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Title:	PBX 9502 Ratchet Growth Experiments on a Dilatometer
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PBX 9502 Ratchet Growth Experiments on a Dilatometer

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Abstract

A Netzsch dilatometer has been used to probe the ratchet growth response of TATB-containing PBX 9502. Preliminary data are presented, showing test reproducibility and examining possible effects of density and/or the specific sequencing of different thermal ranges. We have also shown effects of thermal ramp rate on the test data, likely due to thermal equilibrium of the specimen environment.

Introduction

All TATB-based composites are known to undergo ratchet growth--- irreversible volume increase upon thermal cycling. While the mechanism of this phenomenon is not well understood, a single TATB crystal possesses highly anisotropic coefficient of thermal expansion (CTE) values and this is believed to be responsible for the effect [1]. Indeed, single TATB crystals are graphitic in nature, with a sheet-like structure (the highest CTE value being normal to the sheet surface); similarly, graphite and boron nitride have similar structures, CTE values, and ratchet growth behavior.

PBX 9502 is a plastic bonded explosive composite containing 95 weight% TATB. Howard Cady has [2] explored many aspects of the ratchet growth response of this and similar materials. Some of Howard's previous studies employed a thermal mechanical analyzer to measure uniaxial growth of a specimen in real time, upon thermal cycling. In this paper we report our first results in using a dilatometer to conduct these types of experiments. Our goal is to determine if the dilatometer is capable of performing such measurements reliably and reproducibly, and if so, to use this instrument to provide ratchet growth data for modeling purposes. By ultimately designing appropriate experiments, we hope to provide insight into ratchet growth mechanisms.

Experimental

All dilatometer measurements were performed on the Netzsch, Model 402C. Due to programming limitations in the software, thermal cycles were programmed in segments, 10 cycles each, and these segments were applied to a given specimen sequentially until the desired profile was attained. When working up the data for analysis, these segments were "knitted" together in the order they were performed.

Test segments (10 cycles each)

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

PBX 9502 specimens were machined from a stockpile return charge, Virgin lot 890-019. All specimens were 0.261 inches in diameter and 0.18 inches thick, approximately 0.3 grams each. The small specimen requirement is derived from the use of a 1-inch long copper cylinder as a standard reference, and the need for the reference and test material to undergo similar dimensional variations over the temperature range to be tested. Because the CTE of PBX 9502 is so much larger than that of the copper standard, the length of the specimen must be reduced proportionally.

Specimen densities were obtained for all 30 dilatometer specimens using both immersion methods, in water, and using a micrometer to calculate volume. The results are shown in Figure 1.

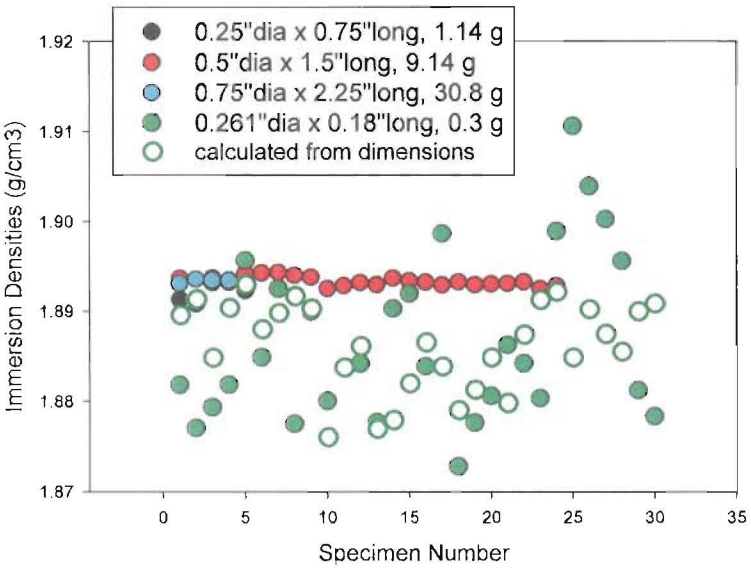

Figure 1: Specimens obtained by immersion methods (solid) and calculated from dimensions (open).

Figure 1 also contains immersion density results for other, significantly larger PBX 9502 specimens, taken from a second stockpile return charge of the same lot of Virgin material. The average densities of the two charges may not be identical, but their density variation should be similar (they were prepared identically and fell within bulk density specifications). Note the minimal spread in densities for the larger specimens. Even they begin to show more variation as the size is reduced towards 1 gram. One may conclude that immersion methods are likely not so accurate for small specimens (dominated by surface effects, wire weights, etc.), however, it must be considered that small specimens could very well display a density inhomogeneity that is real, due to nonuniformities in the local composition. If one compares the relative densities obtained for the small dilatometer specimens using immersion and dimensional measurement techniques, there appears to be no correlation. Dimensional determination tends to underestimate density (by determining the longest dimensions of the part, not the shortest), and we believe the actual densities of the small dilatometer specimens are probably very near to those of the larger parts cut from the different charge. Identical tests were performed on one of the highest and one of the lowest density parts, as determined by the immersion method. By this means we could identify the maximal effect that this magnitude of density difference could have on our data. Seven specimens have been tested to date and they are listed in Table 1.

Table 1: Test plan showing specimen immersion density values. Thermal ramp rates are 5°C/min unless otherwise indicated.

Specimen#	Initial Immersion Density Value (g/cm3)	Test segment order
24	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)

Results and Discussion:

In Figure 2 are plotted the thermal traces of the first 5 specimens in Table 1 as a function of time. In these plots, the time axis of test segments 2 and 3 were shifted to match up with each previous segment. Sometimes, the temperature at the end of one segment did not match perfectly with the starting temperature of the next segment (many hours could elapse between the actual end of one segment and start of the next, however during that time the specimen temperature remained very near to ambient, and the mismatch was never more than 1 to 2°C). The expected effect of this temperature mismatch on the strain data (i.e. due to CTE) was calculated and determined to be minimal. The data in Figure 2 confirm that the temperature profiles are very reproducible.

In Figure 3 are plotted the strain plots versus the shifted time axes in Figure 2. Note that we lost the data for segment C of specimen #18. 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 4, all of the warm (A) segments have been overlayed, regardless of whether they came first or second in the sequence. In Figure 5, all the cold (B) segments have likewise been overlayed, whether they were 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 4, the asymptotic growth is the same for all the tests, regardless whether segment A was run first or second. However, for cycles going to cold temperatures, Figure 5, the specimens that were cycled to warm first, grew more during the cold cycles. Note that in both Figure 4 and 5, the high density specimen (#24, shown in green) shows a higher CTE (more growth 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 6 come from the full range segment (C). Here, as a way of monitoring ratchet growth at ambient temperature, and following previous work established by Howard Cady, the strain values are captured every time the test passes through 23°C. Specifically, the time and strain data were captured where the corresponding temperature value was between 23 and 23.5°C, as the temperature moved up and down through the cycles of segment C. In Figure 6, we see the typical asymptotic ratchet growth response, but with an additional subtlety: 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 this observation in his previous work, confident it was a real effect and not due to a lack of thermal equilibrium. Howard has discussed CTE value being different for ascending versus descending temperatures and he has suggested that this may hint towards important details of the ratchet growth mechanism.

To investigate the question of thermal equilibrium and possible rate effects, the last two specimens in Table 1 were measured using segment C only, at a rate of 5 and 1°C/min, respectively.

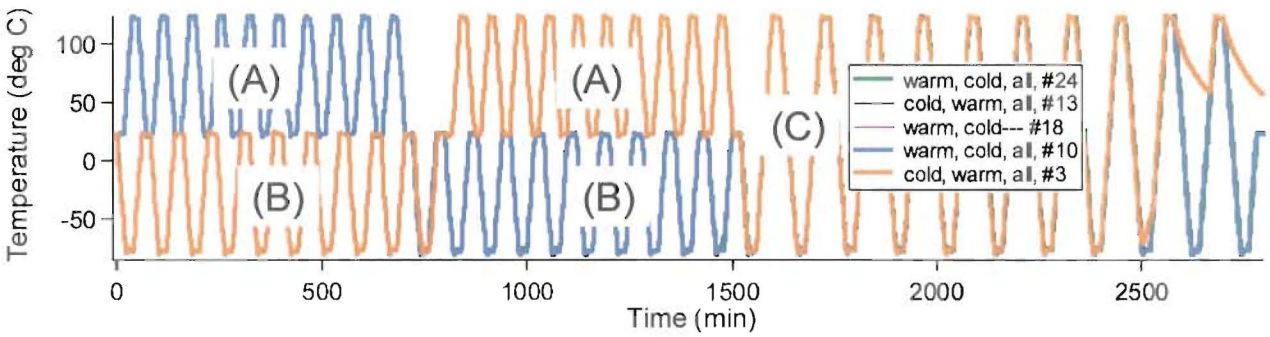

Figure 2: Temperature vs. Time for all A, B, and C segments of all five specimens listed in Table 1.

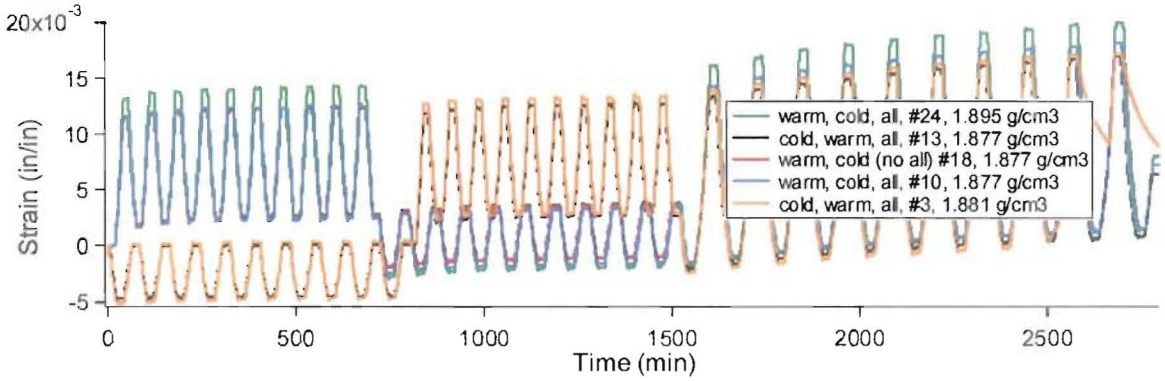

Figure 3: Strain vs. Time for all A, B, and C segments of all five specimens listed in Table 1.

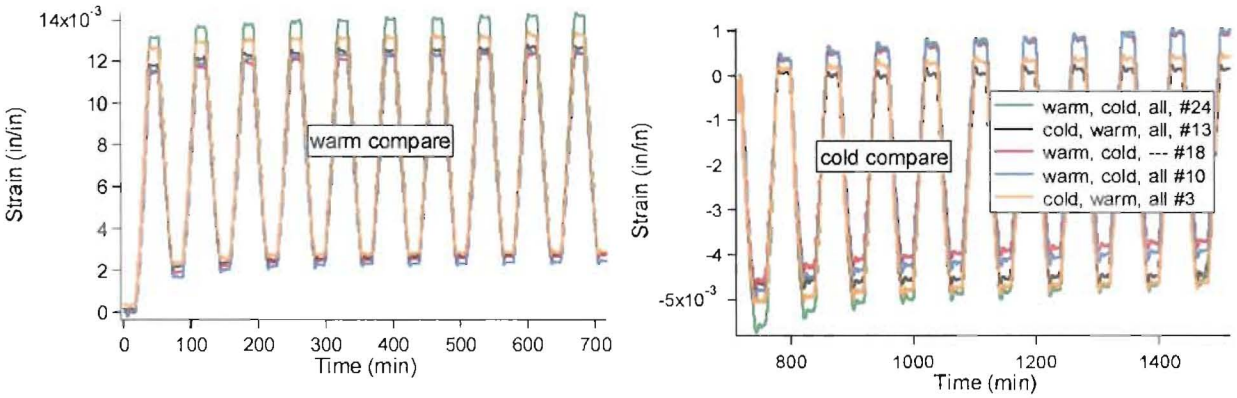

Figure 4: a) Test segment A for all specimens, regardless of segment ordering. (b) Test segment B for all specimens, regardless of segment ordering

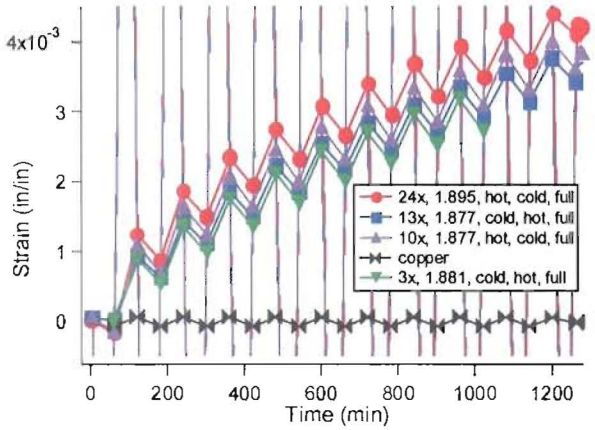

Figure 5: Strain value overlays for segment C, specimens 24, 13, 10, 3 and copper; solid symbols are strain values between 23 and 23.5°C.

Figure 6 shows strain values corresponding to three sets of temperatures: greater than 122°C, between 23 and 23.5°C, and less than -77.5°C, for the last two specimens listed in Table 1. Strain values are plotted versus cycle#, to compare the ratchet growth per cycle at the two rates. All strain values were shifted by a constant such that the initial strain at temperatures between 23 and 23.5°C matched exactly.

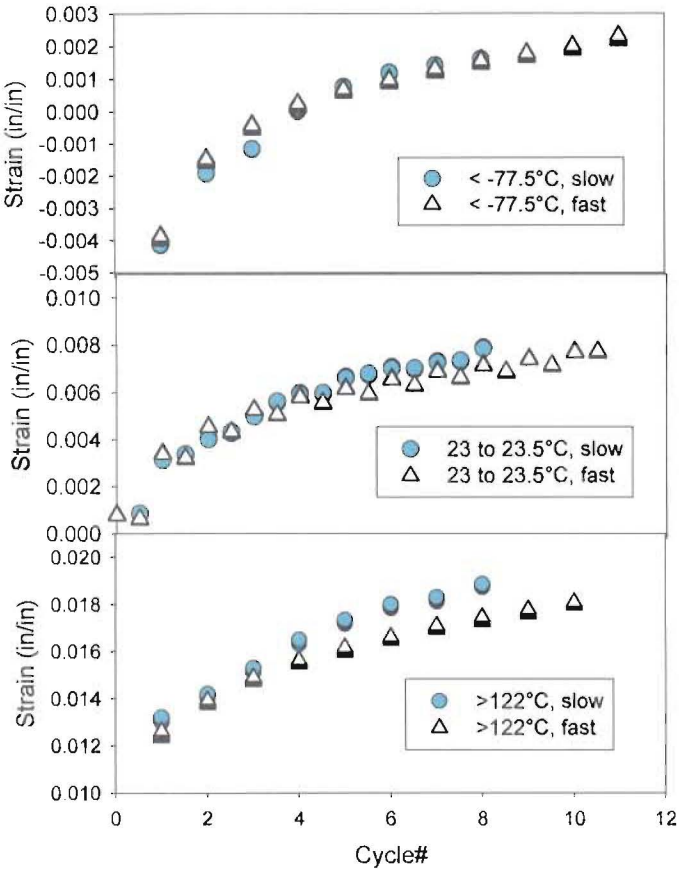

Figure 6: Strain values per cycle# for the last two tests in Table 1, fast data (5°C/min) in open triangles, slow data (1°C/min) in filled circles. Strain values correspond to temperatures (a) less than -77.5°C, (b) between 23 and 23.5°C, and (c) greater than 122°C.

In Figure 6 the fast rate data (5°C /min) do show a stronger "zig-zag" response in the 23 to 23.5°C strain values than the slower data, indicating that the specimen is likely not in full thermal equilibrium at the faster rate. However, at ambient and cold temperatures, the overall ratchet growth rate per cycle appears to be quite independent of the fast or slow thermal ramp rate. Interestingly, the strain data at temperatures above 122°C appear to indicate more growth at the slower 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 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.

[1] Kolb, J. R., Rizzo, H.F., *Prop, Explos., and Pyrotech., 4,* 10, 1979.
[2] Howard Cady, Los Alamos National Laboratory, unpulished results.

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