these bonds had deteriorated until the data were reduced, the test was continued for 48 hours. At 48 hours, the specimens were removed from the oven and their fixtures, and then placed in a cool storage room.

The reduced acoustic data and the temperature history of the specimens are plotted in Fig. 1, and their color changes are noted. As indicated earlier, the data scatter is much greater than one would expect for this type of experiment. There are at least three major causes for the increased scatter: (1) the long electrical leads between the specimens and the ultrasonic equipment, (2) the relatively high temperature of the samples, and (3) sample-to-sample material variations, especially with time at high temperature. Every effort was made to minimize the scatter (see Ref. 3).

DISCUSSION OF THE DATA

The phase velocity-time data shown in Fig. 1 really have two regimes of behavior. For approximately 12 hours following the start of the test, the samples were in diminishing shades of yellow and the phase velocity was nearly constant at 2.2 km/s. The diminishing color of the samples indicated that the diphenylamine stabilizer was absorbing NO_2 liberated by NC decomposition. This is consistent with data obtained by Rogers [4]. He performed thermal decomposition experiments and measured the time it takes for the stabilizer to be completely depleted at a fixed temperature. The stabilizer is essentially depleted as a getter of NO_2 when about 10% of the NC has decomposed, and thereafter the decomposition can be expected to accelerate due to autocatalytic effects of the NO_2 and NO product gases. Rogers' data

are summarized in Fig. 2 and show that at 116°C, the temperature in our experiments, the stabilizer is depleted in approximately 12 hrs.

Thus, it appears that the slow increase in phase velocity observed in our experiments essentially starts after the stabilizer has been depleted. This increase in velocity was unexpected. Physically, we had expected that as the various components of the explosive decomposed, the material would become more dispersive and the phase velocity would decrease.[†] This discrepancy led us to have some post-test chemical studies carried out.

POST-TEST CHEMICAL ANALYSES

The samples were subdivided after the test to permit properties of interest to be measured. A 15-mm-diameter pellet was machined from the center of each sample and from material near the edge of each sample. The surface layer of lacquer was removed by taking thin lathe cuts on each surface. The average density of each pellet was determined from weight, diameter and thickness measurements, and is reported in Table 1.

It appears that the density of pellets from sample centers (designated "C" in the table) does not vary in a systematic way from pellets formed from the edges of the samples. It is noted that the average density decreased by about 1.5% as a result of the 48-hour exposure at 116°C.

Schwartz and co-workers [8] determined the NC and CEF contents of the exposed samples. The results in Table 1 show that loss of the fluidizer CEF, due to evaporation, was comparable to the loss of nitrates

[†]Static tests performed at Los Alamos Scientific Laboratory on similar samples indicate that thermal decomposition at these temperatures results in increased porosity and a decrease in the elastic modulus [7].

from the cellulose nitrate; the actual weight loss from the NC was nearly equal to that of the CEF.

Since the longitudinal sound velocity, c_l , increased by 7% while the density, ρ , decreased by only 1.5%, it can be seen from the relation

$$c_l = \sqrt{E/\rho} \quad (1)$$

that the longitudinal elastic modulus E increased with time and decomposition. The reason for this increase in modulus appears to be that the evaporation of fluidizer and decomposition of cellulose nitrate toward cellulose both tend to increase the stiffness and brittleness of the PRX-9404.

We considered the possibility of relating the acoustic velocity to the extent of NC decomposition, since that might provide a rapid and non-destructive test method for use during aging studies. Our data (Fig. 1) suggests that such a relationship may exist. Unfortunately the effect due to NC decomposition is confounded in our data with the effect of CEF evaporation. After depletion of the stabilizer, the NC decomposition reaction is extremely complex and can interact with the oxygen in any air adjacent to the sample. This makes the course and rate of reaction dependent upon sample thickness, diffusion conditions and vessel size. Thus we were unable to calculate decomposition of cellulose nitrate for comparison with the acoustic data.

CONCLUDING REMARKS

After depletion of the stabilizer, a progressive increase in elastic modulus was observed in these decomposition experiments despite a slight increase in sample porosity. This suggests that in the early stages of

reaction in a shock initiation experiment, in which the pores have been collapsed, we can expect the sound velocity to increase due to reaction to a value higher than one would expect simply due to the state of compression of the material.

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We greatly appreciate interaction with the Los Alamos Scientific Laboratory throughout this study. In particular, A. Popolato made the PBX-9404 material available to us and provided data on LASL physical testing of aged samples. Valuable discussions on decomposition process in cellulose nitrate were held with R. N. Rogers and M. Schwartz, who also supervised the post-test chemical analyses.

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Table 1. PBX-9404 SAMPLES FROM 48-HR., 116°C ACOUSTIC TESTS

Sample No.	Thickness mm	Initial Conditions			Post-Test Measurements				
		ρ_o , Mg/m ³	NC, %*	CEF, %*	Pellet	ρ , Mg/m ³	NC, %	CEF, %	$\Delta\rho$, %
7	6.36	1.839	3.5	3.0	7 C	1.813	2.2	2.3	-1.4
					7	1.801	2.1		-2.1
3	8.92	1.842	3.5	3.0	3 C	1.809	2.1	2.6	-1.8
					3	1.815	2.0		-1.5
10	12.71	1.843	3.5	3.0	10 C	1.825	2.1	2.4	-1.0
					10	1.822	2.1		-1.1

* Derived from other samples from same lot of material.

Note: NC and CEF determinations were made by M. Schwartz, WX-3, LASL. NC was determined as $-\text{ONO}_2$; none of the cellulosic content was lost.

Figure 1. The variation of temperature, color, and longitudinal phase velocity in PBX-9404 with time.

Figure 2. Rogers' estimate [4] of the depletion of the diphenylamine stabilizer in PBX-9404 as a function of temperature.

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