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Thermal Expansion of LX-17, PBX 9502 and Ultrafine TATB

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Abstract

A large quantity of linear strain and LCTE data from -55 °C to 75 °C on LX-17, PBX 9502 and ultrafine TATB (ufTATB) is presented. Axial and diametral measurements are blended to give final densities, which agree with the liquid immersion values of Baytos, et. al. The nominal densities at 21, -55 and 75 °C in g cm⁻³ are: LX-17 1.90, 1.920, 1.874; PBX 9502 1.89, 1.907, 1.867; ufTATB 1.80, 1.822, 1.778. Data taken radially show more thermal expansion than that taken transversely in cut-up parts; both must be combined to get the density. There is no difference between virgin and recycled TATB. Rachet growth data is presented, both at low pressure and at higher pressure, where the swelling is diminished. A Kel-F strain curve is presented and the theoretical maximum densities are computed.

Keywords: density, thermal expansion, LCTE, strain

1 Introduction

The thermal expansion of high-% TATB explosives has been measured for 30 years and still questions persist. The major explosives are LX-17 (wet-aminated TATB 92.5 wt%/kel-F 7.5), PBX 9502 (dry-aminated TATB 95%/kel-F 5) and ultrafine TATB (ufTATB; wet-aminated), which is used as a booster. The type of amination refers to the last step in the production synthesis of the TATB made 30 years ago. Dry-aminated TATB has 0.8 % ammonium chloride left from the process whereas wet-aminated TATB has 0.1%. The Micromeritics Saturn 5200 DigiSizer was used to measure the particle sizes by laser light scattering, and the results are shown in Figure 1. Basic wet and dry-aminated TATB have a mean size of about 75-80 µm, but ultrafine TATB has been micronized to bi-modal peaks at 0.3 and 8 µm.

Figure 1. Particle size distribution for three kinds of TATB.

Rizzo, Humphrey and Kolb measured the linear coefficient of thermal expansion (LCTE) of TATB and LX-17 and found it varied as a function of grain size and pressing method [1,2]. Further, they found that thermal cycling of small parts caused them to swell in a phenomenon called ratchet growth. Cady was perhaps the first to make large parts, cut them up, and to discover that LCTE's measured parallel to a radius are different from those measured transversely [3]. The field was summarized by Skidmore [4], who labeled the PBX 9502 LCTE's as "elusive" and showed a $\pm 20 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ variation in the literature LCTE's. Not included in Skidmore were important immersion densities of PBX 9502 done by Baytos and Martinez [5].

The Skidmore review [4] points out that almost all thermal expansion data has been presented in terms of LCTE's. This seems to have derived from the study of metals, where the LCTE's are fairly constant with temperature. For explosives, they are not, although early work sought to define them as constant over limited temperature ranges. LCTE's contain some error caused by performing another step on the original data, but the historical desire to somehow make LCTE's seem constant is a larger problem in considering old data.

Our particular interest is to obtain density data at specific cold and elevated temperatures for inclusion into a computer code. Immersion measurements speak directly to this. Because thermal mechanical analyzers (TMAs) generally only measure thickness changes in a single direction, multiple measurements

must be made in order to characterize a material's anisotropic behavior. The expansion data from these separate experiments must then be combined to estimate volumetric, and subsequently, density changes.

Assuming constant mass, and if the sample is isotropic, we can convert the relative linear strain, S_l , at some temperature to density at that temperature, ρ_T , by using the expression

$$\rho_T = \frac{\rho_o}{1 + 3S_l}, \quad (1)$$

where ρ_o is the initial reference temperature density. For samples ram-pressed as cylinders, the strain in the axial direction of the cylinder is different from that at right angles- the diametral direction. The two results may be averaged using

$$\langle S_l \rangle = \frac{1}{3} [S_l(axial) + 2S_l(diametral)] \quad (2)$$

This value can be used in Eq. (1) in place of S_l , and a similar expression would apply to LCTE's as well. Other samples are pressed as hemispheres but are cut up into cylinders. These pieces are measured axially, but the sample axis could have been aligned either along the complete part-radius (radial) or perpendicular to the complete part-radius (transverse). The average of the two directions is computed the same way in Eq. (3).

$$\langle S_l \rangle = \frac{1}{3} [S_l(radial) + 2S_l(transverse)] \quad (3)$$

Axial/diametral and radial/transverse are similar but refer to the individual cylinder part and the complete part from which the cylinder may have come. Many samples were cylinders with lengths and radii varying from 6.35 to 20 mm. Some were rectangular solids with dimensions varying from 3 to 63.5 mm.

2. Experimental

Most of our measurements reported here were done with a TA Instruments 2940 thermal mechanical analyzer. In this instrument, the expansion of the sample causes a core attached to a quartz rod probe to move inside a coil, causing a change in voltage. The instrument is calibrated using factory-supplied aluminum standards, which are run over a temperature range of 47 °C to 147 °C. In addition, 6061 T-6 aluminum samples were measured from -60 °C to 150 °C, and the results agreed with the data of Nix and

McNair [6]. Also, a Digital Image Correlation (DIC) machine is now also being used, and results from it agreed with Nix and McNair's aluminum from 25 °C to 75 °C. This optical method can see the tiny strain of ZeroDur glass, albeit with scatter. A few measurements were made with an Ares G2 mechanical spectrometer, which was not designed to do thermal expansion. This was calibrated against Nix and McNair aluminum [6], with the correction being about half the measured strain. It was further calibrated by running the same LX-17 sample on the Ares and on the DIC, so that the LX-17 became a secondary standard. The Ares is good for looking for major possible changes in thermal expansion.

All of our data was taken with temperature increasing, following a 10-minute dwell time cold. The upward rate was 1-3 degrees/minute. The loads on the sample were minimal, being about 275-3450 Pa (0.04-0.5 psi). By increasing the load by a hundred, slightly smaller strains and LCTE's were obtained, so that pressure is a factor.

There are three kinds of pressing used to compact the samples. "Isostatic" or "billet" pressing is pressing done in a fluid with molding powder placed in a sack and situated so hydrostatic pressure may be applied relatively uniformly to all sides. Once pressed, the billet then must be machined into finished parts. Parts produced in this way tend to show the least amount of anisotropy, on average. A second technique, also using hydrostatic fluid, includes the use of a mandrel inside the sack, which causes the powder to be roughly shaped around it. This technique produces parts that are roughly pre-shaped and that may be subsequently machined. Parts such as these tend to show much more directionality than do those produced using the first pressing technique and are called "quasi-isostatic". Finally, "ram" or "die" pressed refers to parts pressed directly to their final size using small and relatively inexpensive pistons and cylinders. No subsequent machining is needed and the products tend to be anisotropic with considerable variability.

2 Pristine Results

Ten years worth of measurements are condensed into Table 1. Samples are "pristine", meaning that no significant ratchet growth is thought to have occurred prior to testing. The cold temperature at -55 °C represents the low end of the temperature spectrum, and +75 °C represents the high end. Linear strain, referenced to 21 °C on the first up-cycle, is the baseline. The ability to compare results to the liquid immersion densities determined by Baytos [5] justifies the conversion of strain data into densities.

Table 1. TMA/DIC linear strain data collected for this paper. The liquid immersion results of Baytos are also included.

	Density (g cm ⁻³)	Ave. Linear Strain	Density (g cm ⁻³)		Ave. LCTE (x10 ⁻⁶ °C ⁻¹)			
		at -55 °C	at 75 °C	-55 °C	75 °C	-55 °C	21 °C	75 °C
LX-17, 1st 4	1.90	-3.5E-03	4.0E-03	1.919	1.875	34	61	110
isostatic	1.90	-3.7E-03	4.6E-03	1.921	1.874	47	59	111
TMA and	1.90	-3.7E-03	4.1E-03	1.922	1.877	36	63	92
DIC	1.894	-3.8E-03	4.7E-03	1.916	1.868	47	64	108
ram	1.90	-3.5E-03	4.6E-03	1.920	1.874	20	69	103
PBX 9502	1.885	-3.4E-03	3.4E-03	1.904	1.866	40	53	85
quasi-static	1.894	-3.9E-03	3.9E-03	1.916	1.872	50	62	96
TMA; all	1.894	-4.0E-03	3.9E-03	1.917	1.872	48	58	84
nine are	1.890	-3.6E-03	3.6E-03	1.911	1.870	44	58	91
hemispheres	1.891	-3.8E-03	3.9E-03	1.913	1.869	49	57	90
	1.891	-3.5E-03	3.7E-03	1.911	1.870	45	51	88
	1.888	-3.8E-03	3.7E-03	1.909	1.867	51	54	87
	1.885	-3.7E-03	3.4E-03	1.906	1.866	48	53	76
	1.891	-3.5E-03	3.6E-03	1.911	1.871	48	50	86
PBX 9502	1.874			1.892	1.858			
liquid	1.883			1.901	1.868			
immersion	1.875			1.897	1.860			
[ref. 5]	1.883			1.902	1.867			
	1.891			1.907	1.871			
	1.891			1.907	1.871			
ufTATB, ram	1.80	-4.2E-03	4.4E-03	1.823	1.777	50	64	96
TMA & DIC	1.80	-3.8E-03	4.1E-03	1.821	1.778	43	61	93

Table 2 summarizes the averaged isotropic results, cold and hot, for samples of the nominal ambient values, and these may be used as code input for generic material. If the densities are different from the nominal, then the fractional density may be used to estimate. Interpolating may be done using a second-order polynomial fit to the -55, 21 and 75 °C points for each property by itself. For example, the densities become

$$\begin{aligned}
 \rho_o(LX-17) &\approx 1.9075 - 3.20 \times 10^{-4} T - 1.68 \times 10^{-6} T^2 \\
 \rho_o(PBX9502) &\approx 1.8965 - 2.77 \times 10^{-4} T - 1.56 \times 10^{-6} T^2 \\
 \rho_o(ufTATB) &\approx 1.8071 - 3.20 \times 10^{-4} T - 9.07 \times 10^{-7} T^2
 \end{aligned} \tag{4}$$

across the temperature range. It is not possible to take a second-order fit of the strain, differentiate it and get good values for the LCTE. The LCTE's must be interpolated separately.

Table 2. Summarized isotropic thermal expansion results at cold and hot temperatures.

	Density (g cm ⁻³)	Linear Strain (x10 ⁻³)		Density (g cm ⁻³)	
		at -55 °C	at 75 °C	-55 °C	75 °C
LX-17	1.90	-3.7 ± 0.2	4.3 ± 0.4	1.920 ± 0.01	1.874 ± 0.01
PBX 9502	1.89	-3.7 ± 0.2	3.7 ± 0.3	1.907 ± 0.005	1.867 ± 0.005
ufTATB	1.80	-4.0 ± 0.2	4.2 ± 0.2	1.822 ± 0.01	1.778 ± 0.01
		Ave. LCTE (x10 ⁻⁶ °C ⁻¹)		Fractional Density	
		-55 °C	21 °C	75 °C	
LX-17	41 ± 8	62 ± 8	105 ± 15		
PBX 9502	46 ± 5	54 ± 5	87 ± 10	1.010 ± 0.006	0.988 ± 0.006
ufTATB	46 ± 10	62 ± 10	94 ± 15		

Table 3 summarizes the directional differences seen in various samples, including two from the literature [3,7]. The top part includes individual cylindrical samples, which have been measured axially and diametrically. Because the parts were made by different processes, it is not surprising that the axial/diametral ratios vary considerably. The lower part of Table 3 contains axially-measured samples taken from large quasi-isostatic parts cut into many smaller parts. The lower result is data taken for this report.

Table 3. Directional thermal expansion differences seen in LX-17 and PBX 9502. LCTE is in x10⁻⁶ °C⁻¹.

	Temp (°C)	Strain	Strain	LCTE	LCTE	ratio	ratio
		Axial	Diametral	Axial	Diametral	strain	LCTE
LX-17 ram- pressed, DIC	-55	-4.11E-03	-3.13E-03	23	19	1.3	1.2
	21	0	0	79	63		1.3
	75	5.12E-03	4.26E-03	119	95	1.2	1.3
PBX 9502 [7]	-55			64	39		1.6
	75			125	68		1.8
ufTATB ram- pressed, DIC	-55	-6.27E-03	-2.94E-03	71	24	2.1	3.0
	21	0	0	102	45		2.3
	75	6.86E-03	3.11E-03	146	73	2.2	2.0
		Strain Radial	Strain Transverse	LCTE Radial	LCTE Transverse	ratio strain	ratio LCTE
PBX 9502 [3] quasi-isostatic	-40			50	42		1.2
	20			66	56		1.2
	60			84	73		1.2
PBX 9502 quasi-isostatic	-55	-4.41E-03	-3.32E-03	57	43	1.3	1.3
	21	0	0	66	47		1.4

75	4.65E-03	3.20E-03	103	72	1.5	1.4
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3 Thermal Cycling

A considerable number of measurements were done for this paper. Table 4 contains LX-17 and PBX 9502 data for samples that were thermal-cycled and had their densities measured at room temperature on the down side of every cycle. The swelling appears to approach about 1-1.5 volume %. Table 5 shows the strain and LCTE results for a cycled LX-17 sample. The strain (swelling) increases with each cycle but the LCTE is constant at cold and ambient and decreases slightly hot. This shows that using only LCTE values can be misleading.

All this data is combined with that of Rizzo [1] and Johnson [8] to give Figure 2. This displays final fractional densities from samples thermal-cycled 20 or more times so that the result is perhaps equilibrated. The X-axis is the temperature span of the thermal cycle from bottom to top each time. The four kinds of symbols show what the initial temperature was. Figure 3 shows that the larger the temperature span, the more ratchet growth is obtained.

A special run was done to consider the properties of Kel-F 800. Old samples of LX-17-1 were heated to 100 °C for 24 hours to remove all traces of crystallinity in the binder. The samples were then cooked at 40 °C for various times, because this temperature is where Kel-F crystals grow most rapidly. Strain was then measured with the Ares G2 at room temperature. No effects on the sample strain or LCTE were seen.

Table 4. Rachet growth in samples with room temperature density measured after every cycle. All cycles are -50 °C to 70 °C.

Cycle No.	End Density	Cycle No.	End Density	Cycle No.	End Density	Cycle No.	End Density
LX-17, ram, 25.4 x 12.7 mm		0	1.910	3	1.901	5	1.898
		2	1.903	4	1.900	6	1.898
0	1.918	3	1.902	5	1.899	PBX 9502, ram, 25.4 x 12.7 mm	
1	1.917	4	1.900	6	1.897		
2	1.912	5	1.899	7	1.896	0	1.901
3	1.910	6	1.897	8	1.896	1	1.897
4	1.908	LX-17, ram, 25.4 x 12.7 mm		9	1.894	2	1.893
5	1.907			10	1.894	3	1.890
6	1.906	0	1.896	11	1.893	4	1.889
7	1.905	1	1.891	12	1.893	5	1.888
8	1.905	2	1.887	13	1.893	6	1.886
9	1.904	3	1.884	14	1.892	7	1.885
10	1.904	4	1.882	15	1.892	8	1.884
11	1.904	5	1.880	16	1.891	9	1.883
12	1.903	6	1.879	17	1.892	10	1.883
13	1.902	7	1.878	18	1.892	11	1.882
16	1.902	8	1.877	19	1.891	12	1.882
19	1.901	9	1.876	20	1.891	13	1.882
22	1.900	10	1.876	23	1.890	14	1.881
28	1.899	11	1.875	26	1.889	15	1.881
34	1.898	12	1.875	29	1.889	16	1.881
40	1.897	13	1.875	32	1.888	17	1.881
LX-17, ram, 19.05 x 12.7 mm		16	1.874	35	1.888	18	1.880
		19	1.872	41	1.887	19	1.881
0	1.915	22	1.872	47	1.887	22	1.880
2	1.906	28	1.871	53	1.886	25	1.879
4	1.900	34	1.869	LX-17, isostatic, 25.4 x 12.7 mm		28	1.880
5	1.899	40	1.869			31	1.879
6	1.898	LX-17, isostatic, 25.4 x 12.7 mm		0	1.915	34	1.879
7	1.896			1	1.909	40	1.879
8	1.895	0	1.914	2	1.906	46	1.878
LX-17, ram, 19.05 x 12.7 mm		1	1.909	3	1.902	52	1.878
		2	1.904	4	1.901		

Table 5. Rachet growth as measured from strain and LCTE for PBX 9502 between -54 °C to 74 °C. The data is extrapolated 1 degree to either side. The initial density was 1.894 g/cm³, a cylinder 25.4 x 12.7 mm, isostatically-pressed and measured by TMA.

cycle no.	Strain (x10 ⁻³)			LCTE (x10 ⁻⁶ °C ⁻¹)		
	est -55 °C	21 °C	est 75 °C	est -55 °C	21 °C	est 75 °C
1	-3.8	0.0	4.5	47	64	108
2	-3.0	0.77	5.0	48	64	94
3	-2.6	1.2	5.4	50	65	90
4	-2.2	1.6	5.8	47	63	79
5	-1.9	1.9	6.1	47	63	81
6	-1.6	2.1	6.3	47	61	84
7	-1.4	2.4	6.5	46	63	80
8	-1.3	2.6	6.6	45	63	84
9	-1.2	2.7	6.8	47	63	88
10	-1.0	2.8	6.9	46	62	84
11	-0.85	3.0	7.2	48	63	79

Figure 2. The fractional density in rachet growth increases with the temperature span.

Figure 2 shows that pressure applied to the sample during rachet growth helps to suppress the effect. The data seems to suggest that pressure is more effective on LX-17 growth than on PBX 9502. Other samples were subjected to 5170 kPa (750 psi) to study creep. At 25, 50 and 75 °C, the fractional density change after 4 weeks was 1.000, 0.999 and 0.997.

Figure 3. Effect of 517 kPa (75 psi) and 827 kPa (120 psi) on fractional density of rachet growth. LX-17 at low pressure is shown by the small triangles.

Finally, Kel-F 800 was run for linear strain, which is shown in Figure 4. The downward turn could be caused by sample softening with the probe sinking in. The linear strain at -55°C and 75°C is -3.9×10^{-3} and 1.9×10^{-3} , with the high temperature point being uncertain. These axial strains were tripled for volumetric use; there being no diametral data. If we use Dobratz' ambient density of 2.02 g/cm^3 [9], we get cold and hot values of 2.044 and 2.009 g/cm^3 .

Figure 4. Linear strain curve for Kel-F 800.

We move one step further and consider the X-Ray diffraction data of Kolb and Rizzo [10]. They measured the unit cell volumes, which can be converted to density knowing that there are two molecules per unit cell in the triclinic structure [11]. We also assume that the Kel-F data is theoretically dense, which is not quite true because of an amorphous component. The resulting maximum densities are listed in Table 6.

Table 6. Theoretical maximum densities (TMD) measured for TATB and calculated for LX-17 and PBX 9502.

Temp (°C)	TMD (g cm ⁻³)		
	TATB	LX-17	PBX 9502
-55	1.972	1.977	1.975
21	1.936	1.942	1.940
75	1.900	1.908	1.905

4 Discussion and Summary

By converting strain to density, the strain and liquid immersion results agree and the thermal expansion of TATB no longer seems elusive. The combined LCTE data has smaller error bars, partly because the

three explosives considered here are precisely made, compared to an arbitrary large-grained TATB. Directional effects must be accounted for in any sample if the final step to density is to be made.

The greatest gap in the data lies in the ram-pressed area, where the difference in axial and diametral measurements is clearly a function of how the pressing is done. A complete study should be done in this area. Quasi-isostatic data on LX-17 to balance all that taken on PBX 9502 would also be good.

There is a bewildering array of ratchet growth-as-a-function-of-pressure data, which is insufficient to predict what will happen to a given small sample. Remaining “pristine” can hold for several cycles with a wide temperature spread and it takes 20 cycles or more to greatly change the density. A systematic study of the kind done by Rizzo [1] should be undertaken.

5 References

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