LA-UR- 09-01448

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Intended for: Proceedings of the Society for Experimental Mechanics Annual Conference, Albuquerque, NM, 1-3 June 2009.

Ratchet Growth in Recycled PBX 9502

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ABSTRACT

PBX 9502 is a plastic-bonded high explosive (PBX) containing 95 weight% TATB crystals in a polymer binder. TATB crystals are graphitic in nature, with a sheet-like structure and anisotropic CTE. Although the mechanism is not understood, solid-pressed TATB composites have been observed to undergo irreversible volume change ("ratchet growth") upon thermal cycling. This phenomenon has been studied but many aspects remain elusive and uncharacterized. Engineering or performance changes associated with ratchet growth have often been attributed to changes in density alone. We propose that the density changes which accompany ratchet growth involve a unique form of micro-damage distinguishable from the pore structure associated with low-pressed density.

We have performed ratchet growth studies on Recycled PBX 9502 between -54 to 80°C with density changes of about 1.5%. Specimens of the same density were obtained using a lower pressure in the manufacturing process. Comparative measurements were made using quasi-static uniaxial tension tests, as well as micro x-ray computed tomography and ultra-small angle neutron scattering experiments. Through these measurements we have shown that ratchet grown PBX 9502 has properties quite different from predictions based on density alone. The pore size distribution of ratchet grown specimens is unique and easily distinguished from parts pressed to an equivalent density.

Introduction

Thermally-induced irreversible volume change, or "ratchet growth," is a phenomenon observed in pressed composites that contain a high volume percentage of crystals with highly-anisotropic coefficient of thermal expansion (CTE) values. Such materials include pressed composites containing graphite and boron nitride [1,2], while our interest lies in plastic bonded explosives (PBX) such as PBX 9502, containing 95 weight% (wt) TATB (triaminotrinitrobenzene).

Dimension changes are asymptotic as specimens are thermal cycled again and again over a range of temperatures; growth will begin anew if the temperature range is then increased. Previous ratchet growth studies [3,4] on TATB-containing PBXs have shown that the magnitude of volume change depends to some extent on the thermal properties of the binder relative to the range of thermal cycling, however, neat-pressed TATB (with no binder) demonstrates the effect as well. These and other studies [5] have shown significant effects of pressing conditions and initial specimen density on ratchet growth; in addition, they have summarized that 80 psi of applied load is enough to entirely stop dimensional growth.

PBX 9502 molding powder is obtained by slurry mixing TATB with the binder, 5 wt% Kel-F (3:1 chlorotrifluoroethylene/vinylidine fluoride copolymer). Powders are then isostatically pressed to form solid parts. In an effort to stem the high cost of TATB manufacture, many lots of "recycled" PBX 9502 were made using a 50/50 mixture of original (or "Virgin") material and re-dissolved machining scraps from post-process Virgin material. Because of the extra processing, recycled PBX 9502 has been shown to possess smaller TATB particles, on average, than Virgin material. We are studying both material types, however, this paper will present only the ratchet growth behavior in recycled PBX 9502.

Experimental

PBX 9502, Lot HOL88A891-006 was used in this study. Three hemispherical charges were pressed isostatically at 110 deg C, 20 kpsi, for 4 cycles with 5 minute dwell times. A fourth charge was pressed using identical conditions except that the pressure was reduced to 10 kpsi. See Table 1 for charge numbering scheme. Cylindrical cores (2.54 cm diameter by 110.16 cm long) were removed perpendicular to the equatorial plane of each charge, resulting in two distinct groups of initial core densities (see Figure 1). The higher density cores were removed adjacent to the inner charge cavity, the lower density cores were adjacent to the outer charge surface. Charge 4 cores were removed from a single layer.

Table 1: Test Matrix for Specimens: Core Numbers and Immersion Densities (in g/cm^3)

	Charge 01	Charge 02	Charge 03	Charge 04
Charge/Core Preparation	Pressed to high density (20 kpsi).	Pressed to high density(20 kpsi), thermal cycled to low density.	Pressed to low density (10 kpsi).	Pressed to high density(20 kpsi), thermal cycled to low density under 100 psi axial load.
Ultra-Small Angle Neutron Scattering	01- 02 *(1.8909)*	02- 26 *(1.8712)*	03- 03 *(1.8711)*	N/A
Uniaxial Tension 50°C 0.0001 s^{-1}	01- 01 (1.8905)	02- 02 (1.8714)	03- 01 (1.8705)	04-21
	01- 02 (1.8907)	02- 39 (1.8663)	03- 27 (1.8654)	04-18
	01-08 (1.8911)	02- 26 (1.8712)	03-03 (1.8717)	04-04
		02- 08 (1.8716)	03-10 (1.8723)	04-01
		02-37 (1.8645)	03-39 (1.8644)	04-14
		02-06 (1.8728)	03-24 (1.8710)	04-06
Uniaxial Tension -20°C 0.00000167 s^{-1}	01- 13 (1.8905)	02- 04 (1.8717)	03- 05 (1.8729)	04-08
	01- 15 (1.8909)	02- 35 (1.8636)	03- 32 (1.8653)	04-05
X-Ray Tomography	N/A	02-04 *(1.8720)*	03-05 *(1.8721)*	N/A

An additional set of data from nominal recycled PBX 9502, Lot 891-007, has been included in this discussion for reference. Lot 007 charges were isostatically pressed to nominal density and the relevant specimens machined at B&W Pantex.

Densities of all cores, and subsequently-machined tensile specimens, were measured using immersion methods in water and a NIST standard reference. The density of the baseline specimens were also measured using the same procedure/standards in the same analytical laboratory.

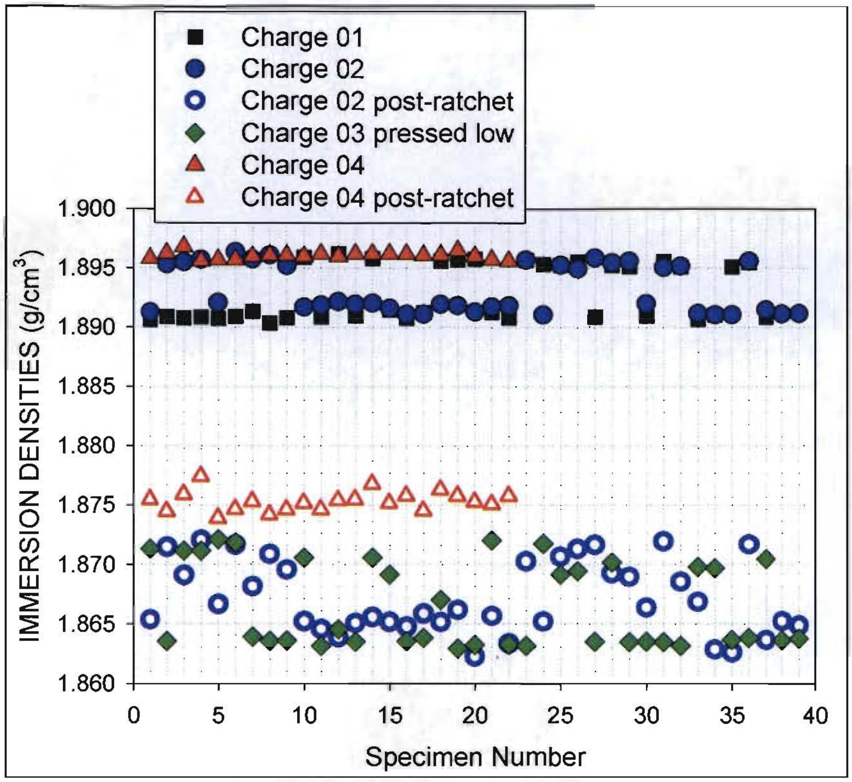


Figure 1: Immersion densities of as-pressed and post thermal-cycling cores from Charges 01 thru 04. Specimen numbers are arbitrary.

A custom-built, explosion-proof Tenney Benchmaster, model BTC-SPL, was used to thermal cycle cores from Charges 02 and 04 in batches of 8 to 10 cores. The Charge 04 cores were loaded into spring-loaded steel fixtures, Figure 2, with 100 psi load applied. Charge 02 cores were placed, unloaded, in the steel fixtures. Each fixture was equipped with a thermocouple and subjected to 30 cycles of the following profile: ~1°C/min ramp from ambient up to 85°C, one hour hold, 1°C/min ramp down to -65°C, 1 hour hold, 1°C/min ramp back to ambient. The outputs of 8 thermocouples were consistent and reproducible.

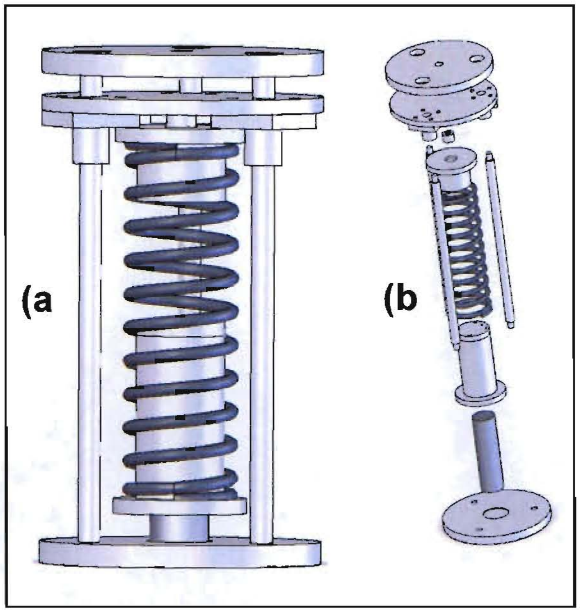


Figure 2: Spring-rig fixture used to apply 100 psi axial load to the cores of Charge 04.

As seen in Figure 1, the final ratchet grown densities of Charge 02 cores were almost identical to the densities of the as-pressed low density cores from Charge 03. Charge 04 densities, thermal cycled under load, showed a somewhat intermediate level of density.

Lengths and diameters of Charge 02 and 04 cores were measured with a micrometer before and after thermal cycling in order to capture the directionality of volume growth. Lengths at three locations, and diameters at three locations, were averaged and the normalized dimensional changes are plotted in Figure 3a and 3b. The effect of the 100 psi axial confinement is clearly seen, reducing the normalized length change from 0.4% to zero. Interestingly, the normalized diameter change *increases* for the axially confined specimens, demonstrating the limitation of uniaxial confinement in reducing overall volume change. In Figure 3c are shown the normalized density changes for post-ratchet Charge 02 and 04 cores; the 100 psi uniaxial confinement reduced the overall volume change from 1.4% to 1.1%. Further experiments are underway to explore the effect of a triaxial 100 psi mechanical confinement.

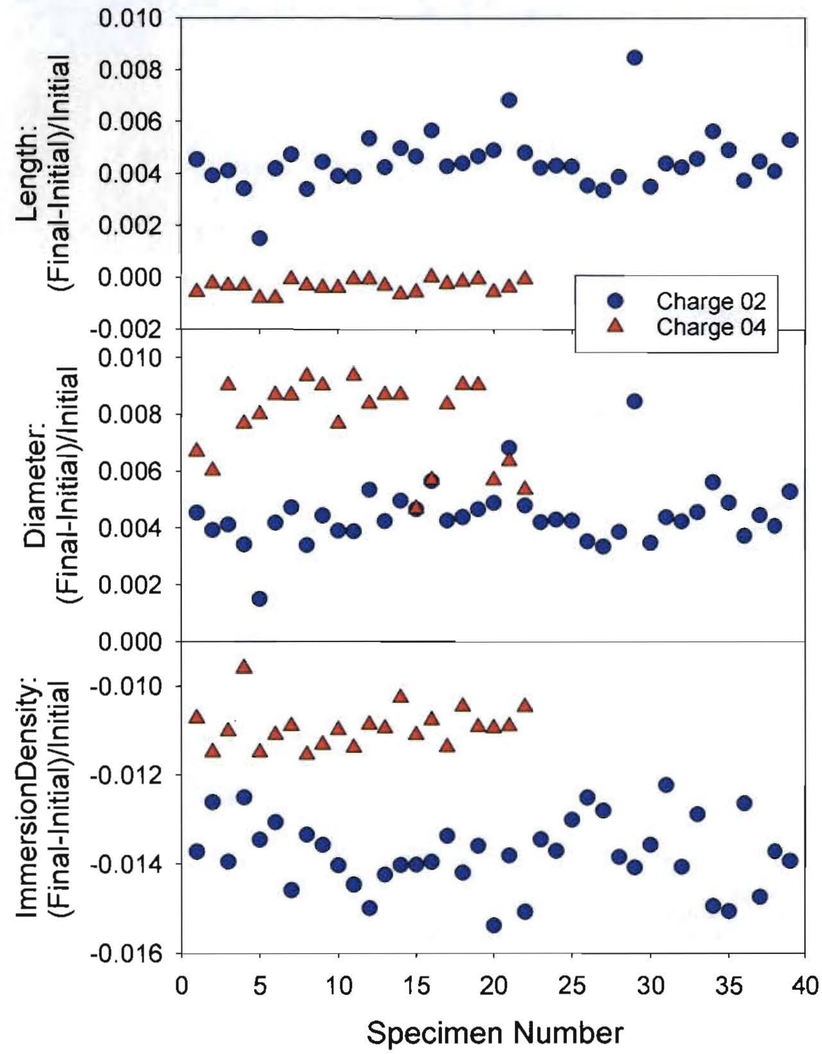


Figure 3: Normalized change in average core dimensions from Charge 02 and 04, before and after thermal cycling (a) length; (b) diameter; normalized change in immersion density before and after thermal cycling (c).

A subset of cores from Charges 01 thru 04 were machined into tensile dogbones, Figure 4. These specimens were tested under quasi-static conditions to failure on an Instron 5567. Two knife-blade extensometers, 2.54 cm gauge length, were mounted on opposite sides of the specimen, and tests were run in strain rate control using the averaged extensometer output. A Bemco environmental chamber was used to control the temperature to within 0.1 deg C, and tests were run at 50°C and 0.0001 s^{-1}, and at -20°C and 0.00000167 s^{-1}. The stress-strain curves are shown in Figure 5a and 5b, including the results for "nominal" Lot 007 specimens tested under the same condition.

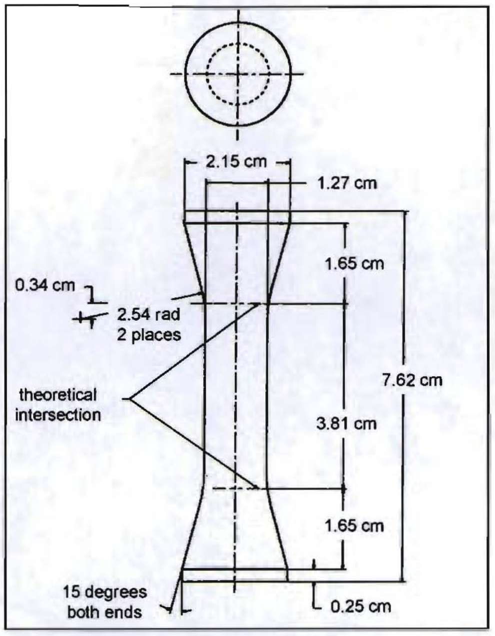
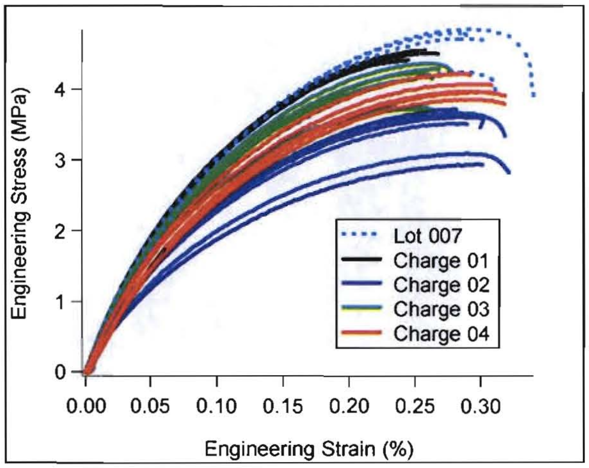


Figure 4: Dimensions of standard 3-inch tensile dogbone.

There are obvious differences in the tensile response of the various charges. The question is whether those differences correlate with specimen density, regardless of how that density was obtained, or whether the differences more specifically correlate with the thermal (ratchet growth) history of the specimens. It is our hypothesis that the mechanism of ratchet growth induces unique and measureable micro-damage in the specimen, endowing specimens with a unique pore-size distribution and corresponding bulk properties.



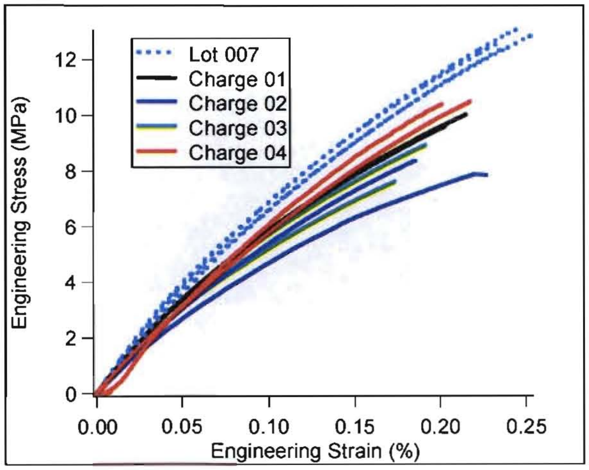


Figure 5: Tensile stress-strain curves of specimens taken from Charge 01 thru 04 cores, as well as from Lot 007. (a) Test conditions were 50°C and 0.0001 s^{-1}. (b) Test conditions were -20°C and 0.00000167 s^{-1}.

Three parameters are used to indicate stress-strain trends as a function of PBX 9502 specimen density in Figures 6 and 7. The ultimate stress (MPa) is the highest stress achieved during the test, the strain at ultimate stress (%) is the strain value corresponding to the ultimate stress, and the modulus (MPa/%) is the slope of the stress-strain curve measured at 40% of the ultimate stress value. In Figures 6 and 7, ratchet grown specimens are indicated by open symbols and as-pressed specimens are shown in solid symbols.

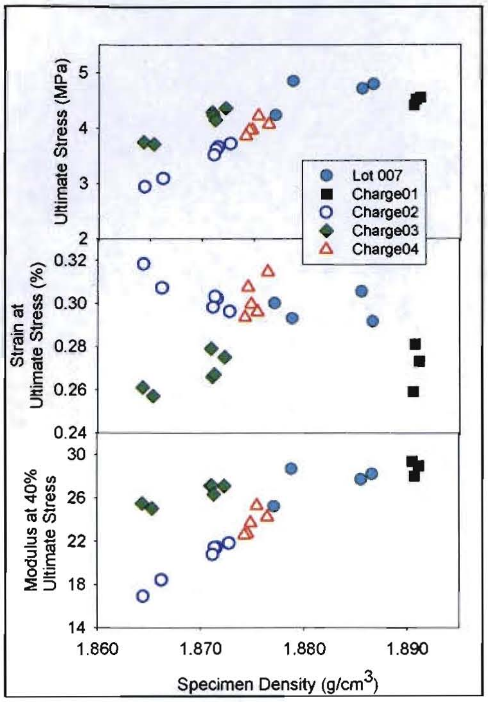


Figure 6: Tensile parameters at 50°C and 0.0001 s^{-1} plotted versus specimen immersion density for specimens from Charges 01 thru 04 as well as Lot 007. Data include: ultimate stress in MPa (a), strain at ultimate stress in % (b), and the modulus measured at 40% of the ultimate stress (c).

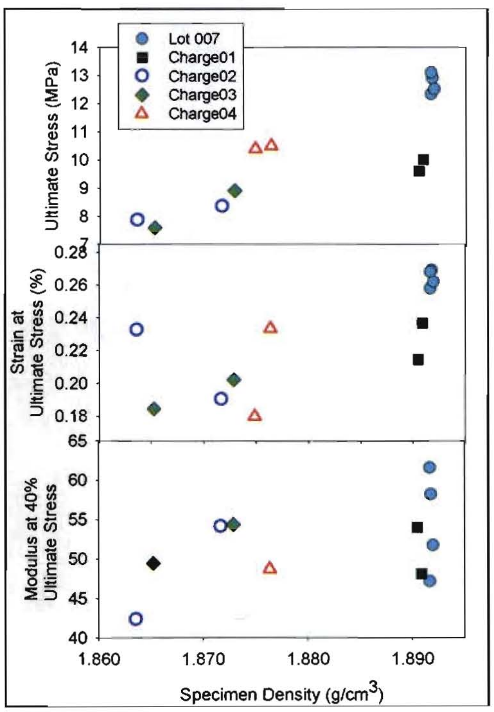


Figure 7: Tensile parameters at -20°C and 0.00000167 s^{-1} plotted versus specimen immersion density for specimens from Charges 01 thru 04 as well as Lot 007. Data include: ultimate stress in MPa (a), strain at ultimate stress in % (b), and the modulus measured at 40% of the ultimate stress (c).

In Figure 6 are shown the tensile parameters measured at 50°C plotted versus the specimen densities. Two distinct trend lines are observed for each of the three parameters, one following the as-pressed specimens and one following the ratchet grown. Ratchet grown specimens have a significantly lower modulus, fail at lower pressures, and can accommodate larger strains at failure than their as-pressed, equivalent-density counterparts. Interestingly, the uniaxially-confined specimens of Charge 04 appear to follow the same trend line as the unconfined specimens of Charge 02, even though their growth was entirely limited to the radial direction of the cores. If the Charge 04 micro-damage was oriented, the effect is not distinguishable in the 50°C tensile properties.

In Figure 7, the tensile parameters measured at -20°C are plotted versus their specimen densities. Here, the trends of ratchet-grown versus as-pressed specimen response are not so well-distinguished. The glass transition temperature of the PBX 9502 binder is 28 °C [6]. At -20°C, tensile failure is very brittle and shows a significantly broader distribution than at warmer temperatures. Note that the lot-to-lot variability in tensile parameters at this temperature, for "nominal density" specimens, is nearly as large as the changes observed over the entire range of as-pressed and ratchet-grown density.

We are using ultra-small angle neutron scattering (USANS) and micro x-ray computed tomography methods [7] to characterize the pore structure of specimens from Charges 01 thru 04. These techniques span pore sizes ranging from 0.1 – 20 μm for USANS and 1 μm to larger for tomography. Results to date have indicated that the ratchet grown specimens of Charge 02 possess a significantly smaller average pore size distribution than the equivalent-density specimens from Charge 03. For tomography, two specimens with identical densities were selected from each of the two charges. Three slices from each 3D image were analyzed using three different grayscale-threshold values in Clemex Vision software. The averaged pore-size distributions for each slice of the four specimens are plotted in Figure 8. The average radius of the ratchet-grown Charge 02 specimens is significantly lower than the average radius of the as-pressed specimens from Charge 03. The USANS and tomography results will be summarized elsewhere in greater detail [7].

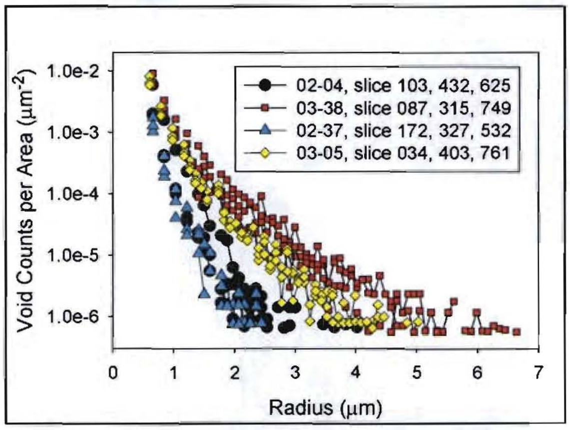


Figure 8: Pore size distribution from micro x-ray computed tomography images. See legend for specimen identification. Specimens 02-04 and 02-37 are from Charge 02, ratchet grown, while specimens 03-38 and 03-05 are from Charge 03, as-pressed.

While the tensile results presented here show a significant difference between ratchet-grown and as-pressed specimens of the same density, they do not indicate a significantly different response of confined and unconfined ratchet grown specimens. This is somewhat surprising due to the oriented nature of the volume change in the confined specimens. Of particular interest to us will be the USANS and tomography results for the Charge 04 specimens, where we anticipate we will distinguish significant orientation of the pore structure. Other types of mechanical response are being evaluated in these specimens with the hope of quantifying the engineering effects of oriented damage.

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