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Linear Thermal Expansion of PBX 9501 and PBX 9502 Plastic-Bonded Explosives

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ABSTRACT

Two applications of thermal expansion measurements on plastic-bonded explosive (PBX) composites are described. In the first dilatometer application, thermal expansion properties of HMX-based PBX 9501 are measured over a broad thermal range that includes glass and domain-restructuring transitions in the polymeric binder. Results are consistent with other thermal measurements and analyses performed on the composite, as well as on the binder itself. The second application used the dilatometer to distinguish the reversible and irreversible components of thermal expansion in PBX 9502, a TATB-based explosive. Irreversible expansion of the composite is believed to derive from the highly-anisotropic coefficient of thermal expansion (CTE) values measured on single TATB crystals, although the mechanism is not well understood. Effects of specimen density, thermal ramp rate, and thermal range variation (warm first or cold first) were explored, and the results are presented and discussed. Dilatometer measurements are ongoing towards gaining insight into the mechanism(s) responsible for PBX 9502 irreversible thermal expansion.

INTRODUCTION

The safety and reliability of devices employing plastic bonded explosives (PBX) are achieved in part through engineering designs that accommodate the complicated thermal expansion properties of those materials. These designs may be constructed to account for thermal expansion during device assembly or storage. An additional complicating issue is the fact that two nominally identical lots of an explosive material may not exhibit the exact same thermal behavior because of details related to material processing history. A better understanding of the thermal expansion of plastic bonded explosives and the development of models that reproduce the expansion behavior will aid engineering efforts and improve the ability of the devices to withstand a variety of thermal environments. In this work we have used dilatometry to measure the linear thermal expansion of two important plastic bonded explosives that are used in a variety of high performance weapons.

MATERIALS AND SAMPLES

The two explosive materials that we have examined are PBX 9501 and PBX 9502. Both of these composite PBX materials are formulated through a solvent-slurry process where inert binder is first dissolved in a solvent that does not dissolve the explosive. Powdered explosive is added to the solution and then the solvent is driven off with heat while the slurry is mixed. The PBX prills that result from this process are then pressed at elevated temperatures in a steel-die or isostatic press to form solid charges. These charges can be used directly for applications or machined into more precise or complicated shapes.

PBX 9501 is a plastic-bonded explosive made of 95% by weight HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) in 5% binder. The HMX is added in powder form as a bimodal distribution of coarse crystallites (10 micron mean) and fine crystallites (1 micron mean) mixed in a 3 to 1 ratio by weight. The binder is a 1:1 mix of polyester-polyurethane block copolymer with BDNPA/F (bis(2,2-dinitropropyl)acetal-formal) plasticizer. In the PBX formulation, the glass transition of the binder is around –35 to -40°C. The thermal expansion of PBX 9501 has not been well characterized. The Lawrence Livermore National Laboratory explosives handbook lists a mean coefficient of thermal expansion between 211 and 344 K of $\sim 55 \times 10^{-6}$. To our knowledge, no other thermal expansion values have been published. Other thermophysical properties of the binder and the PBX 9501 formulation have been examined by other authors [1]. From differential scanning calorimetry and dynamic mechanical analysis measurements it is known that, in addition to the glass transition near -35°C, the binder also undergoes hard/soft domain phase mixing between 50 and 100°C. This phase mixing has also been interpreted as a glass transition in the hard domain component. Thermal expansion data for an explosive formulation similar to PBX 9501 shows a value of greater than 50×10^{-6} near room temperature, a slow increase with increasing temperature, and small peaks at -38 and 41°C.

In the work we report here, all PBX 9501 samples were cylinders, 11 mm long and 6 mm in diameter. Three sets of samples were examined. The first set (two samples), was cut from the outer surface of an isostatically pressed hemispherical part. The second set (three samples), was cut from the inner surface of the same part. The third set (three samples), was taken from the outer surface of a part that was isostatically pressed, but formulated with a different lot of HMX and pressed using slightly different conditions. Table 1 shows the details of the sample dimensions and densities calculated from the sample sizes and masses.

PBX 9502 is a plastic-bonded explosive made of 95% (by weight) TATB (2,4,6-trinitro-1,3,5-benzenetriamine) in 5% chlorotriflouroethylene-based polymer binder. This binder has a glass transition near 28C. The thermal expansion of PBX 9502 is characterized by an irreversible volume expansion that occurs during thermal cycling and is termed "ratchet growth." The permanent

expansion can be significant for cycles running between -60 and 80°C, and growth is diminished at later cycles over a given thermal range. The ratchet growth, largest in the initial cycles, tapers off entirely after about 30 cycles. There are various microscopic models that attempt to explain the ratchet growth mechanism but no definite evidence that suggests one particularly favorable candidate. Early work [2,3] showed that single TATB crystals possess highly anisotropic CTE values, but do not undergo ratchet growth. Dry-pressed TATB powders, with no binder, were observed to undergo ratchet growth, indicating it is a property of the compressed crystals and not the binder itself, nor specific binder-crystal interactions. In addition, graphite and boron-nitride crystals, similarly sheet-like and with anisotropic CTE values, also demonstrate ratchet growth behavior.

For PBX 9502, test segments were performed over three different temperatures ranges, 10 cycles each:

Test Segment (A) Between 23 and 123°C
Test Segment (B) Between 23 and -77°C
Test Segment (C) Between 123 and -77°C.

Table 1 lists the sample parameters and test segments for each.

Table 1. Sample dimensions, masses, and densities

PBX-9501	Height (mm)	Diameter (mm)	Mass (g)	Density (g/cc)	Test Segments
1-1	11.0	6.6	0.3807	1.821	
1-2	11.0	6.6	0.3807	1.812	
2-1	11.0	6.6	0.3824	1.817	
2-2	11.0	6.6	0.3813	1.821	
2-3	11.0	6.6	0.3811	1.821	
3-1	10.9	6.6	0.3776	1.820	
3-2	11.0	6.6	0.3796	1.824	
3-3	11.0	6.6	0.3792	1.820	
PBX-9502					
24	4.57	6.63	0.300	1.895	A, B, C
13	"	"	"	1.877	B, A, C
18	"	"	"	1.877	A, B (no C)
10	"	"	"	1.877	A, B, C
3	"	"	"	1.881	B, A, C
1	"	"	"	1.882	C
19	"	"	"	1.878	C (1°C/min)

METHODS

All of the thermal expansion data was acquired with a Netzsch Instruments 402C dilatometer. A NIST traceable copper standard sample was used for the correction file that is applied to each explosive sample run. The copper standard is run with the same thermal profile used for the samples so that the response of the instrument can be normalized out to produce accurate measurements of the sample behavior. By examining trial samples of each material, we were able to adjust heater control parameters and instrument settings to provide accurate sample temperature control and linear ramps. The Netzsch software was used to calculate the coefficient of thermal expansion without smoothing.

RESULTS for PBX 9501

All of the PBX 9501 runs have been compiled into a single plot in Figure 1.

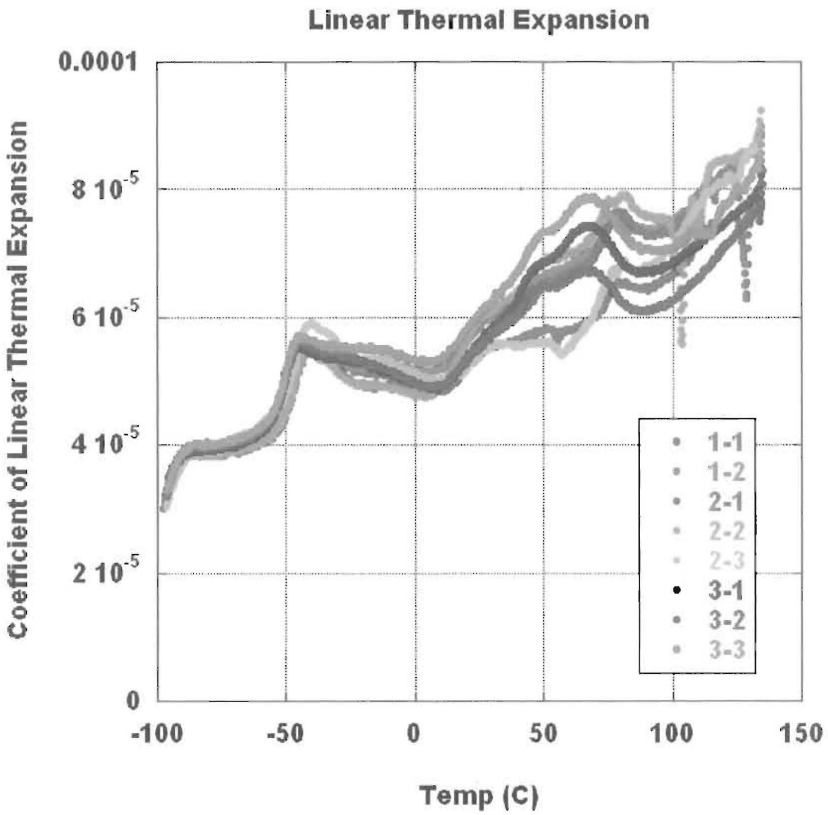

Figure 1. Thermal expansion data for three sets of samples. The first number in the legend is the part number that the samples were taken from and the second number is the sample number.

In Figure 1 we can see features that are common to the three sets of samples and several that differ. The low temperature peak, near -35°C, is roughly the same for all samples and corresponds to the glass transition in the binder. The details of the shape and precise peak location are all probably within the scatter that we would expect from nominally identical samples.

The higher temperature peak or peaks in the scans vary with the larger parts that the sample sets were taken from. The first and second sets of samples, being taken from inner and outer surfaces of the same part have peaks in the 75 to 80°C range. The third set of samples, taken from a different part, showed a lowered and separated set of peaks, occurring near 50 and 70°C. Regardless of whether these features result from a glass transition or from domain mixing, they are all related to motion of polymer strands within the matrix. As a result the differences between the parts likely reflect variations in microscopic details of the HMX particle size distributions or in HMX/binder distribution occurring in the prill formation or during pressing.

No density dependence is obvious from Figure 1. There does not appear to be a trend within each set of samples or across the sets. Some of this could be due to error associated with dimensional-based density measurements, which are not sensitive to machining errors such as non-parallel faces or cylinder axis angles deviating from 90 degrees.

We characterize the thermal expansions by averaging all of the runs for samples taken from a single part and fitting a line to the resulting plot. The plots are shown in Figure 2

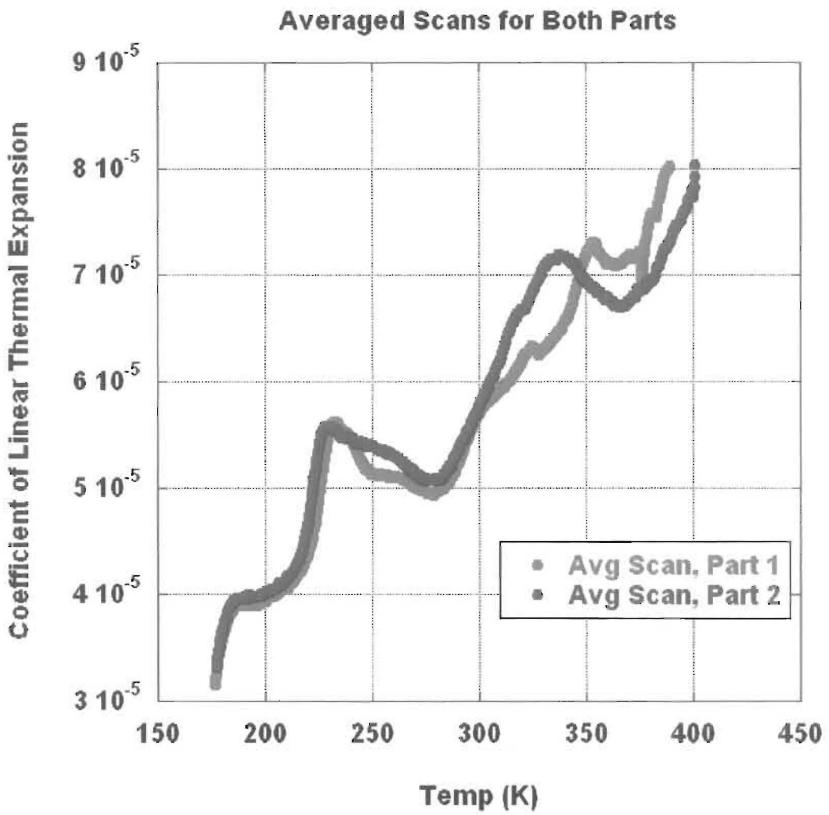

Figure 2. Average thermal expansion data for each part from the data in Figure 1.

By averaging the data from samples 1-1, 1-2, 2-1, 2-2, and 2-3 we obtain, for temperatures between 175 K and 400 K,

$$\alpha(K^{-1}) = 4.0103\times10^{-6} + 1.8327\times10^{-7}\cdot T(K) \quad (1)$$

For the samples taken from the second part (averaging 3-1, 3-2, and 3-3) we obtain

$$\alpha(K^{-1}) = 9.4258\times10^{-6} + 1.6755\times10^{-7}\cdot T(K) \quad (2)$$

The slope of these thermal expansion functions average to around $1.75\text{x}10^{-7}$. The average value of the plots near room temperature is near $50\text{x}10^{-6}$, consistent with previously published values. The shape of our plots is similar to that shown for a similar formulation noted above [1] with the exception that we observe peaks between 50 and 80°C as opposed to the peak at 41°C.

RESULTS FOR PBX 9502

For PBX 9502, we intended to probe reproducibility and temperature cycle directionality (warm first versus cold first) in our application of the dilatometer to study ratchet growth. In Figure

3a are plotted the thermal traces of the first 5 specimens in Table 1 as a function of time. In these plots, the time axes of test segments 2 and 3 were shifted to match up with each previous segment. In Figure 3b are plotted the corresponding strain plots versus the shifted time axes. Note that the data for segment C of specimen #18 was lost. Note also that thermal control was lost during the final two cycles of segment C, specimen #3; all data prior to that are valid.

In Figure 3c, all of the warm (A) segments have been overlayed, whether they came first or second in the sequence. In Figure 3d, all the cold (B) segments have likewise been overlayed, whether they came first or second in the sequence. If we examine these data for irreversible growth every time the temperature returns to 23°C, we can see that at warm temperatures, Figure 3c, the asymptotic growth is the same for all the tests, regardless of whether segment A was run first or second. However, for cycles going to cold temperatures, Figure 3d, the specimens that were cycled to warm first, grew more during the cold cycles. Note that in both Figure 3c and 3d, the high density specimen (#24, shown in green) shows a higher CTE (more expansion at the temperature extremes) but does not stand out as having unique ratchet growth properties in terms of irreversible growth measured at 23°C.

The data plotted in Figure 4 come from the last two specimens in Table 1, comprised of segment C only, at a rate of 5 and 1°C/min, respectively. Here, as a way of monitoring ratchet growth at ambient temperature, and following previous work established by Howard Cady [4], the strain values are captured every time the test passes through the two temperature extremes and through ambient, 23°C, plotted on an axis of sequential cycle number. Specifically, strain data were captured where the corresponding temperature values were less than -77.5°C (top), between 23 and 23.5°C (middle) and greater than 122°C (bottom), as the temperature moved up and down through the cycles of segment C. In Figure 4, generally speaking, we see the typical asymptotic ratchet growth response. However, there are some additional subtleties. At the warm temperature extreme, >122°C, although the thermal data indicate that the two tests reach nearly identical temperatures (not shown), the strain values indicate that the specimen may actually achieve a warmer temperature during the slow (1°C/min) test. For the 23°C fast data, 5°C/min, note that strain values are slightly higher if the temperature is passing through 23°C on its way down, than if it is on its way up. Howard Cady made a similar observation in his previous work using thermal mechanical analysis (TMA), confident it was a real effect and not due to a lack of thermal equilibrium in the system. Howard has discussed CTE values being different for ascending versus descending temperatures and he has suggested that this may hint towards important details of the ratchet growth mechanism. However our results at the slower rate show that this effect is minimized and very nearly goes away. We therefore attribute the mis-matched CTEs as being due to a lack of thermal equilibrium, and intend to perform future tests at the slower rate of 1°C/min. At all temperatures, the overall ratchet growth rate per cycle appears to be independent of the fast or slow thermal ramp rate.

In summary, the dilatometer appears to be a satisfactory method for monitoring PBX 9502 ratchet growth response in real time. The data appear to be reproducible, and the software limitation of running long tests in ~10 cycle segments does not seem to diminish the quality of the data in any way. Our tests suggest that higher density parts (by ~0.02 g/cm^3) may result in higher CTE values, with only a minimal effect on the magnitude of ratchet growth. We have shown that specimens thermal cycled between ambient and cold appear to grow more if the specimen has already been thermal cycled between ambient and warm. However, the opposite is not true; warm cycles grow samples by the same amount whether the specimen has been first cycled to cold or not. We have observed the CTE mismatch at ambient for ascending versus descending temperatures, as mentioned by Howard Cady. We have seen possible differences in the magnitude of this phenomenon as a function of the thermal rate, slow heating and cooling giving rise to a reduced ascending/descending mismatch in CTE. The overall ratchet growth per cycle is not significantly dependent on thermal

ramp rate, except possibly at warmer temperatures. However, our system may not be well-equilibrated at these elevated temperatures.

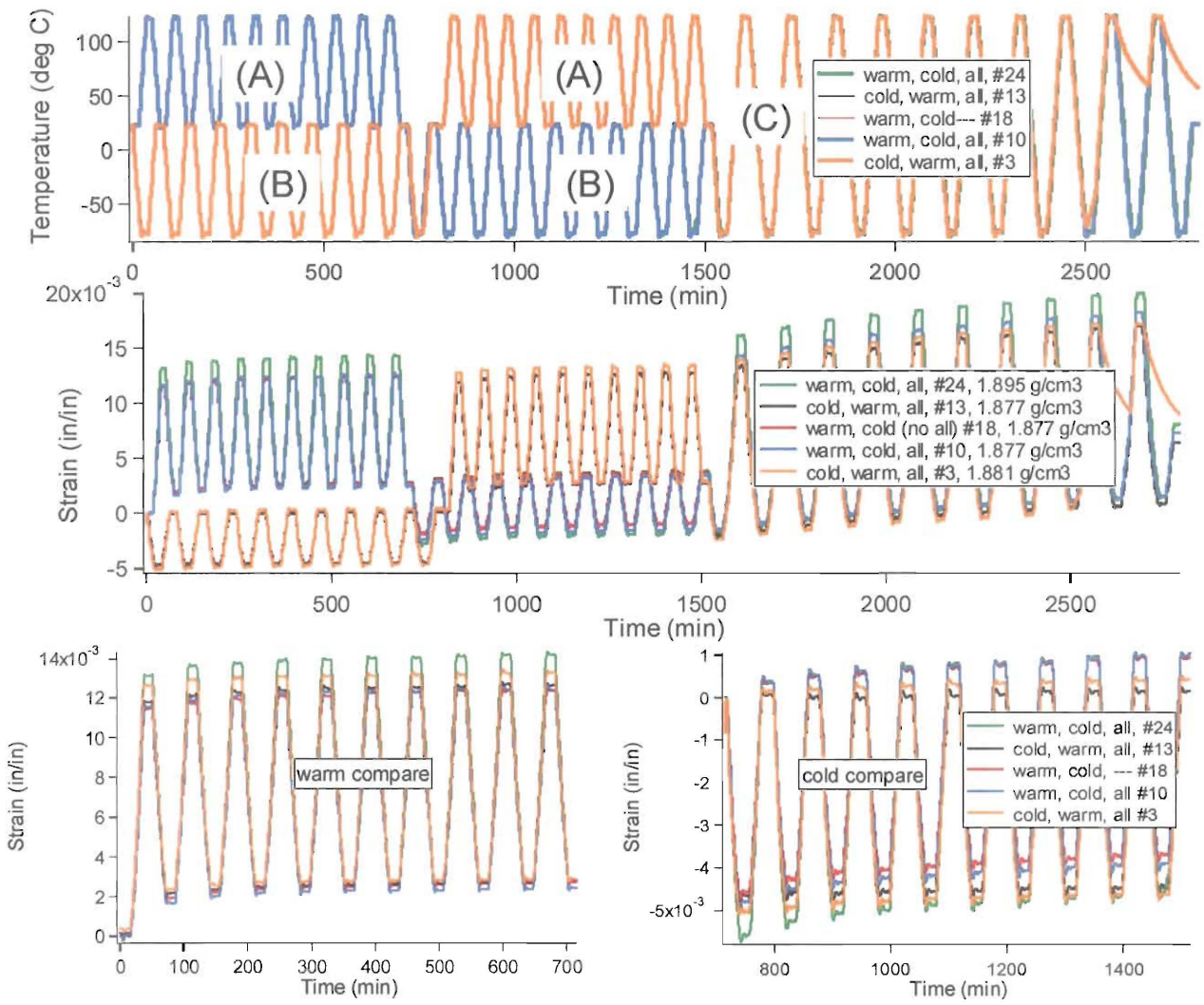

Figure 3: (a, top) Temperature vs. Time, all A, B, and C segments of the first five PBX 9502 specimens listed in Table 1; (b, middle) Strain vs. Time for all A, B, and C segments of all five specimens listed in Table 1; (c, bottom left) Test segment A for all specimens, regardless of segment ordering. (d, bottom right) Test segment B for all specimens, regardless of segment ordering.

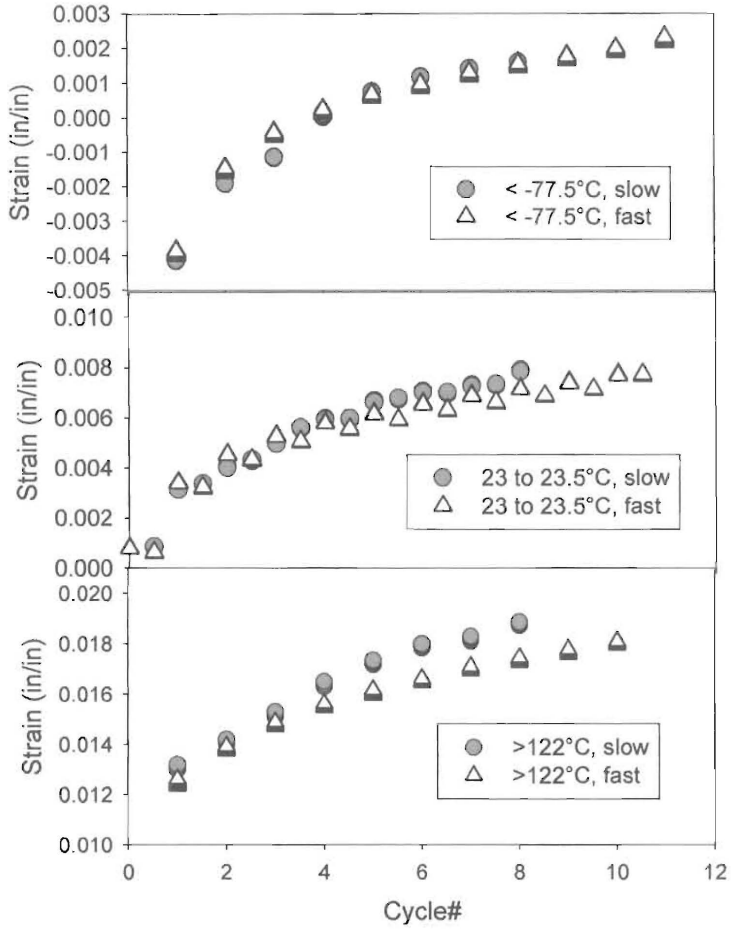

Figure 4: Strain values per cycle# for the last two tests in Table 1, fast data (5°C/min) in open triangles, slow data (1°C/min) in filled circles. Strain values correspond to temperatures (a) less than -77.5°C, (b) between 23 and 23.5°C, and (c) greater than 122°C.

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