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DDT of hot, thermally damaged PBX 9501 in heavy confinement

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Abstract

The research presented examines DDT of cylinders of PBX 9501 damaged above 180˚C in heavy confinement for 0-3 hours and end-ignited or ramped until self-ignition (cookoff) occurred. Progression of luminous reaction was observed by streak photography through a glass-filled slit running the length of the cylinder. Post-mortem analysis of the steel DDT tubes was also done for correlation with the optical records. Results indicate that repeatable, Type I DDT was observed to occur in hot, thermally damaged PBX 9501 with low levels of porosity. It was demonstrated that multiple parameters affect DDT behavior, most likely in a coupled fashion. These parameters are porosity, ignition temperature and thermal soak duration. Conditions leading up to cookoff were shown to sensitize the HE to DDT by increasing likelihood and decreasing run length. Over the range of porosities (0-37%) and ignition temperatures (180-235˚C), run lengths and detonation velocities varied, respectively, from approximately 22–109 mm and 6.0–8.3 mm μs^{-1}. This work fills a valuable and realistic space in the understanding of high explosive violent reaction, including DDT, in abnormal thermal environments.

Background

The behavior of high explosives (HE) in abnormally hot thermal environments remains an area of significant concern from a safety standpoint. The concerns arise from the often violent reactions that have been observed when the temperatures cross a sufficiently high threshold for ignition to occur (i.e. cookoff). Once ignited, the subsequent reaction may quench, or advance through increasingly rapid modes of combustion and violence. If certain conditions are met, a deflagration-to-detonation (DDT) transition will occur; this outcome resides on the worst-case end of the violence scale. As a result, over the course of many decades, research has been performed to understand the mechanisms and critical conditions for cookoff and DDT events and to relate them to violence. Our understanding of these high explosive violent reactions has improved, but still has a long way to go before reasonable predictive capabilities are attained.

DDT research for condensed phase explosives has most often been done with relatively high porosity, granular beds, at ambient temperatures. Most of the classic designs incorporated a rigid, round tube loaded with explosives that were ignited on an end so that reaction progression would be pseudo one-dimensional. The progression of reaction was monitored with discreet pressure, temperature or luminosity gauges (Cite), or in some more spatially-continuous designs, with a streak camera accessing the explosive column through a slit running lengthwise along the tube (cite). Observations and analysis from these experiments converged on a well-supported classification scheme (Type I or Type II) and descriptions of DDT mechanics (cite).

Briefly, Type I DDT begins with a laminar burn that increases pressure in the tube rapidly. In short time the pressure becomes high enough to lead to a transition to convective burning through the porosity (cite Boggs, Berghout). As a result of the additional burning surface area, the free volume in the tube pressurizes even faster (Cite parker). The combustive flow velocity increases as does drag on the particles (cite Asay, Shepard). The particles entrained in the flow compress until the bed strength is exceeded and collapse ensues resulting in a nearly impermeable compact at ~90% theoretical maximum density (TMD). This relatively impermeable compaction wave runs up the column. All the while, the upstream surface of the compact continues to burn supplying continuous propulsive force, stress waves and compressive heating. Eventually, a second compaction occurs and a 100% TMD *plug* forms. The plug acts as a piston, driven by the high-pressure combustion products, that accelerates until a shock forms and a normal shock-to-detonation-transition (SDT) finishes the process.

The extent and morphology of the porosity in these experiments was shown to be the most important factor for influencing the run length (distance) over which this DDT process occurred. It was shown that porosity provided increased surface area for early stage burning, void space for compaction during the intermediate stages building to shock formation and, finally, as a means of sensitizing the explosive during the SDT stage (cite). At higher levels, porosity allowed for multi-dimensional phenomena like longitudinal channeling and axial compaction (Cite). Results from these higher porosity experiments are grouped into the less-precisely described classification of Type II DDT (cite Leubcke). For a more thorough review of these classic experiments and DDT mechanics, the authors direct readers to the chapter on DDT found here [Asay]

For the purposes of understanding the fundamentals of DDT, porous, granular beds were ideal. However, for most applications where safety is a concern, the explosives of interest have been prepared at high densities with necessarily low porosity. Additionally, most cookoff scenarios result in a large fraction of the charge being heated and damaged as a result. Whether or not the conclusions from ambient temperature, high porosity granular beds can or should be applied to full-density, consolidated, plastic bonded explosives at elevated temperatures was one of the questions this work was intended to address. The authors chose to test the HMX-based plastic bonded explosive PBX 9501 because it has been studied extensively in abnormal thermal environments and has been observed to react violently during cookoff. Its kinetics [Henson, Dickson, Smilowitz] and mechanical properties [Rae] have been measured at high temperatures. Morphological changes as a result of thermal damage have been characterized [Parker, Peterson, Asay]. Its burn rate and behaviors are well described [Son, Berghout, Jackson, Hill, Parker] and its violence as a function of confinement has been studied [Dickson and Lee]. This experiment has been designed to tie all of these individual elements together and observe the integrated response under realistic conditions.

Methods and Design

The Apparatus

Figure 1 shows a cutout view and a dimensioned schematic of the DDT tube used for this work. The inner diameter and *keyhole* slit were cut within high tolerances by electrical discharge machining (EDM). This created a smooth surface finish and slip-fit for both the glass slide and the HE cylinders. Custom-sized float glass microscope slides were used for their good optical properties, high temperature resilience and constant width. As can be seen, the slit runs lengthwise through the tube providing a pseudo-one-dimensional view of the HE column. Inserted into the bottom of the tube was an ignition device. For the earliest shots, ignition was accomplished with a NiChrome wire threaded through a polyether ether ketone (PEEK) feedthrough. This method of ignition was prone to failure and was replaced with a more robust diesel engine glow plug (also inserted into the end of the tube) for the remainder of the series. The top end of the tube contained a conical aluminum feedthrough that was inserted the same length as the glow plug. Being conical, it would resist ejection during pressurization. With inserts in both ends, the length of tube available for filling with explosive was 149.6 mm. The inner diameter ranged from 6.35-6.401 mm.

The tube itself was manufactured from 1018 steel. To prevent the glass slide from being ejected during pressurization, the slit width stepped down by half to create a lip (this step-down is reminiscent in shape to a keyhole, thus it is described as such). On each end, a stainless steel retaining ring was used to provide extra hoop strength to keep the tube closed against the glass as long as possible during pressurization. This design was intentionally not gas-tight so that decomposition products could vent. The tolerances between the glass and steel were tight enough, however, to dynamically choke flow and effectively seal the system during combustion. Two radially oriented through-holes, 9 and 34 mm from the end, provided additional diagnostic access to the HE column.

The tube was designed to have thick walls (38.1 mm) for several reasons. The primary reason was to isolate the HE from boundary effects; maintaining one-dimensionality as best as possible so that results would be more representative of expected behavior in much larger charge geometries. Additionally, by being thick enough not to fragment, the tubes could be used as a post-mortem diagnostic. Finally, this level of confinement bounds the parameter space as a worst-case scenario.

Both a steel and PEEK disc were placed on either end of the tube and the whole assembly was bolted in place between two 25 mm thick steel plates. The steel discs had a conical hole to mate with the aluminum feedthrough and the PEEK disc was there to thermally insulate the tube from the clamping plates.

Heating

The tube was wrapped either in heating tape or with a flexible, kapton-insulated heater. Temperature was monitored by five thermocouples. Two of the thermocouples were internal; one passed through the aluminum feedthrough on the top end, while the other was potted with epoxy in the lower radial through-hole. The external thermocouples were located on the bottom, middle and top of the tube. Once assembled, the tube was insulted with fiberglass. A PID temperature controller was used to maintain the temperature profile. The heating rate varied from approximately 8-10°C/min. Temperature was sampled and logged every second.

Three types of thermal profile were imposed: 1) ramp to ignition, 2) ramp to soak for a specified duration, then ignition and 3) ramp to soak for a specified duration, then ramp again to ignition. All shots were soaked or ignited above 180°C. Ignition was accomplished either on one end by an electrically heated device (NiChrome wire or glow plug) or by thermal runaway (cookoff).

Explosives

All but one of the tests reported were performed with PBX 9501. The other was done with LX-07 molding powder. A variety of methods were used to form the PBX 9501 cylinders. For the lower and intermediate porosity tests, they were either machined from isostatically-pressed billets, or pressed-to-size uniaxially in a die. The cylinders were stacked end-to-end to fill the tube. The pressing density was nominally 1.834 g/cc, with slight variations noted. The higher porosity tests were done with molding powder that was hand-packed with a dowel into the tube.

Parameters Tested

A primary focus of this work was to identify variables that had significant effects on DDT behavior. Attempts were made to control for these variables as well as possible and indentify trends when different behaviors were observed. Table I summarizes parameters that were tested.

Table I. Parameters tested.

	Estimated Porosity (%)	Pore-field Characteristics	Ignition Temperature (°C)	Soak Duration (hrs)	Ignition Mode
Variables	0-5 5-8 18-25 33-37	Isotropic or Anisotropic	180-190 220-230 >235	0 1 3	End-ignition Cookoff

Porosity Creation and Estimation

As mentioned in the introduction, porosity is recognized as being of paramount importance to DDT mechanics. We relied on several techniques to create porosity and different methods to estimate it. Experimentally, the degree of porosity was varied by three means: 1) expansion of HE into ullage (free-volume), 2) initial loading density and 3) variation of thermal soak duration.

Despite our best efforts to control porosity, there are some factors for which we have high uncertainty. For example, HMX undergoes a β–δ polymorphic phase transition to varying degrees of completion between 160-180°C. With this transition comes a 6.7% increase in crystal volume. Depending on the kinetics of this transition, our porosity estimate could vary significantly. However, according to (Cite) above 180°C complete transition should occur in a matter of minutes. For this reason, the authors consider the transition to have gone to completion for the samples soaked at 180°C for 1 hour or more. For those samples that were heated above 180°C, but not soaked before ignition, our porosity estimates have greater uncertainty. Another high-uncertainty factor is solid loss due to volatilization and decomposition. Based on work by (Cite Zerkle, Parker) we have chosen to estimate a 0.8%-hr^{-1} increase in porosity for the first 3 hours at or above 180°C.

After 3 hours the mass loss rate reduces dramatically, though for this work we did not damage for durations beyond this. Again, reported uncertainty spans this range in case mass was not vented from the system.

With those caveats, porosity was estimated by two methods. The first method was reported by Jackson (Cite) for PBX 9501 and accounts for initial porosity, thermal expansion and the phase transition. It assumes the material swells isotropically and flows into the ullage in the tube. Its applicability is limited to experimental configurations with $\leq 15\%$ ullage. Percent ullage (U) is calculated as follows:

$$U = \left(\frac{V_\tau - V_e}{V_\tau} \right) \cdot 100 \qquad \text{Eqn. 1}$$

where V_τ and V_e are, respectively, the volumes of the tube and the pristine explosive. This first method does not address creation of porosity due to volatilization and decomposition, so represents the lower bound of the reported range of the porosity estimates.

The second method also assumes the material swells and flows into the ullage in the tube. It is only applicable for PBX 9501 heated above 180°C, for configurations with $\leq 15\%$ ullage and for soak durations not exceeding 3 hours. It does not account for thermal expansion of the HE, but does address creation of porosity due to volatilization and decomposition. Both of these differences increase the porosity value, thus this method is used for the upper bounding estimate of the reported range. It is calculated as follows:

$$\phi_{>180^\circ C} = \left(\frac{\rho_\delta - \rho'}{\rho_\delta} \right) \cdot 100 + 0.8 \cdot t \qquad \text{Eqn. 2}$$

where $\phi_{>180^\circ C}$ is the percent porosity for an HMX-based explosive heated above 180°C and through the β–δ phase transition, t is time in hrs, ρ' is the bulk density of material in the tube and ρ_δ is the TMD (in g cm^{-3}) of the HMX-based explosive with δ-phase HMX. Bulk density, ρ', is calculated as follows:

$$\rho' = \frac{m}{V_\tau} \qquad \text{Eqn. 3}$$

where m is the HE mass in g and V_τ is the volume of the tube in cm^3. Finally, ρ_δ is calculated as follows:

$$\rho_\delta = 0.933 \cdot \rho_\beta \chi_e + \rho_\beta \chi_b \qquad \text{Eqn. 4}$$

where ρ_β is the TMD (in g cm^{-3}) of HMX-based explosive with β-phase HMX. χ_e and χ_b are, respectively, the mass fractions of the explosive and binder components. For PBX 9501 χ_e=0.95 and χ_b= 0.05 and for LX-07, χ_e=0.9 and χ_b= 0.1.

Pore-field Characteristics
An important assumption was that the HE would swell and completely fill the ullage. This assumption was made based on observations that unconfined PBX 9501 undergoes a bulk expansion of approximately 15% when heated through the phase transition. Since 6.7% of that expansion is due to the HMX phase transition, the remaining 8.3% must be void volume. By dimensioning the HE and/or the tube to impose ullage ranging from 0-13% it was thought that porosity could be controlled, accordingly, to be between 0-6.3%.

For these tests, the radial ullage was sufficiently small that the HE would expand and come tight against the walls before expansion was complete. Once tight, internal stresses would increases as more material expanded. It was assumed that these stresses would be relieved through flow in the longitudinal direction. This approach inevitably led to anisotropic expansion and, subsequently, as noted by (Cite), anisotropy in the morphology and distribution of the pore-field. To account for this possibility, tests were performed to compare the effects of the degree of anisotropy on cookoff/DDT behavior (*see* results section).

Diagnostics
The progression of luminous reaction was monitored through the slit in the tube with a high-speed Phantom™ v12.1 color video camera for the earliest tests and a Phantom™ v710 monochromatic camera for the later tests. The maximum frame rates were 763,941 and 985,507 frames s^{-1}, respectively, with a resolution of 8 x 512 pixels. These cameras can be set to maintain the entire frame sequence (i.e. 1-2 s duration) in a volatile memory rolling buffer allowing for extensive pre-trigger capture. With this capability, unpredictable events, like cookoff in HE, were easily observed. An optical fiber attached to a photodiode and potted into a radial through-hole 30 mm from the end of the explosive column was used to trigger the camera.

In keeping with analysis methods from classic DDT research, streak-type images were produced from the video record with image processing software. In short, this was accomplished by cropping each frame to be 1 pixel wide and then assembling the temporally successive frames into a composite image. The resulting composite conveys reaction progress in a standard position vs. time image (x-t diagram). A detailed description of this technique, including a discussion of its advantages and disadvantages can be found here (Cite). With streak images, burn rates and detonation velocities can be measured and identification of relevant structures and classification of DDT mechanism type can be made (*see* figures 3-13).

After each shot, the damaged tube was sectioned to examine the degree of deformation of the steel. The depth of the dent in the tube was profiled and normalized by the dent depth from a reference shot that was performed with pristine PBX 9501 detonated in a tube at ambient temperature. Further, the color and surface texture of the inner diameter clearly correlated with the streak image. Specifically, on shots where DDT occurred, the tube displayed a distinct darkening and roughening from the point where the detonation began. This provided a reliable back-up diagnostic for run length and proved useful for shot #5 where the camera failed to trigger.

Results and discussion
Table II contains the information pertinent to the analysis that follows. Figure 2 displays these data mapped on a DDT-run distance vs. estimated porosity plot. This plot is useful for indentifying general trends. Finally, figures 3-13 are each a composite of a streak image, a photograph of the sectioned tube (on the right edge of the streak) and the profile of the dent for select tests.

Table II

Shot #	Material	ϕ (%) from Cite	ϕ (%) from Eqn 2	Soak Temp. (°C)	Soak Time (hrs)	Ignition Temp. (°C)	Ignition Mode	Run Distance (mm)	Detonation Velocity (mm μs^{-1})
1	9501	6.0	7.8	180	1	184.8	End, NiCr	No DDT	No DDT
2	9501	5.9	7.8	180	1	>235	Cookoff	55	7.5
3	9501	2.3	3.3	180	1	>235	Cookoff	58	8.3
4	9501	5.9	7.8	180	1	>235	Cookoff	No DDT	No DDT
5	9501	2.3	3.3	180	1	>235	Cookoff	64	NA
7	9501	0.7	1.3	180	1	187.5	End, GP**	109	7.4
9	9501	4.7	6.0	180	1	188.4	End, GP**	No DDT	No DDT
10	9501	0	1.0	-	-	185.8	End, GP**	No DDT	No DDT
11	9501 MP*	20.1	25.1	-	-	185.3	End, GP**	51	7.3
17	9501	6.3	8.3	180	1	186.3	End, GP**	No DDT	No DDT
18	9501 MP*	18.0	23.2	-	-	>235	Cookoff	22	7.2
20	LX-07 MP*	33.4	37.4	-	-	195.9	End, GP**	56	6.0
22	9501	0.0	0.5	-	-	>235	Cookoff	32	7.9
23	9501	2.5	3.2	180	1	227.9	End, GP**	76	8.0
24	9501	2.7	4.8	180	3	187.2	End, GP**	54	7.7
25	9501	0	3.1	180	1	211.1	End, GP**	81	8.0

*MP = molding powder
** GP = glow plug

By examining figure 2, it can be seen that the degree of porosity, the ignition temperature (and/or ignition mode) act to decrease run length. Shots ignited at similar temperatures and by similar means (i.e. end-ignited vs. cooked off) show a trend towards shorter run lengths with higher porosity. Those shots with comparable porosity, but different ignition temperatures also show this same trend. Shots that did not DDT (represented as dashed, vertically-oriented lines on the plot) when ignited on an end at cooler temperatures did tend to DDT when allowed to cook off. Ultimately, it appears that porosity and temperature (both of which increase rapidly during cookoff) act in a coupled fashion to sensitize the HE and consequently shorten the run length. Despite these trends being highly coupled, other trends can be gleaned from certain side-by-side comparisons. Whether or not these other trends are of primary importance, is difficult to conclude, but their mention is of value in the opinion of the authors. Following are some of the more informative comparisons:

Effect of Porosity
To examine the effect of degree of porosity, refer to shots #7, #24, #11 and #20, (figures 3, 4 and 5). All of these shots were end-ignited at a temperature between 180-190°C; the primary variable was porosity. In agreement with other DDT research, the trend indicates that increasing porosity decreases the run length to an extent. This trend levels off and even reverses at the highest levels of porosity. This effect is attributed to voids acting as hot spot generators under shock conditions.

Effect of Isotropy
As described in the methods section, it was believed that porosity could be controlled by varying the amount of ullage and assuming the HE would expand and flow to fill it. Subsequently, there would be varying degrees of isotropy in the pore-field of the damaged explosive. To elucidate the effect of isotropy shot #25 (fig. 6) was performed with pellets that were pressed to 1.72 g/cc. These pellets were dimensioned so that the HE would fill the tube completely at ambient temperature (in fact, liquid nitrogen was needed to shrink the pellets for loading into the tube). This density is about 6.7% lower than the nominal specification for pressed PBX 9501 and would allow for expansion due to the phase transition to be isotropic. Shots #25 and #23 (fig. 7) are similar in most ways (i.e. degree of porosity, thermal history, and ignition mode). The main difference between the two is that shot #23 had a high degree on non-uniformity in the distribution of the ullage (i.e. there was not much space to expand radially; most of the ullage was in the longitudinal orientation). Shot #23 should, therefore, have had a high degree of anisotropy in its pore-field. With similar detonation velocities, dent depths and run lengths, the effect of this anisotropy appears to be negligible.

Effect of Temperature
Comparison of shots #7, #23 and #3 (figures 3, 7 and 8) demonstrate the trend that increasing ignition temperature decreases run length. A reasonable explanation for this sensitization is that higher temperature material is at a higher energy state, thus requiring less energy input to exceed its activation energy barrier.

Effect of Cookoff
Many of the tests that were end ignited at 180-190°C did not DDT. However, when similar tests were repeated and allowed to cook off, DDT was observed. A comparison between shots #2 and #17 (figures 9 and10) demonstrates this. Additionally, for those lower-temperature, end-ignited tests that did DDT, for example shot #11 (fig. 5), its cooked off replicate, shot #18 (fig. 11), exhibited a shorter run length. Again this behavior is probably due to the sensitizing effect of elevated temperature.

Effect of Soak Duration

To address thermal response issues where the duration of thermal insult is greater, shot #24 (fig. 4) was soaked above 180°C for 3 hours. Its response puts it in the run length neighborhood of shots #2 and #3 (figures 9 and 8) which where both higher-temperature cookoff shots. This apparent advancement in sensitivity could be due to it having a greater degree of porosity from more advanced decomposition, chemical effects of decomposed intermediate species, or both. Regardless of the reason, this increased sensitivity is significant.

Effect of Having No Ullage
Shots #10 and #22 (figures 12 and 13) were both prepared to have as little ullage as practically possible. To minimize the creation of porosity, Shot # 10 was heated at the maximum rate until reaching its target temperature when it was ignited. In contrast, the temperature for shot #22 was ramped until self-ignition occurred. Shot #10 burned rapidly (approximately 1.8 mm μs^{-1}), but did not DDT, whereas Shot #22 transitioned in a short run distance. Unfortunately, the streak image for shot #22 is of poor quality, but the tube was deformed to the greatest extent observed in this body of work. As with the long-duration soak, this increased level of violence is significant.

Conclusions

A 1-dimensional, hot DDT tube experiment was designed and used to successfully field experiments with PBX 9501 under a variety of realistic thermal insult conditions. Starting with full density, pristine material, damage was induced and reaction was monitored from ignition through to completion. The low levels of porosity examined in this work fill in an important gap that had not been addressed in the classic DDT tube experiments with powder beds. Additionally, to the authors' knowledge, this is the first time DDT experiments have been performed where self-ignition (cookoff) of the material was allowed and recorded. Again, these cookoff observations fill in a missing piece of the thermal safety puzzle and they do so in a more realistic and valuable way.

From a safety perspective, four results stand out. First, hot, thermally damaged PBX 9501 does DDT. This result is repeatable, as is the Type I mechanism by which it progresses. Second, the advancement of thermal insult to the point where cookoff occurs appears to exacerbate the parameters (e.g. temperature and porosity) that sensitize the HE and shorten the DDT run length. Third, increased soak duration appears to advance the sensitization beyond what would be expected simply from increasing porosity. This result needs further investigation to better understand why it is so. Fourth, tight-fitting (i.e. with little or no ullage), strong casing can lead to high-violence cookoff and DDT despite having almost no porosity. Lastly, for those situations where DDT did not occur, the resulting reaction was still somewhat rapid and violent.

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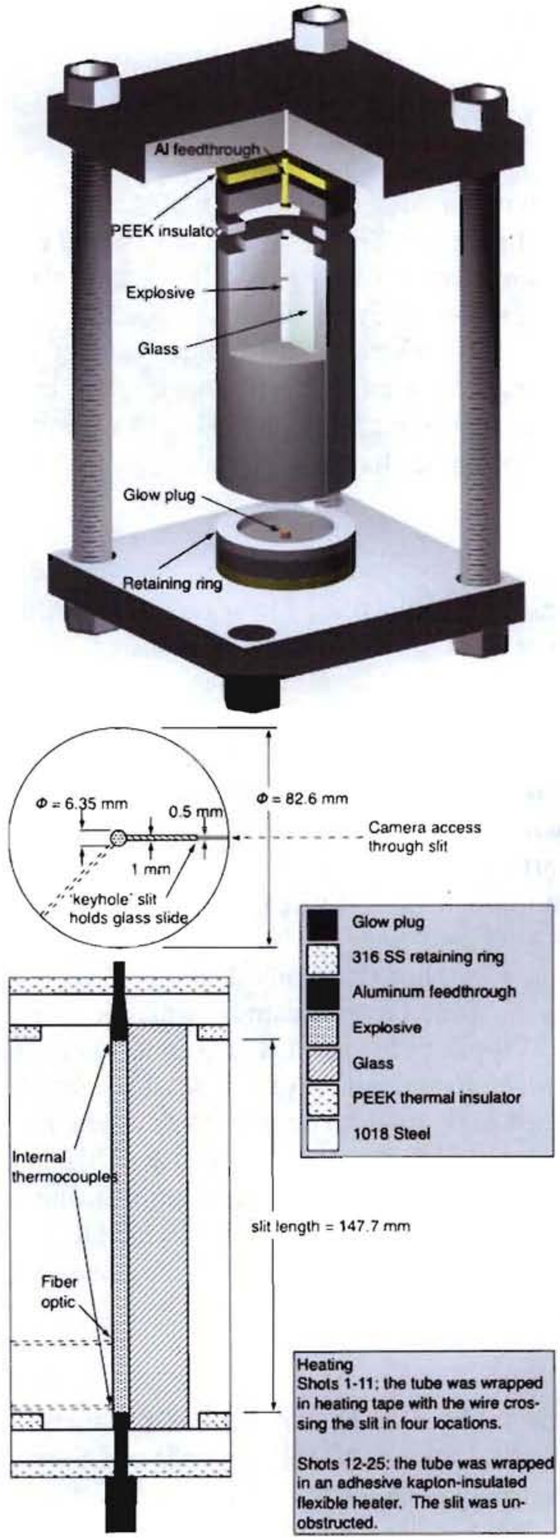


Figure 1. Schematic of the DDT tube

assembly

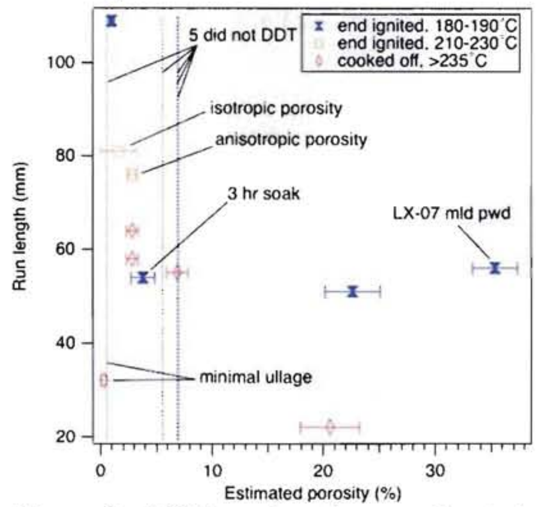


Figure 2. DDT run length vs. estimated porosity for the tests listed in Table II.

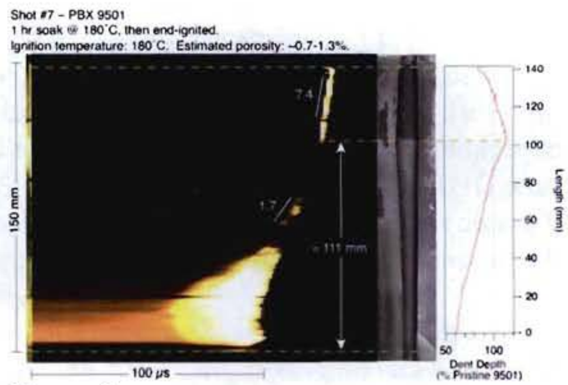
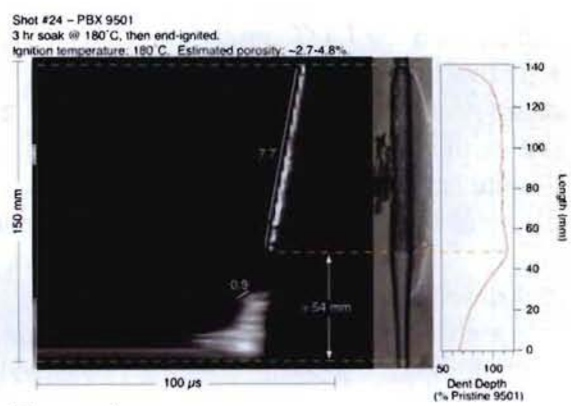


Figure 3.



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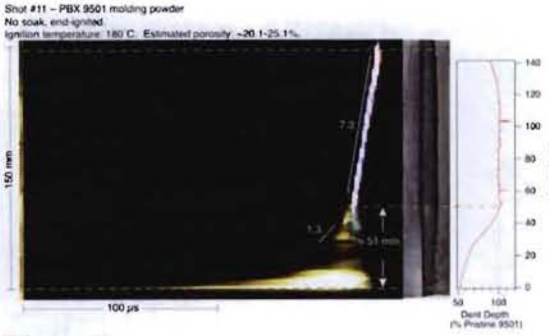

Figure 5.

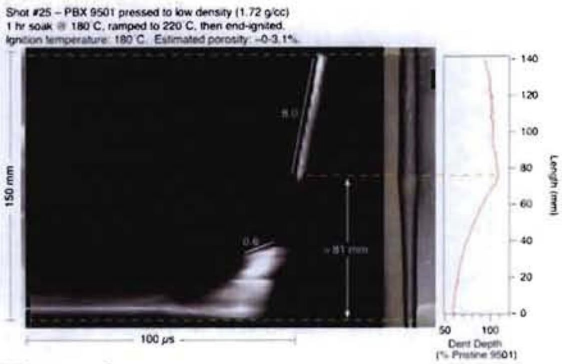

Figure 6.

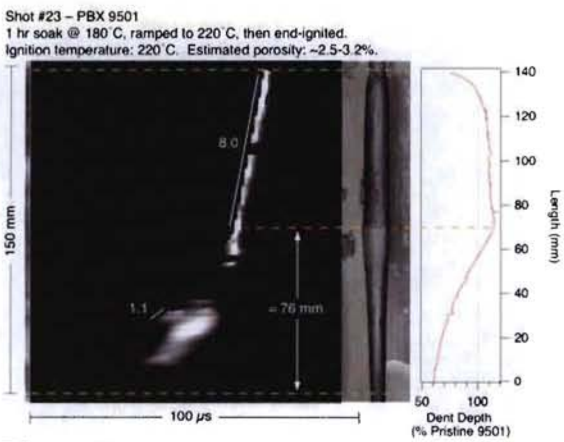

Figure 7.

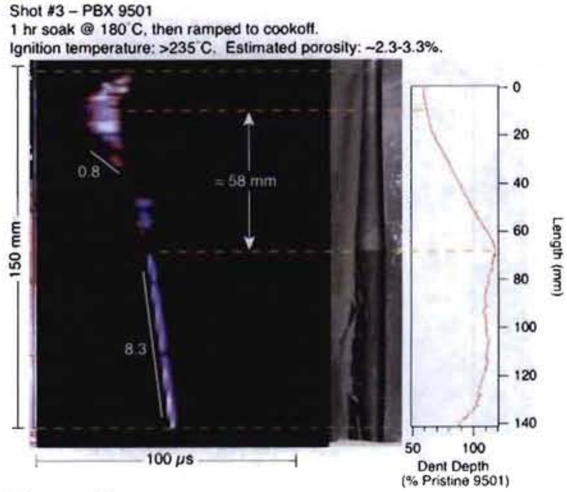

Figure 8.

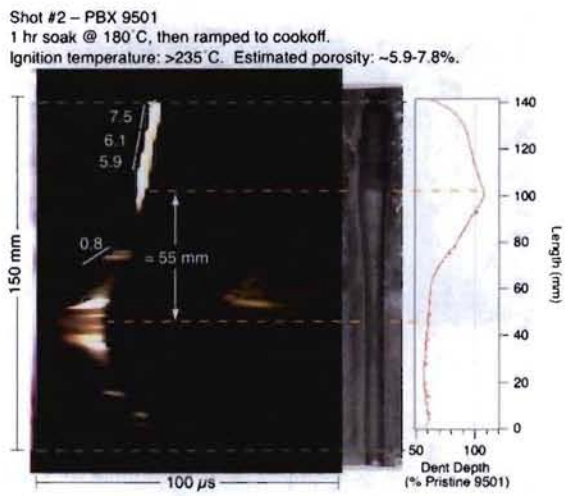

Figure 9.

Figure 10.

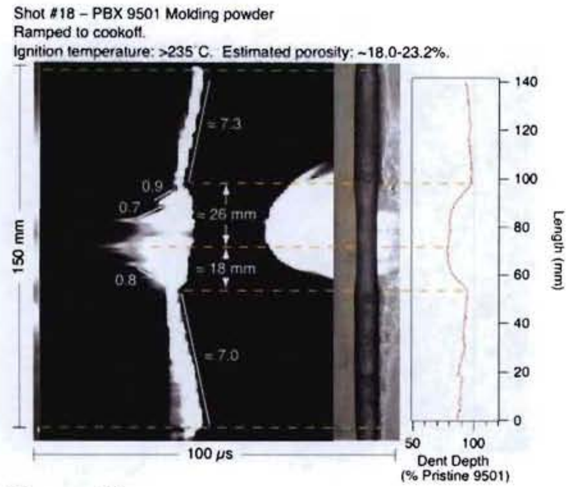

Figure 11.

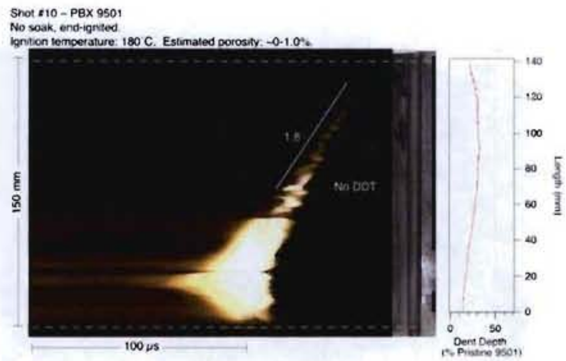

Figure 12.

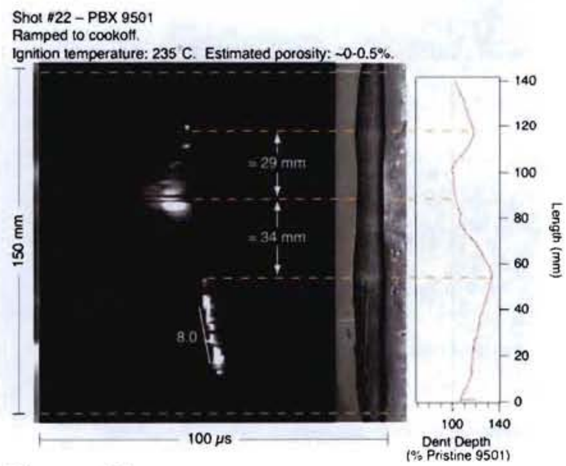

Figure 13.