Explosive Properties of Melt Cast ETN

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Abstract: Erythritol tetranitrate (ETN) is a low melting solid nitric acid ester with significant explosive properties. Increased availability of its precursor (erythritol) which is now used as a sweetener attracted attention to a possible misuse of ETN as an improvised explosive. However, ETN has also some potential to be used as a component of military explosives or propellants. The article is focused on properties of melt cast ETN. Sensitivity of the compound towards impact and friction was tested. Explosive performance was evaluated based on cylinder expansion tests and detonation velocity measurements. Impact energy and friction force required for 50% probability of initiation was 3.79 J and 47.7 N, respectively. Gurney velocity value of G = 2771 m s^{-1} and detonation velocity of 8027 m s^{-1} at the charge density of 1.700 g cm^{-3} were found for the melt cast material. The sensitivity characteristics of the melt cast ETN does not differ significantly from both literature and authors' data measured using the crystalline material. Explosive performance properties were found to be close to PETN.

Keywords:

Sensitivity, Detonation velocity, Melt cast, Erythritol tetranitrate, Gurney velocity

Introduction

Erythritol tetranitrate (ETN) is a solid four-carbon unbranched ester of nitric acid structurally similar to the two-carbon ethyleneglycol dinitrate or three-carbon nitroglycerine. Although ETN is an easily synthesized powerful explosive it has not really attracted the attention of scientists as a useful explosive [1], with the high cost of erythritol, a necessary starting material for ETN, being one of the main reasons for this lack of interest. The early books in the field of explosives simply mention its basic explosive parameters [2-4]. However new technology for erythritol production has been developed recently [5] and the price of erythritol has thus been significantly reduced. The consequent current availability and affordability of erythritol has fueled the extensive research into the explosive properties of ETN which started just a few years ago.

The first paper was published by Oxley et al. [6] who presented some analytical and thermoanalytical data for ETN. Manner et al. focused on analytical data and the influence of crystal morphology on the sensitivity of ETN to mechanical stimuli [7]. Our research group investigated the fundamental physical properties of ETN [1] and recently some analytical properties of ETN [8]. Yan et al. [9] studied the thermal behavior and decomposition kinetics of pure ETN and its mixtures with both pentaerythritol tetranitrate (PETN) and hexogen (1,3,5-trinitro-1,3,5-triazinane, RDX). We also investigated the explosive properties of mixtures based on ammonium nitrate sensitized with erythritol tetranitrate [10]. Manner et al. recently reported the detonation parameters of pressed ETN determined by cylinder expansion tests [11].

All studies of the explosive properties of ETN have been focused on crystalline material in the form in which it is obtained from synthesis or recrystallization. ETN is a compound with a low melting point, 61°C [2, 3], which is substantially lower than the temperature of 158°C at which exothermic decomposition occurs [9]. The significant difference between melting and decomposition temperatures allows ETN to be melt casted. To the best of our knowledge the properties of melt cast ETN have not yet been published, and therefore we focused on research into the sensitivity and performance of melt cast ETN.

Materials and Methods

Caution: No problems have occurred during the synthesis and handling of erythritol tetranitrate, but the material is still an explosive. Laboratories and personnel should be properly prepared and safety equipment such as protective gloves, shields, and ear plugs should be used, even when working with small quantities of this substance.

Materials

Erythritol tetranitrate was prepared according to the method patented by Bergeim [12] and described recently in detail [10]. Erythritol (a meso form - (2R,3S)-butane-1,2,3,4-tetraol) with declared purity of 99.5% was obtained from a local pharmacy (trade name Extra-linie). Other chemicals used were of analytical purity (p.a.). The ETN was crystalized from ethanol which resulted in a crystalline powder consisting of needle-like crystals with average length of 230 μm and length to width ratio of 6.5. The product analysis, yield, crystal size and shape of ETN have already been described in detail in our previous work [1]. Melt cast ETN samples were prepared in the form of small pellets by dropping molten ETN onto a cold tile – the appearance of the samples is presented in Figure 1.

Mercury fulminate (MF), pentaerythritol tetranitrate (PETN) and hexogen (RDX) were used as reference explosives for comparisons with ETN sensitivity. The preparation of brown mercury fulminate, its crystal size and shape have been published in our previous paper [13]. PETN with particles smaller than 200 μm was provided by Explosia a. s. (Czech Republic) under the trade name “Pentrit NS” and RDX was sourced from Chemko Strazske (Slovakia).

Impact sensitivity

Impact sensitivity was measured using Kast fall hammer, produced by OZM Research, as were the pistons (BFH-SR) and cylinders (BFH-SC). A 0.5 kg hammer was used for MF, a 1 kg one for PETN and ETN and a 2 kg hammer for RDX. Probit analysis [14] was used for evaluation of the data and for the construction of sensitivity curves. Each sample was measured at five energy levels with fifteen trials at each level. One pellet of ETN with weight of about 20 mg was used for each trial. Crystalline ETN and other explosives were used in the powdered state in volumes of 40 mm^3 for each trial.

Friction sensitivity

Sensitivity to friction was determined using an FKSM-08 BAM device supplied by OZM Research. BFST-Pt-100S type test plates and BFST-Pn-200 pestles were used, all produced by OZM Research. Each sample was measured at five energy levels with fifteen trials on each level. Probit analysis was again used for evaluation of the data obtained and for the construction of sensitivity curves. Melt cast ETN samples were prepared by direct dropping of ETN melt onto a rough test plate and allowing it to solidify. Other explosives were used in their crystalline state.

Gurney velocity

Four reduced scale cylinder tests were performed to determine the Gurney velocity of melt cast ETN. Copper tubes, 200 mm in length, with a 15 mm internal diameter and a wall thickness of 1.4 mm, were used. The exact dimensions of the tubes were measured within 0.01 mm accuracy to produce an actual metal to explosive mass (M/C) ratio. The tubes were filled gradually with molten ETN at 75°C in a vertical position to obtain homogeneous charges without cavities. The final charge densities were 1.700 ± 0.003 g cm^{-3}. The expansion of the tubes was recorded photographically using a UHSi 12/24 high speed framing camera (Invisible Vision). Back lighting was provided by an argon flash bomb. Expanding wall velocities were measured by a first generation photonic Doppler velocimeter (PDV, prototype device produced by OZM Research) with three active channels and bare fiber probes [15]. Original voltage-time oscilloscope records were evaluated using short-time Fourier transform (STFT) in a MATLAB based software to obtain velocity vs. time profiles in a way which is described in detail in [16]. The PDV probes were fixed in a position of about 120, 135 and 150 mm from the upper end of the tube with the probes' axes angled to the copper surface normal by 5° towards the detonator. The distance of the probes from the cylinder surface was kept at 11.5 mm which allowed undisturbed observation of a seven-fold cylinder volume expansion ($V/V_0 \approx 7$). Wall velocity at $V/V_0 \approx 7$ is sometimes referred to as the terminal velocity (v) in the case of the standard copper cylinder test with reference values available in the literature [17-19]. Using terminal expansion velocity, the Gurney velocity (G) for ETN was calculated according to the Gurney equation for cylindrical charges [20]:

$$\frac{v}{G} = \left(\frac{M}{C} + \frac{1}{2} \right)^{-1/2}$$

Detonation velocity

Detonation velocity of erythritol tetranitrate was measured using ionization probes and digital oscilloscope. Ionization probes were prepared from 0.1 mm twisted copper wire. Four charges of erythritol tetranitrate were prepared by filling polypropylene tubes having an internal diameter of 16.6 mm and wall thickness of 4.2 mm. Two of these tubes were filled by careful hand pressing of ETN crystalline powder which resulted in charge densities of 0.83 g cm^{-3} and 0.86 g cm^{-3}. Fine powder was added in small increments in order to achieve a regular density distribution along the charge. The remaining two tubes were filled with molten ETN, in the same way as cylinder test charges, resulting in charge densities of 1.64 g cm^{-3} and 1.66 g cm^{-3}.

Detonation velocity was also measured in four cylinder expansion tests using the fiber optic probe method (FOP) [21]. The probes were prepared by perpendicular drilling of 8 holes with a diameter of 0.3 mm into a plastic optic fiber with 1 mm core diameter and 2.2 mm outer diameter. The FOP was inserted into the last 40 mm of the charge parallel with the charge axis. Air cavities in the holes are compressed by the passing detonation wave which causes them to produce a bright flash of light. The light signal is transported by the fiber to optoelectronic receiver and is then recorded by digital oscilloscope. Typical raw signal and data evaluation methods are presented in figure 3.

Calculation of detonation parameters

Detonation parameters of ETN were calculated using the Explo5 V6.03 thermochemical code (OZM Research). The semi-empirical Becker-Kistiakowsky-Wilson (BKW) equation of state was used with the BKWN set of parameters as follows ($\alpha = 0.5$; $\beta = 0.38$; $\kappa = 9.32$; $\theta = 4120$) which is useful for thermochemical calculations of the properties of high explosives in a wide range of densities [22, 23].

Results and Discussion

Sensitivity to mechanical stimuli

Sensitivity of ETN to impact has been evaluated using probit analysis [14]. The resulting sensitivity curves for crystalline and melt cast ETN are presented in Figure 4. We compared the friction sensitivity of ETN with the sensitivities of MF, PETN and RDX (using the same method). The values for 50% probability of initiation (taken from sensitivity curves) for all explosives measured are summarized in Table 1.

The form of ETN does not significantly affect sensitivity to impact. Crystalline ETN is only slightly more sensitive than melt cast ETN. Sensitivity of ETN to impact is about the same as that of PETN and higher than that of RDX. A similar result for crystalline ETN was obtained by Oxley et al. [6] while Manner et al. reported an impact sensitivity for crystalline ETN nearly twice as high as that for PETN [7]. However, our absolute values differ from the values obtained by Oxley et al. [6] and Manner et al. [7]. This can be explained by the use of a different apparatus and evaluation method. Therefore, our sensitivity data for the reference explosives are shown for comparison.

Values of impact sensitivity for the reference explosives (PETN and RDX) in this study differ significantly from our previously published data [24]. The probable reason for this difference is the use of older types of pistons and cylinders in the earlier measurements. Older types of pistons and cylinders were out of range of the diameter tolerance demanded by today's use of STANAG 4489. Other conditions of measurement, methodology and measuring apparatus were the same as in our earlier study.

Table 1. Sensitivity to impact and friction.

	Impact energy for 50% probability of initiation /J	Friction force for 50% probability of initiation /N
MF	0.62	5.3
ETN (crystalline)	3.28	38.9
ETN (melt cast)	3.79	47.7
PETN	3.93	75.1
RDX	6.94	127

Sensitivity to friction was also evaluated using probit analysis. The resulting sensitivity curves for crystalline and melt cast ETN are presented in Figure 5 and the values for 50% probability of initiation (taken from sensitivity curves) for all explosives are summarized in Table 1.

The form of ETN does not have a significant effect on its friction sensitivity. The experiments showed that the sensitivity of melt cast ETN to friction is slightly higher than the sensitivity for crystalline ETN. Sensitivities of both forms of ETN exceed the sensitivity of PETN. The result for crystalline ETN is in agreement with the friction sensitivity previously published by Manner et al. [7].

Explosive properties

Copper tube cylinder expansion tests were performed to characterize the metal acceleration ability of melt cast ETN. A wall velocity for ETN of 1694 ± 8 m s^{-1} (V/V_0 = 7; density 1.700 ± 0.003 g cm^{-3}) was obtained using cylinder tests as the average of 11 available results from the total number of 12 PDV probes. The resulting standard deviation corresponds to a 0.5% variability of results which is caused by slight variations in the cylinder dimensions and the materials' lack of homogeneity. The average Gurney velocity value, G = 2771 ± 8 m s^{-1}, was calculated from the Gurney equation using measured wall velocity. In this case, the variability of results is just 0.3% partly because the slight differences in tube dimensions were taken into account in the calculation. For comparison, wall velocity data presented for the two cylinder tests on pressed ETN were extracted from figure 2 in [11] and the corresponding Gurney velocities for V/V_0 = 7 were calculated. Their results differ from ours by less than 1.5%. Wall velocity profiles and tube expansions obtained by the three PDV probes in one of the cylinder tests are shown in figure 6. The shadow photographs of the expanding charge casing show that some ruptures appeared at V/V_0 = 6.5, but none of them influenced the signal of PDV probes. It can be seen that the expansion of the tubes was fairly symmetrical (figure 7).

Detonation parameters for pressed ETN have been published recently [11]. The detonation velocities of crystalline hand pressed ETN and melt cast ETN were measured at a charge diameter of about 16 mm which should be enough to exclude diameter effects according to [11]. The peak detonation velocity of 8027 ± 27 m s^{-1} at the charge density of 1.700 ± 0.003 g cm^{-3} was determined in four cylinder expansion tests. All the measured values are summarized in Table 2 where the available values are compared with the literature data for PETN [26] and the values of ETN and PETN computed using the Explo5 thermochemical code. Both measured and calculated detonation velocities of ETN at high densities are 1% lower than those for PETN. The observed values are in agreement with Manner et al. [11] with the difference being lower than 1% at the same densities.

Table 2. Detonation velocities of ETN. All values are rounded to the tens.

	Detonation velocity /m s^{-1}			
Density /g cm^{-3}	0.83	0.86	1.65	1.70
ETN experimental	4420[a]	4630[a]	7940[b]	8030[b]
ETN calculated	4800	4900	7890	8100
PETN [26]	4890	5000	7930	8110
PETN calculated	5040	5150	7970	8150

[a] hand pressed crystalline powder

[b] melt cast

Conclusions

The sensitivity and performance properties of erythritol tetranitrate were determined for powdered and melt cast material. Probability curves which describe the sensitivity of ETN towards impact and friction were measured and compared with those of well-known explosives. The friction force required for ETN initiation was found to be nearly half of that required for PETN. However, no significant difference was found between powdered and melt casted material. The Gurney velocity and detonation velocity of melt cast ETN were found to agree with the literature values of pressed samples at similar densities. The detonation velocity of melt cast ETN was found to be 1% lower than that of PETN at the same density.

Acknowledgement

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Figure 1. Shape and size of crystalline ETN (left) and melt cast ETN pellets (right). The fine scale division is in millimeters.

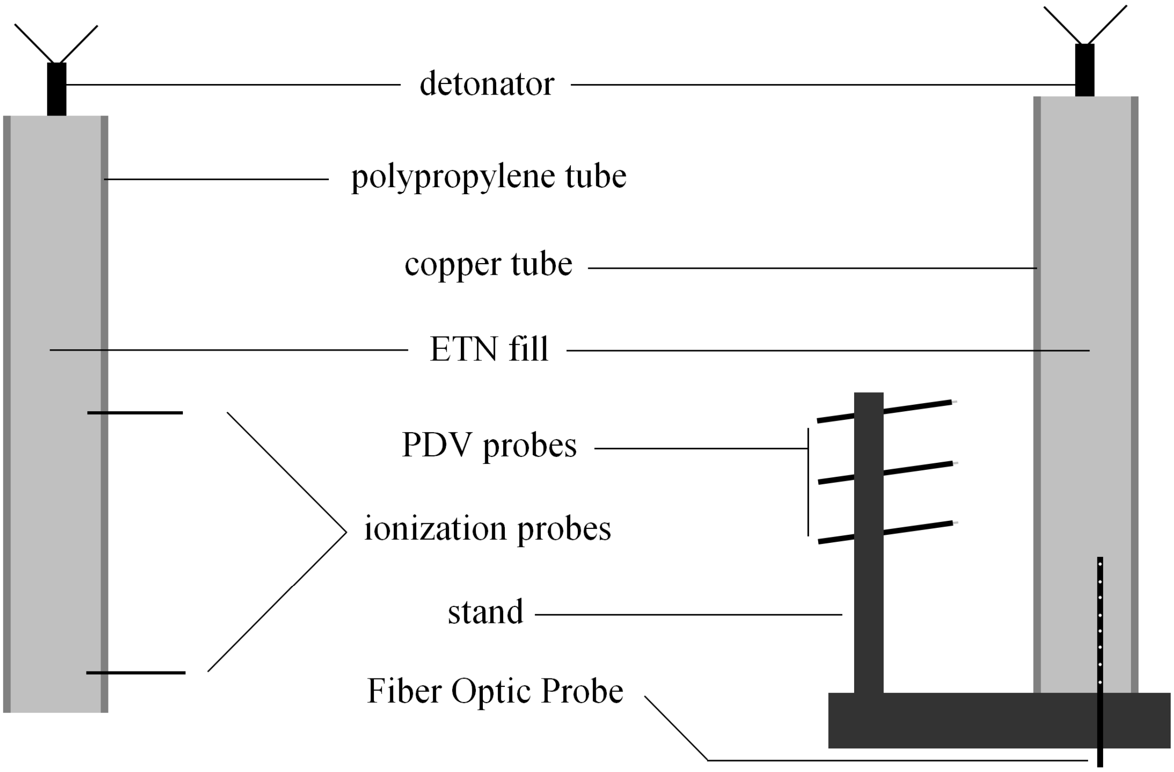

Figure 2. Cross-sections of the detonation velocity (left) and cylinder test (right) measurement setups

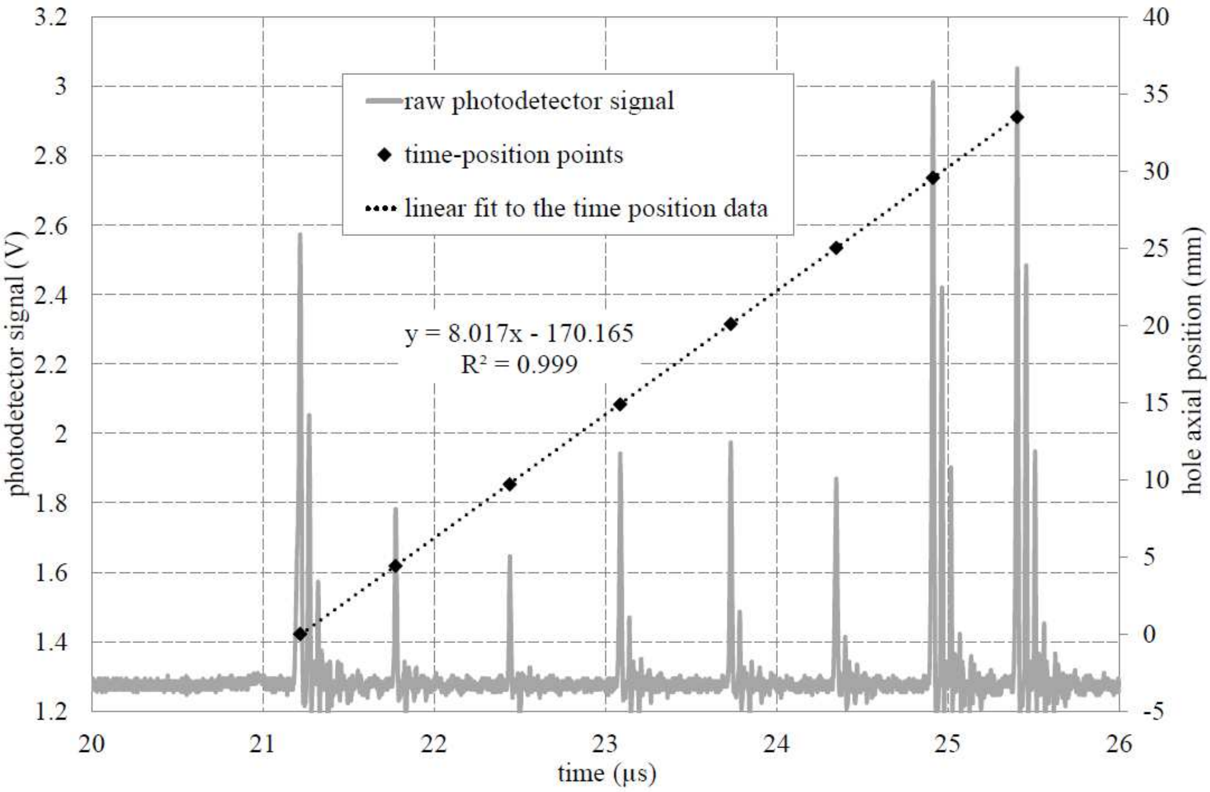

Figure 3. FOP raw signal and detonation velocity evaluation. The peak times taken from the raw signals are plotted against the positions of the holes. The slope of the regression line is a velocity of detonation (mm μs^{-1})

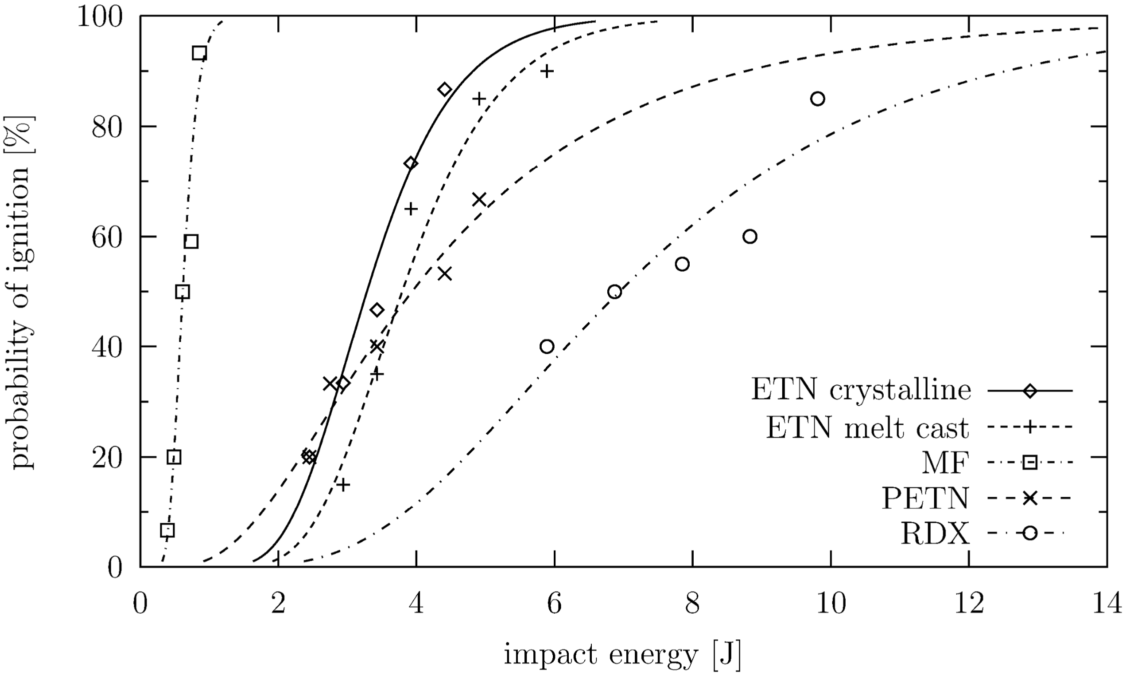

Figure 4. Comparison of impact sensitivity of ETN with that for MF, PETN and RDX.

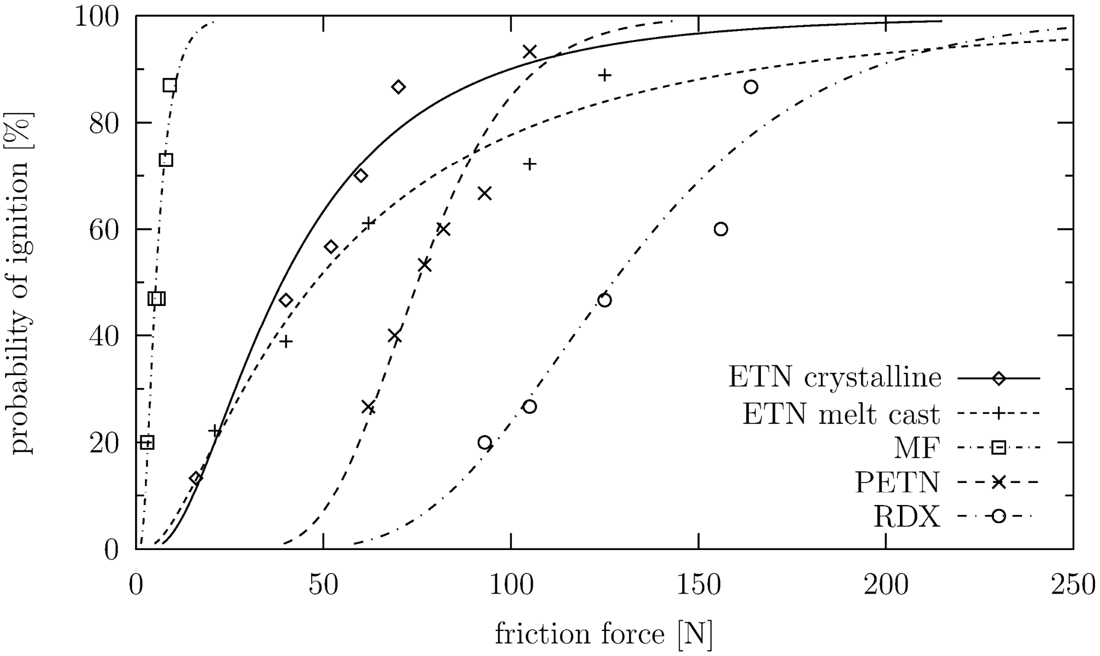

Figure 5. Comparison of friction sensitivity of ETN with that for MF, PETN and RDX.

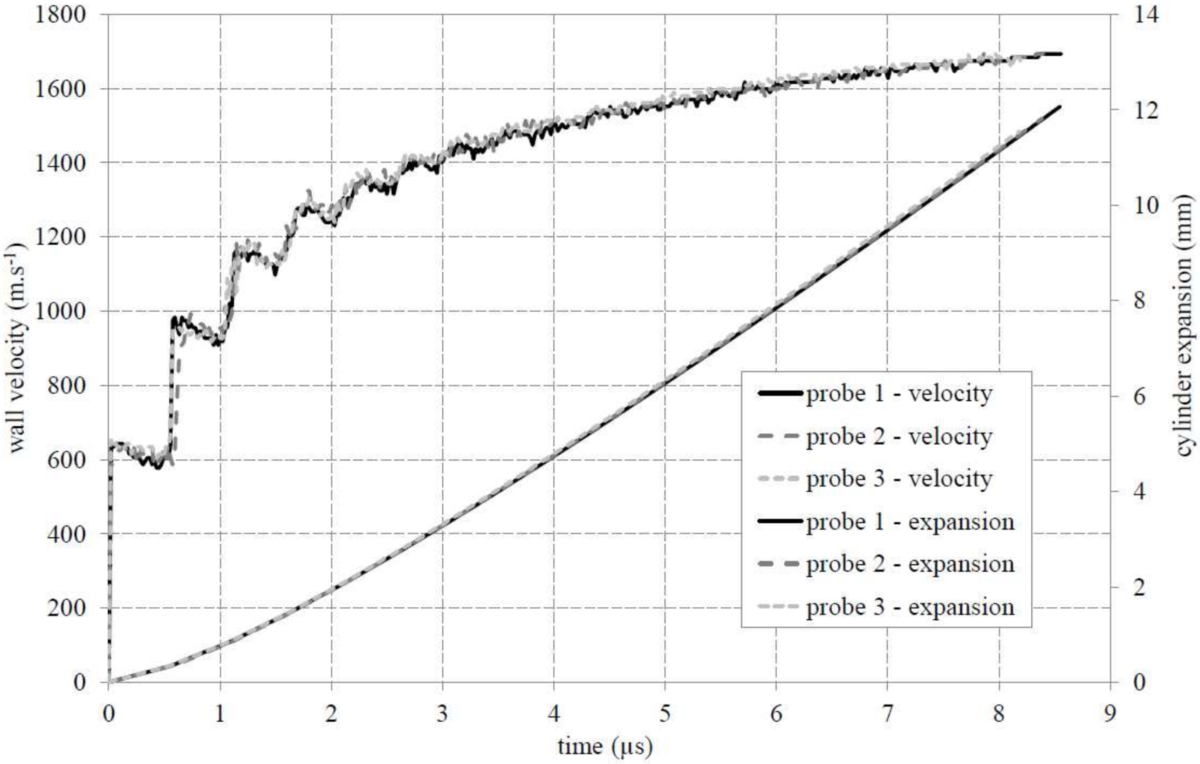

Figure 6. Example of wall velocity and expansion profiles obtained by cylinder expansion test of melt cast ETN.

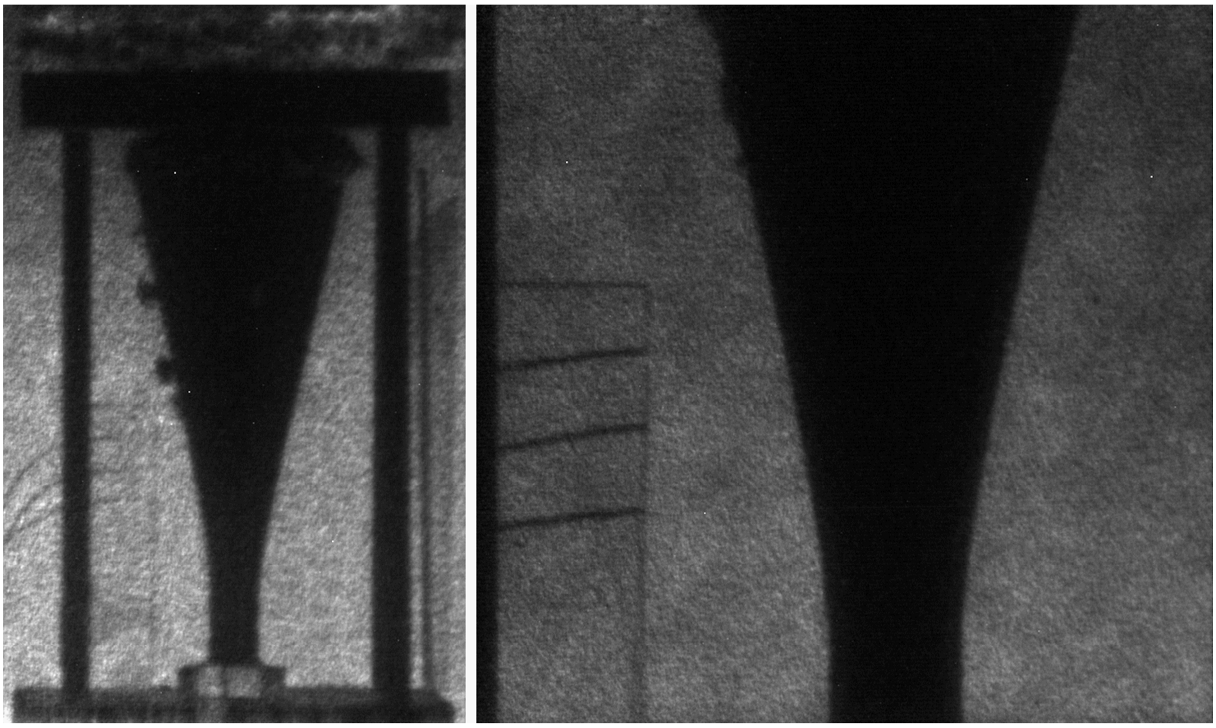

Figure 7. High speed camera shadow photographs of the expanding cylindrical charge (overall on the left and detailed view on the right)