



Evaluation of the Thermo-mechanical and Explosive Properties of Bimodal and Hybrid Polymer Bonded Explosive (PBX) Compositions Based on HNS and HMX

Jatinder KAUR^{1*}, Vandana P. ARYA¹, Gurvinder KAUR¹
and Prem LATA²

¹ Department of Quality Assurance, Terminal Ballistics Research Laboratory, Sector-30, Chandigarh-160030, India

² Department of Applied Sciences, PEC University of Technology, Sector-12, Chandigarh-160012, India

*E-mail: jatinder05tbrl@gmail.com

Abstract: In the present paper, a series of bimodal PBX compositions containing coarse (90 μm) and fine (<1 μm) HNS (2,2',4,4',6,6'-hexanitrostilbene) and hybrid PBX compositions based on HNS and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) in varying mass ratios, along with the fluoropolymer Viton-A, a vinylidene fluoride and hexafluoropropylene copolymer, as a binder (5%), have been prepared on the lab scale. In order to observe any effect of incorporating fine HNS particles with coarse ones and the effect of replacing HNS with HMX in all types of bimodal and hybrid PBX compositions, the samples were characterized for composition analysis, thermal behavior and morphological analysis as well as evaluated for their mechanical and explosive properties including sensitiveness tests and detonic properties. The data showed that incorporation of fine HNS into coarse particles of HNS in the bimodal PBX resulted in an increase in mechanical strength and a decrease in friction and impact sensitivity, as well as an enhanced performance compared to PBXs based on coarse HNS alone. Viton-A based hybrid PBX compositions provided better mechanical and sensitivity properties as compared to conventional explosive compositions based exclusively on HMX or HNS and the performance of the PBX compositions increased with increasing HMX content.

Keywords: HNS, HMX, Viton-A, Bimodal PBX, Hybrid PBX, characterization

Introduction

Defense forces around the world are adopting Insensitive Munitions (IM) in order to minimize the response of ordnance items to accidental stimuli and to increase the survivability of personnel and scarce resources [1]. TNT (2,4,6-trinitrotoluene) based melt-cast compositions no longer meet the new requirements of modern military and aerospace agencies. The development of insensitive munitions (IM) can be achieved through the preparation of polymer bonded explosive (PBX) compositions in which the explosive powder is bound together in a matrix using small quantities of a synthetic polymer. In addition to protecting the explosive crystals from rapid initiation by external stimuli, polymeric binders provide mechanical strength to the explosive charges [2]. PBX compositions have been recognized as providing improved safety during processing, handling, storage and flight conditions, as well as better thermal stability and performance, which are the essential needs of present day weapon systems. For that purpose, polymers such as polyisobutylene, styrene butadiene rubber, hydroxy terminated polybutadiene (HTPB), acrylonitrile-styrene-butadiene, polyurethane, Teflon *etc.*, have been reported as polymeric additives in PBXs. But these polymers were found to be ineffective for high end applications because of certain limitations such as a limited shelf life under ambient conditions [3]. On the other hand, fluorinated polymers have been found to possess properties that are better than those of other polymers. Fluorinated polymers such as Viton-A have been found to be best suited for defense applications for making PBXs because of their chemical inertness, higher density, greater thermal stability and longer shelf life [4].

Despite the good performance of HMX and RDX based PBX compositions presently being used, their comparatively higher sensitivity values find limited applications, since there has been a number of accidents involving initiation of munitions by impact or shock aboard ships, aircraft carriers and ammunition trains [5]. Moreover, specific applications demand a special class of thermally stable high energy materials (HEMs) having decomposition temperatures superior to that of the bench mark explosive HMX. Therefore, PBXs prepared by mixing thermally stable, insensitive high explosives (IHEs) including HNS, TATB (1,3,5-triamino-2,4,6-trinitrobenzene), NTO (3-nitro-1,2,4-triazol-5-one) with a polymer are desirable in advanced armaments.

Apart from polymeric binders for making PBX grains, the solid explosive loadings in a binder also depend on their particle size and shape. In order to achieve maximum solids loading, the particle size is carefully controlled and

bi- or tri-modal mixtures of different particle size are desirable. It is reported that bimodal PBX formulations containing fine and coarse particles of TATB using polyurethane as the binder showed improved mechanical properties in comparison to coarse TATB alone in high explosive PBX compositions. These differences were related to various aspects of TATB particle size and distribution [6]. A number of PBX formulations based on the thermally stable explosive HNS alone has been reported in the literature. HNS based PBX compositions (HNS/Kel-F800; 95/5) were developed by the Atomic Weapons Research Establishment, Aldermaston, UK [7]. For civilian applications, HNS /Teflon explosive charges have also been used for the Apollo 17 seismic tests [8]. Little information is available on the effect on the thermo-mechanical and sensitivity properties of explosive powder compositions of including different proportions of fine HNS particles with the coarse ones. In the present study, using Viton-A as the binder, bimodal PBX compositions containing coarse (90 μm) and fine (<1 μm) HNS mixed in different mass ratios have been prepared on a lab scale to study the effect of particle size variation in the explosive formulations on their thermo-mechanical and explosive properties.

Although in modern ordnance the primary requirements of futuristic weapon systems are high-energy output, good thermal stability, long storage life, improved performance as well as insensitivity, these requirements are not generally found in one explosive. Explosives having good thermal stability and impact insensitivity usually exhibit poorer explosive performance and vice versa. Therefore, one of the ways by which both insensitivity and performance can be enhanced is by making explosive PBX compositions using two explosives, each with at least one desired property. A series of new explosives has been developed with a promising blend of insensitivity, performance and thermal stability [9]. HNS based formulations significantly improve the safety and survivability of munitions, weapons and personnel in the vicinity. However, the performance of HNS in terms of velocity of detonation (VOD) is much lower than that of the high performance explosive HMX. But HMX is more sensitive and has less thermal stability than HNS. Therefore, hybrid PBX compositions containing different proportions of HMX with HNS, along with binder Viton-A, have been studied to see what effect mixing HMX with HNS would have on the explosive powder properties. This was done to enhance the performance on the one hand, but keeping the sensitiveness issue of the explosive powder under control on the other. For this purpose, HMX, which has excellent power performance has been used along with the thermally stable explosive HNS in order to make hybrid PBX compositions.

The present study is an attempt to determine the thermo-mechanical and

hazard assessment of these PBXs, since little information is available on the properties of bimodal and HNS and HMX based hybrid PBX compositions.

Experimental

Materials and methods

HNS, procured from an outside source, was only 93% pure. It was recrystallized in-house by slow cooling recrystallization to give coarse HNS (mean diameter 90 μm) and later submicron sized HNS (mean diameter $<1 \mu\text{m}$) [10]. In-house prepared 99% pure HMX (mean diameter 180 μm), and DuPont manufactured Viton-A fluoropolymer were used for the PBX preparations.

All of the chemicals were of AR grade. For analytical techniques like HPLC, NMR *etc.* spectroscopic grade solvents were used. Deionised water from a Millipore Elix system was used.

PBX compositions were prepared by the slurry coating method on a laboratory scale. The explosive material was dried in an oven at 50 $^{\circ}\text{C}$ for 24 h. A weighed quantity of Viton-A polymer (2.63 g) was dissolved in methyl ethyl ketone (MEK) solvent (53 mL), maintaining the ratio of 1:20 (w/v), and kept overnight to obtain an homogenous lacquer. The explosive powder (50 g) was dispersed in deionized water (750 mL), maintaining the ratio of 1:15 (w/v), in a reaction vessel with stirring at 500 rpm. To raise the temperature of the explosive slurry to 55 $^{\circ}\text{C}$, the reaction vessel was kept in a hot water bath set at 65 $^{\circ}\text{C}$. The lacquer of Viton-A was added drop-wise into the explosive slurry through a dropping funnel, with stirring at 700 rpm in order to maintain a uniform dispersion of the polymeric binder over the crystalline explosive. After the complete addition of the lacquer, the mixture was stirred for another 15 min. The temperature was maintained above 85 $^{\circ}\text{C}$ for about 20-25 minutes to distil off the solvent. The slurry was then cooled to below 40 $^{\circ}\text{C}$ by quenching *i.e.* pouring into ice cold water, which resulted in the formation of the moulding powder. During the cooling step, the agitator speed was slowed. The moulding powder was then filtered off, washed with water to remove any remaining solvent and dried in an oven at 50 $^{\circ}\text{C}$ to obtain a free flowing, PBX moulding powder. The batch size for the preparation of a PBX was 50 g.

Bimodal PBX compositions

For the preparation of bimodal PBX compositions, bimodal HNS consisting of coarse (90 μm) and fine ($<1 \mu\text{m}$) HNS mixed in different mass ratios was used along with Viton-A as the binder. The explosive content in the mixture was

constant, but the proportion of coarse to fine HNS was changed. In all types of bimodal PBX formulations, the Viton-A content was 5% whilst the 95% HNS consisted of different proportion of fine to coarse HNS (these being 100% coarse HNS, 100% fine HNS and 50%, 10%, 5% or 1% fine HNS with the balance being coarse HNS) designated as HV-1, HV-2, HV-3, HV-4, HV-5 and HV-6, respectively. The details of the bimodal PBX compositions prepared on the lab scale are given in Table 1.

Table 1. Composition details, compressive strength, vacuum stability, friction sensitivity and impact sensitivity data of bimodal PBX compositions

Sample ID	Explosive in bimodal PBX	PBX composition Explosive: Viton-A [mass%]	Compressive strength [MPa]	Vacuum stability test [mL/g]	BAM, frictional force [N]	Limiting friction load [N]	Impact sensitivity for 2 kg fall weight	
							$h_{50\%}$ [cm]	Limiting impact energy [J]
HV-1	Coarse HNS	95:5	18	0.04	105	80	24	3.6
HV-2	Fine HNS	95:5	25	0.45	125	96	35	5.6
HV-3	Coarse HNS: Fine HNS (50:50)	95:5	22	0.39	124	96	27	4.0
HV-4	Coarse HNS: Fine HNS (90:10)	95:5	19	0.04	124	96	26	4.0
HV-5	Coarse HNS: Fine HNS (95:5)	95:5	19	0.02	123	96	25	4.0
HV-6	Coarse HNS: Fine HNS (99:1)	95:5	16	0.04	108	80	24	4.0

Hybrid PBX compositions

Hybrid PBX compositions contained 95% of explosive (as a mixture of HNS and HMX) and 5% of Viton-A. The explosive content in the mixture was constant but the proportion of HNS to HMX was changed. The amount of HMX in HNS was varied from 10 to 90%. The series of hybrid PBX compositions prepared at HNS and HMX ratios of 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90 by weight percent were designated as HX9010, HX8020, HX7030, HX6040, HX5050, HX4060, HX3070, HX2080, HX1090, respectively (Table 2).

Table 2. Composition details, compressive strength, vacuum stability, friction sensitivity and impact sensitivity data of hybrid PBX compositions

Sample ID	Explosive in hybrid PBX (HNS:HMX)	PBX composition Explosive: Viton-A [mass%]	Compressive strength [MPa]	Vacuum stability test [mL/g]	BAM, frictional force [N]	Limiting friction load [N]	Impact sensitivity for 2 kg fall weight	
							$h_{50\%}$ [cm]	Limiting impact energy [J]
HX (HMX/Viton)	HNS:HMX (0:100)	95:5	12	0.06	162	120	40	4.5
HS HNS/Viton	HNS:HMX (100:0)	95:5	18	0.04	105	80	24	3.6
HX9010	HNS:HMX (90:10)	95:5	15	0.04	108	80	24	3.6
HX8020	HNS:HMX (80:20)	95:5	15	0.03	108	80	27	4.0
HX7030	HNS:HMX (70:30)	95:5	15	0.04	108	80	37	5.6
HX6040	HNS:HMX (60:40)	95:5	15	0.07	108	80	36	5.6
HX5050	HNS:HMX (50:50)	95:5	16	0.09	152	96	42	6.3
HX4060	HNS:HMX (40:60)	95:5	16	0.04	151	96	42	6.3
HX3070	HNS:HMX (30:70)	95:5	16	0.08	152	96	42	6.3
HX2080	HNS:HMX (20:80)	95:5	16	0.07	156	96	42	6.3
HX1090	HNS:HMX (10:90)	95/5	15	0.03	161	120	42	6.32

All types of bimodal and hybrid PBX compositions were characterized by composition analysis, thermal behaviour and morphological analysis, as well as evaluated for their mechanical and explosive properties, including sensitiveness tests and performance evaluation studies. A structural analysis of the Viton-A polymer was carried out by ^1H , ^{13}C and ^{19}F NMR (300 MHz, Jeol, ECX-300); acetone- d_6 was used the solvent. The IR spectra were recorded by an FT-IR spectrometer (Nicolet-Avtar-360). For FT-IR analysis, the Viton-A sample was prepared as a cast film on a KBr plate using methyl ethyl ketone (MEK) to dissolve the polymer.

Thermo-gravimetric analysis of the polymer, bimodal and hybrid PBX compositions was carried out using a thermogravimetric instrument (Mettler, TGA) and differential scanning calorimetric analysis using a Differential Scanning Calorimeter (Mettler, DSC). For TGA analysis, the amount of sample was ~7 mg with a temperature range 25-600 °C at 10 °C/min under an inert atmosphere using ultra-high purity N₂ gas (flow rate: 40 mL/min). Approximately 5 mg sample in a crimped aluminum pan was heated from -50 °C to 500 °C at 10 °C/min for DSC analysis. A laser diffraction based, particle size analyzer (Malvern Mastersizer-2000, PSA) was used to measure the average particle size and size distribution of the explosives. The morphology was checked by scanning electron microscopy (Carl-Ziess, SEM).

The Viton-A content was determined post-preparation in all types of PBX compositions by a gravimetric method [11]. 2 g of PBX was refluxed in 100 mL of 70% HNO₃ for 4 h. At the end of refluxing, the polymer remained floating in the acid and was filtered off, was washed repeatedly with distilled water, dried overnight in a vacuum oven at 100 °C and weighed.

Bimodal PBX cylindrical pellets, having dimensions of 25 mm diameter and 25 mm height, were prepared by using warm isostatic pressing. A weighed quantity of pre-dried PBX moulding powder was placed in a metallic mould and plunger assembly. Pressure (1.7 tons/cm²) was applied for 15-20 s dwell time on the composition by means of a hydraulic ram and the consolidated pellet was extracted from the mould. Each pellet was checked for weight, dimensions and density for all of the PBX pellets determined.

The mechanical strength (compressive strength) of the PBX pellets was determined on a Universal testing machine (Make Lloyd LR 100K) having a capacity of 100 kN at room temperature and humidity of 55%. The maximum test load was 10 kN at a testing speed of 10 mm/min and the pellet was compressed until the point of rupture. A graph of load versus change in height was recorded on the recorder. From the graph obtained, the compressive strength was calculated.

PBX powder sensitiveness tests, including impact sensitivity and friction sensitivity, were carried out using a standard BAM fall hammer apparatus (OZM, RESEARCH) and BAM friction test apparatus, (OZM, RESEARCH) respectively. In the impact sensitivity test, a small amount of the PBX powder sample (20 ±5 mg) was subjected to the action of a drop weight (2 kg) from different heights in order to initiate decomposition, ignition or explosion. The impact sensitivity ($h_{50\%}$) was expressed as the drop height at which 50% initiation or explosion occurred and was obtained by conducting 30 trials. The results were also expressed in terms of the lowest impact energy (J) at which at least one explosion occurred in six consecutive trials. The test result was considered positive if the lowest impact

energy at which at least one explosion occurred in six trials was 2 J or less and the substance was then considered too dangerous for transport in the form in which it was tested. Otherwise the result was considered negative [12].

In the friction sensitivity test, a small amount of the PBX powder sample (20 ± 5 mg) was uniformly spread on the porcelain plate and the frictional force was provided by keeping standard BAM weights (loads) on the peg dragged across the sample. The frictional force was calculated by finding the 50% probability of initiation or explosion by conducting 30 trials. Friction sensitivity was also measured by finding the lowest frictional load at which at least one explosion occurred in six consecutive trials. The test result was considered positive if the lowest frictional load at which one explosion occurred in six trials was less than 80 N and the substance was then considered too dangerous for transport in the form in which it was tested. Otherwise the result was considered negative [13].

In order to determine the chemical and thermal stability under extreme conditions and also to verify the compatibility of an explosive with the polymer in the PBX compositions, the vacuum stability test was carried out using a vacuum stability tester (STABIL OZM, RESEARCH). A dried and weighed sample (2 g) of PBX was heated at 120 °C for 48 h and the volume of gases (mL/g) evolved was recorded. Duplicate 2.0 g samples were placed in glass sample tubes which were evacuated using a vacuum pump. The sample tubes were then placed in a heating bath at 120 °C. The volume of gas evolved was monitored for 48 h at 120 °C and the results were recorded as an average of duplicate samples. Acceptance criteria for thermal stability by this method was taken as less than 2 mL/g [14].

Performance assessment of PBX charges was carried out by conducting plate dent tests (indentation test) against a mild steel (MS) witness plate (50 mm thick) and the velocity of detonation (VOD) was determined by an electrical measurement technique [15], called the pin oscillographic technique (POT).

Results and Discussion

Polymer characterization

Viton-A was soluble in acetone and methyl ethyl ketone (MEK) but was insoluble in methanol, chloroform and 70% HNO₃.

The FT-IR spectrum showed the following absorption bands for Viton-A (Figure 1): 1397-1074 (C-F bond), 1273, 1191, 1134 and 1111 (C-F₂ bonds); 635, 610 cm⁻¹ (C-F₃ bonds). Fluorine-containing compounds absorb strongly over a wide range between 1400 and 1000 cm⁻¹ because of the C-F stretching modes. A monofluoroalkane shows a strong band in the 1100-1000 cm⁻¹ region.

As the number of fluorine atoms in an aliphatic molecule increases, the band pattern becomes more complex, with multiple strong bands appearing over the broad region of the C-F absorption [16]. The thermal analysis of Viton-A by TGA and DSC is summarized in Table 3. The TG curve for Viton-A (Figure 2) showed that mass loss occurred at high temperature in two steps: 93.2% mass loss at 100-500 °C followed by 4.8% mass loss at 500-550 °C in a second step. This indicated that its thermolysis occurred in two steps due to decomposition of the copolymers VDF and HFP present in Viton-A. DSC analysis (Figure 3) revealed that the glass transition temperature (T_g) of the polymer was -21.4 °C and was followed by the softening point at 55.4 °C. As temperature increases, amorphous solids become less viscous. At some point, the molecules obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process and results in a peak in the DSC signal. In the case of Viton-A, the crystallization temperature of the polymer was recorded at 196 °C. Thermal degradation started at around 450 °C followed by a broad endothermic peak at 495 °C.

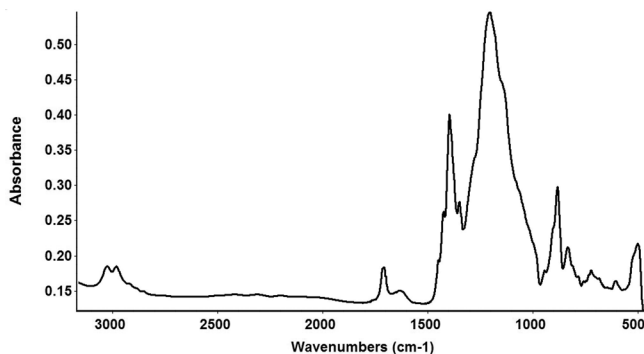


Figure 1. FT-IR spectrum of Viton-A.

Table 3. TGA and DSC analysis data of Viton-A

Viton-A			Temperature range [°C]
TGA analysis	Mass loss [%]	93.2%	100-500
		4.8%	500-550
DSC analysis	Glass transition temperature (T_g)		-21.4
	Softening temperature		55.4
	Crystallization temperature (T_c)		196
	Decomposition temperature		495

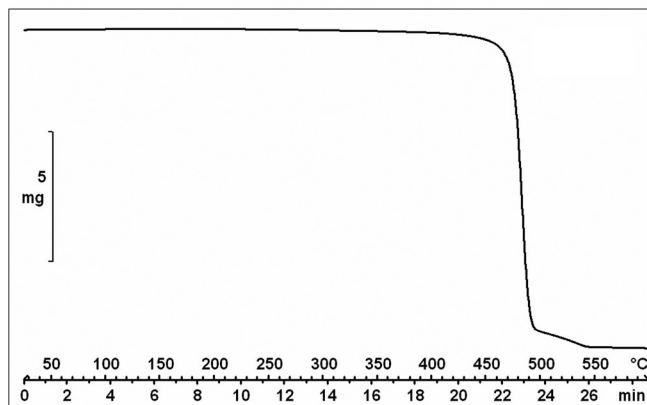


Figure 2. TGA curve of Viton-A.

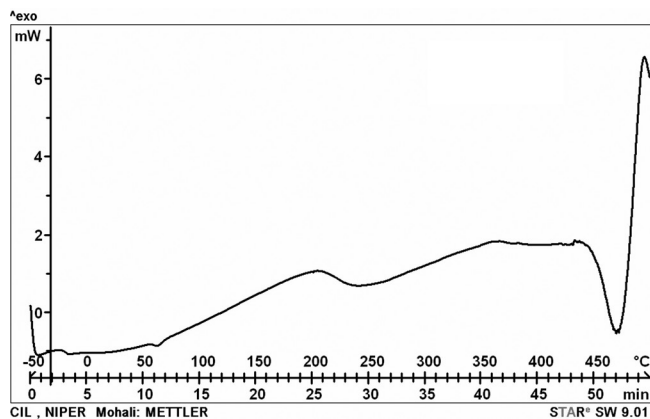


Figure 3. DSC curve of Viton-A.

The ^1H NMR spectrum of Viton-A showed a multiplet at 3.01 ppm which indicated the presence of two protons which exhibit very strong coupling with the neighbouring fluorine atoms present in Viton-A. The ^{13}C NMR spectrum exhibited peaks at 123, 119, 43, and 35 ppm corresponding to CF, CF₂, CF₃ and CH₂ carbons. The microstructure sequence of Viton-A was determined by ^{19}F NMR [17]. The ^{19}F NMR spectrum of the copolymer showed the characteristic signals of vinylidene fluoride (VDF) centered at -92, -114 and -116 ppm (Table 4) assigned to $-\text{CH}_2\text{CF}_2-\text{CH}_2\text{CF}_2$, $-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2$, respectively. The data showed the presence of long VDF sequences in Viton-A, whereas the presence of two adjacent hexafluoropropylene (HFP) units was completely excluded. Thus Viton-A obtained externally was of Viton-A grade (a bipolymer

of hexafluoropropylene and vinylidene fluoride; HFP/VDF).

Table 4. ^{19}F NMR data of Viton-A

Group	Microstructure sequence of Viton-A	^{19}F NMR peak [ppm]
-CF ₃	VDF/HFP/HFP	71.34
	VDF/HFP/VDF	75.85
-CF ₂	VDF/VDF	92.74, 94.42, 111.2, 113.19, 114.54, 116.28
	VDF/HFP/VDF	104.24, 118.71
-CF	VDF/HFP/VDF	184.93

Characterisation and evaluation of the PBX compositions

Composition analysis of PBX compositions by a gravimetric method confirmed the presence of $5 \pm 0.5\%$ Viton-A in the PBX compositions, with no significant loss of Viton-A during processing.

The thermal behavior of bimodal and hybrid PBX compositions (which is an important aspect with respect to safety, performance and stability) was investigated by the TGA and DSC techniques. TGA and DSC analysis of bimodal PBX is presented in Figures 4 and 5. Thermal analysis indicated that the presence of 5% Viton-A binder did not significantly change the thermal decomposition pattern of HNS-based, bimodal PBXs, as the decomposition behavior for all of the PBXs was similar to that of the parent explosive HNS and the binder Viton-A. TG thermograms for hybrid PBX compositions (Figures 6 (a-d)) show the multistep mass loss; mass loss occurred in a 1st step due to HMX decomposition at 285 °C, a 2nd step was due to HNS decomposition at 320 °C, followed by decomposition of Viton-A between 450 to 550 °C. It was noticed that the percentage mass loss of HNS at 320 °C decreased with increasing HMX content. DSC thermograms of hybrid PBX compositions are shown in Figures 7(a-c). The DSC curve for hybrid PBX exhibited three peaks at different temperatures. A first endothermic peak was observed at 190 °C (due to the phase transformation of β -HMX to δ -HMX), followed by another endothermic peak at 285 °C (which corresponds to melting of HMX) and an exothermic peak at 288 °C (which is due to thermal decomposition of β -HMX). HNS exhibited an endothermic peak at 320 °C followed by an exothermic peak at 350 °C. Similar characteristic endothermic and exothermic peaks were observed in all types of hybrid PBX compositions, as found in the parent explosives HNS and HMX, indicating almost the same thermal stability.

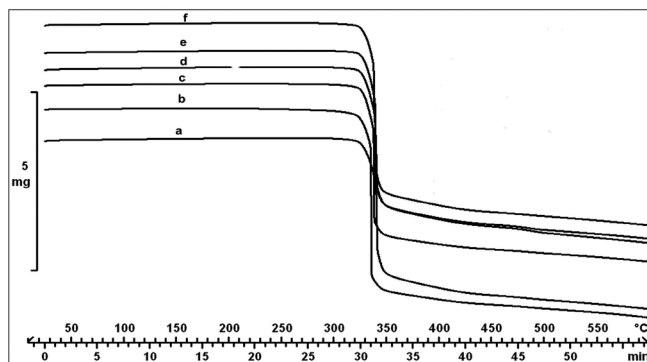


Figure 4. TGA analysis of bimodal PBX compositions: (a)HV-1; (b) HV-2; (c) HV-3; (d) HV-4; (e) HV-5; (f) HV-6.

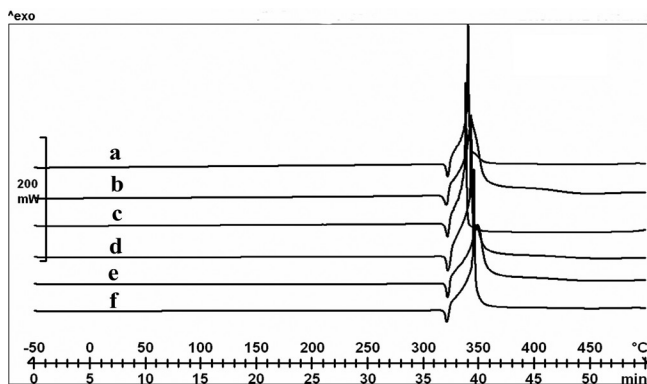


Figure 5. DSC analysis of bimodal PBX compositions: (a) HV-1; (b) HV-2; (c) HV-3; (d) HV-4 (e) HV-5; (f) HV-6.

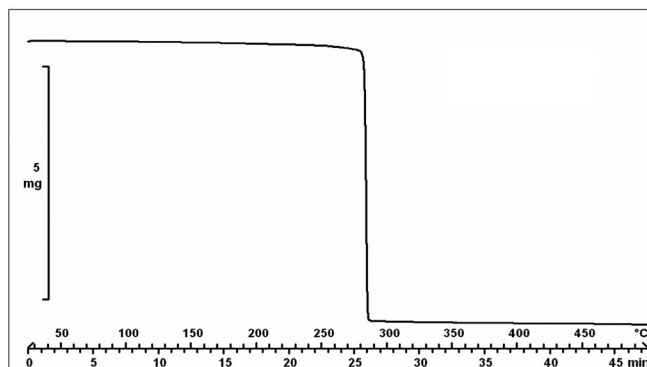


Figure 6(a). TGA curve of HMX.

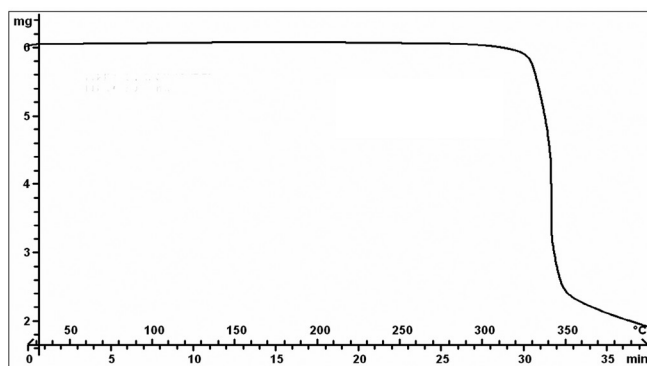


Figure 6(b). TGA curve of HNS.

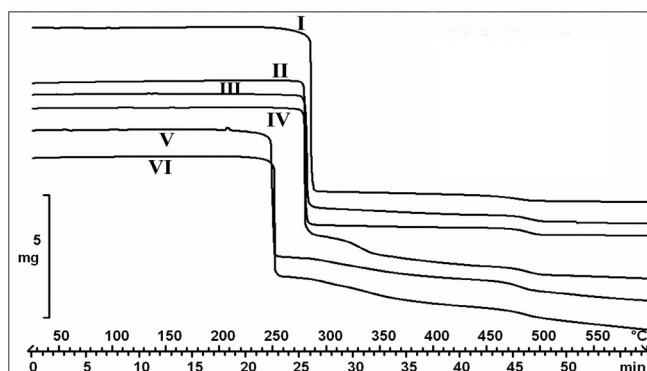


Figure 6(c). TGA analysis of hybrid PBX compositions; (I) HX; (II) HX-1090; (III) HX-2080; (IV) HX-5050; (V) HX-3070; (VI) HX-4060.

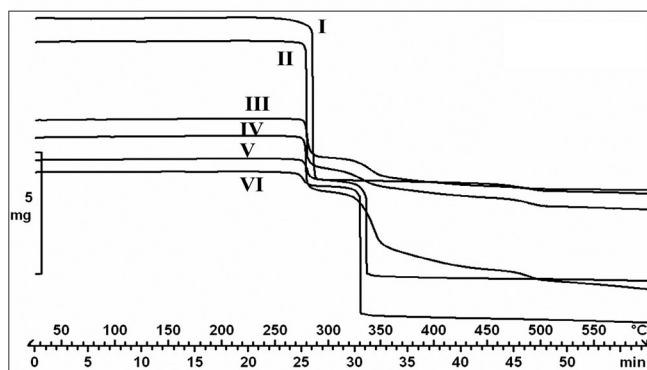


Figure 6(d). TGA analysis of hybrid PBX compositions; (I) HX; (II) HX-5050; (III) HX-6040; (IV) HX-7030; (V) HX-8020; (VI) HX-9010.

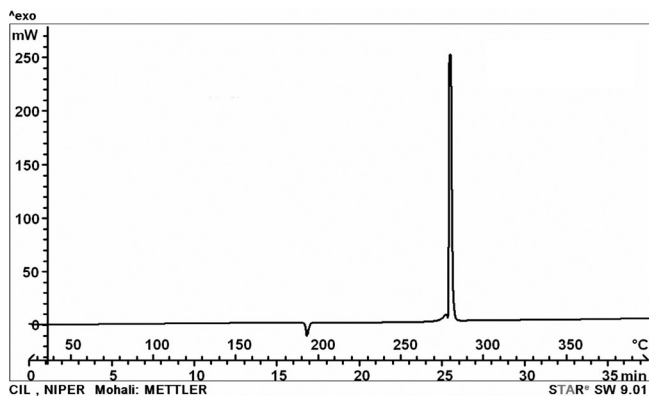


Figure 7(a). DSC curve of HMX.

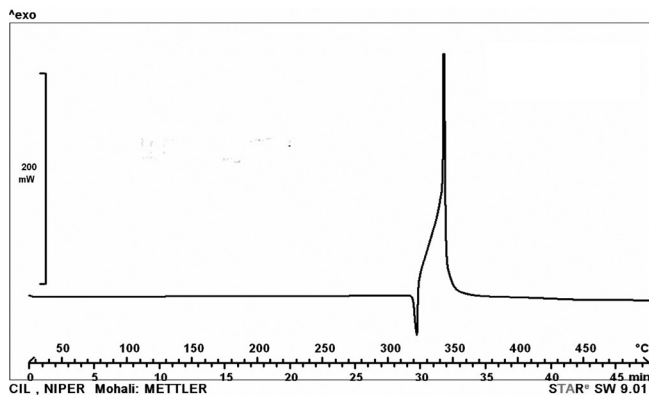


Figure 7(b). DSC curve of HNS.

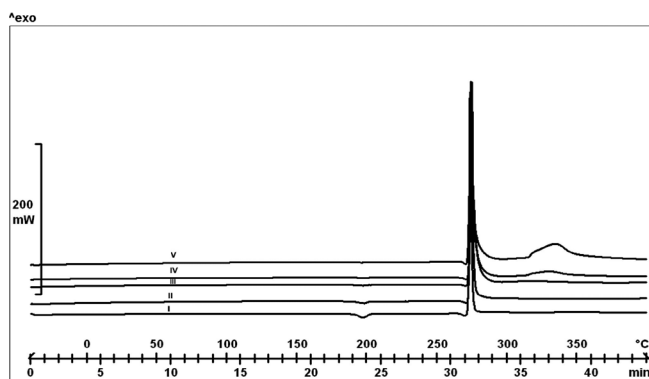


Figure 7(c). DSC analysis of hybrid PBX compositions; (I) HX-1090; (II) HX-2080; (III) HX-3070; (IV) HX-4060; (V) HX-5050.

Thermal analysis indicated that the presence of 5% Viton-A did not significantly change the thermal decomposition pattern of HNS and HMX based hybrid PBX, as the decomposition behavior for all of the PBXs was similar to that of the parent explosives HMX and HNS and the binder Viton-A.

SEM analysis of the PBX compositions showed that the explosive particles were coated with polymer (Figures 8a and 8b), as polymer was present in between the explosive particles in the PBX grains.

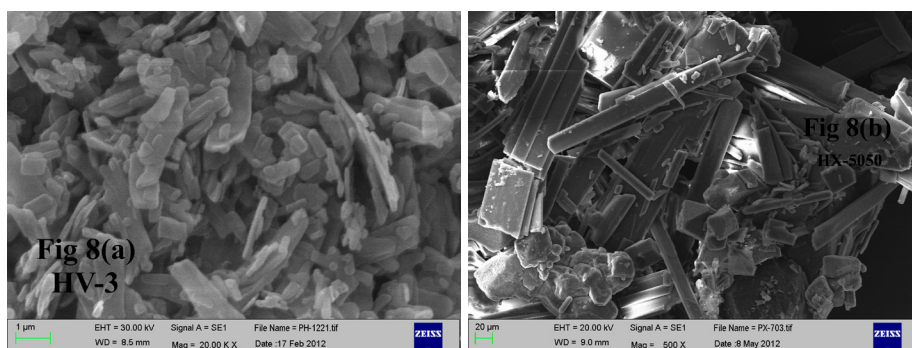


Figure 8. SEM images of PBX; (a) HV-3 (fine HNS: coarse HNS (50:50)/Viton; 95/5); (b) HX-5050 (HNS:HMX/Viton; 95/5).

It was observed that under identical conditions of pressing, PBX containing only fine HNS became pressed to a lower density (1.5 g/cc), whereas all bimodal PBX pellets were pressed to a higher density (1.6 g/cc). This may be due to the interstitial vacancies left in coarse particles becoming occupied by finer ones, leading to an increase in the loading density of bimodal PBXs.

In hybrid PBX pellets, the incorporation of HMX from 10 to 40% (HX9010, HX8020, HX7030, HX6040) resulted in lower densities (1.65 g/cc) compared to hybrid pellets containing HMX contents varying from 50 to 90% (HX5050, HX4060, HX3070, HX2080, HX1090) (1.75 g/cc). This was because the explosive HMX has a higher density (1.9 g/cc) than the explosive HNS (1.7 g/cc).

Mechanical strength/compressive strength data for the bimodal PBX compositions as measured by UTM is given in Table 1. The results revealed that the compressive strength of PBX pellets having fine HNS alone was higher (25 MPa) than the PBXs containing coarse HNS alone (18 MPa). This may be due to higher intraparticle cohesive forces of finer particles. For bimodal PBX pellets, increasing the amount of fine HNS in coarse HNS from 5 to 50% led to an increase in compressive strength from 19 to 22 MPa. This may be because of better packing of the fine particles in the coarse ones.

Mechanical strength/compressive strength data for hybrid PBX compositions (Table 2) revealed that the compressive strength of hybrid PBX pellets containing both HNS and HMX was greater (16 MPa) than the PBX pellets containing HMX alone (12 MPa). This may be due to the contribution of the higher mechanical strength of PBXs based on HNS alone (18 MPa) compared to PBXs based on HMX alone. The compressive strength of pellets was almost constant (16 ± 1 MPa) for compositions containing HMX in amounts varying from 10 to 90% (HX9010, HX8020, HX7030, HX6040, HX5050, HX4060, HX3070, HX2080, HX1090).

The results of impact and friction sensitivity testing of bimodal PBX compositions are presented in Table 1. Impact sensitivity data of bimodal PBXs revealed that $h_{50\%}$ was more in the case of the PBX based on fine HNS alone (35 cm) than the PBX with coarse HNS alone (24 cm). In bimodal PBX compositions, $h_{50\%}$ increased from 24 to 27 cm with increasing amounts of fine HNS in coarse HNS (1 to 50%). The limiting impact energy was 4 J for all of the bimodal PBX compositions.

The frictional force was greater in the case of the PBX based on fine HNS alone (125 N) as compared to the PBX based on coarse HNS alone (105 N). The frictional force increased from 108 to 124 N with increasing amounts of fine HNS in coarse HNS (1 to 50%) in bimodal PBXs (Table 1). The limiting frictional load of PBXs based on fine HNS alone and bimodal PBX compositions was greater (96 N) than for PBXs based on coarse HNS alone (80 N). This increase in insensitivity of fine particles to impact and friction may be because the average pore diameter in fine explosive particles is too small to become a hot spot under the impact and frictional stimulus.

The results of sensitiveness to impact and friction of hybrid PBX compositions are presented in Table 2. The $h_{50\%}$ increased from 24 to 42 cm on increasing the amount of HMX in the hybrid PBXs from 10 to 50% (HX9010, HX8020, HX7030, HX6040, HX5050). The $h_{50\%}$ was almost constant (42 cm) in hybrid PBX compositions containing HMX from 50 to 90% (HX5050, HX4060, HX3070, HX2080, HX1090), but was higher than with PBXs based on HNS alone (24 cm).

The frictional force increased from 108 to 161 N as the amount of HMX increased from 10 to 90% in hybrid PBXs (Table 2). The limiting frictional load was more for hybrid PBXs (120 N) compared to PBXs based on HNS alone (80 N).

Thus all bimodal and hybrid PBX compositions were safe to transport as the limiting impact energy was more than 2 J and the limiting frictional load was more than 80 N for all of the compositions.

The vacuum stability testing results of bimodal (Table 1) and hybrid PBX compositions (Table 2) indicated good compatibility of the polymer with the explosives HNS and HMX. The data on vacuum stability indicated that all of the developed PBX compositions evolved gas at less than 0.5 mL/g. Thus the PBX compositions were thermally and chemically stable even under extreme conditions and the polymer Viton-A was compatible with HNS and HMX. The vacuum stability results were corroborated by the TGA and DSC analysis.

In terms of performance evaluation, all PBX charges were initiated when fired against Mild Steel (MS) witness plates and a clear dent was recorded on the witness plate, which was an indication of detonation.

A comparison of the detonation velocity of different bimodal PBX compositions is presented in Figure 9 and Table 5. The VOD results showed that in the case of bimodal PBX compositions, the detonation velocity of PBXs based on fine HNS alone was 12% higher than for PBXs based on coarse HNS alone. The detonation velocity of bimodal PBX compositions containing fine and coarse HNS in the proportion of 1:1 was 16% more than for PBXs based on coarse HNS alone, and there was a decrease in VOD as the amount of fine HNS in coarse HNS was reduced to 5%. This was because, in the case of bimodal PBXs, the maximum packing density was achieved with smaller particles packing the interstices between the larger ones.

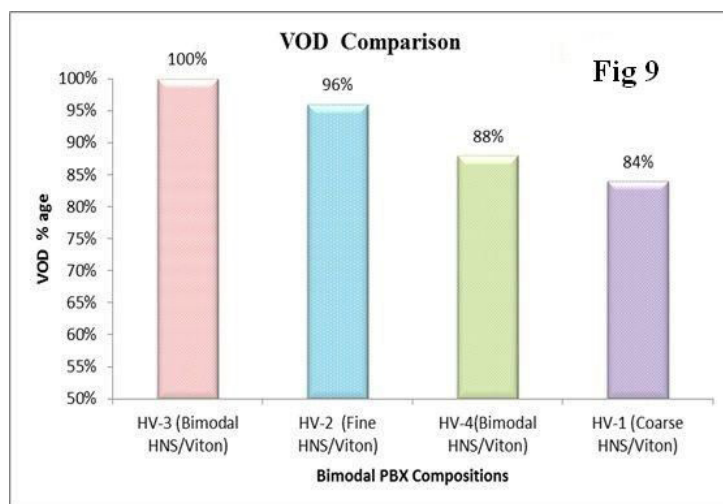


Figure 9. VOD comparison of bimodal PBX compositions.

Table 5. VOD comparison of bimodal PBX compositions

PBX compositions	Pellet density [g/cc]	VOD [km/s]	VOD/unit density	VOD* [in %age]
HV-1	1.65	6.45	3.91	84
HV-2	1.48	6.61	4.47	96
HV-3	1.59	7.38	4.64	100
HV-4	1.65	6.73	4.08	88

*VVOD of HV-3 being taken as 100%.

In the case of hybrid PBX compositions, the detonation velocity of hybrid PBX compositions containing HNS and HMX in the proportion of 1:1 was 12% higher than for PBXs based on HNS alone, and there was a decrease in detonation velocity on decreasing the amount of HMX in HNS. The VOD of PBXs based on HMX alone was higher, as expected, since HMX is a more powerful explosive than HNS. Thus the higher performance of hybrid PBXs was achieved due to the incorporation of the more powerful explosive HMX in HNS. A comparison of the detonation velocities of different hybrid PBX compositions is presented in Figure 10 and Table 6.

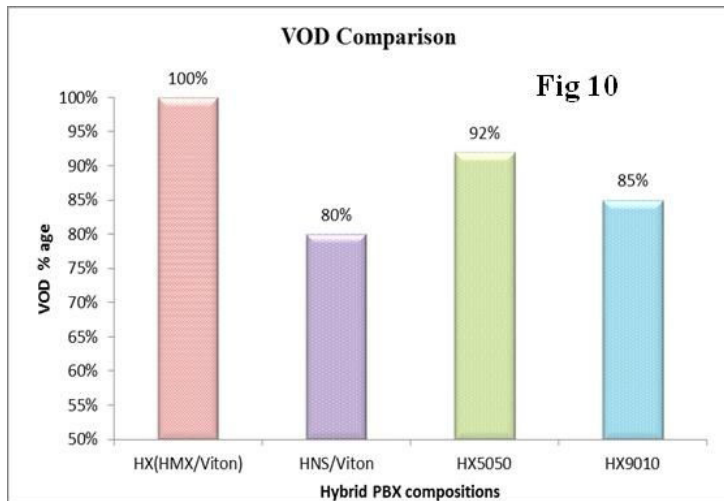
**Figure 10.** VOD comparison of hybrid PBX compositions.

Table 6. VOD comparison of hybrid PBX compositions

PBX compositions	Pellet density [g/cc]	VOD [km/s]	VOD/unit density	VOD* [in %age]
HX	1.75	8.54	4.88	100
HS	1.65	6.45	3.91	80
HX5050	1.71	7.68	4.49	92
HX9010	1.68	6.97	4.15	85

*VOD of HX being taken 100%.

Conclusions

In bimodal PBX compositions, incorporation of fine HNS into coarse HNS particles, from 5-50%, resulted in an increase in mechanical strength. There was a decrease in both friction and impact sensitivity in the bimodal PBXs compared to PBXs based on coarse HNS alone. When pressed under identical conditions, the density of bimodal PBX pellets was greater than that of PBX pellets containing only fine HNS. Bimodal PBX compositions also had enhanced performance (higher VOD) in comparison to PBXs based on either fine or coarse HNS alone.

In hybrid PBX compositions, the inclusion of 10-90% HMX in HNS resulted in an increase in the density of the pellets and a decrease in both impact and friction sensitivity, as well as enhanced performance compared to PBXs based on HNS alone. The mechanical strength of hybrid PBX pellets was found to be higher than that of PBX pellets based on HMX alone. In all types of PBX compositions, the explosives HNS and HMX were found to be compatible with each other and also with the fluoropolymer Viton-A.

From the present work, it can be concluded that Viton-A based bimodal and hybrid PBX compositions provide better mechanical and explosive properties compared to conventional PBX compositions based exclusively on HMX or HNS.

Acknowledgements

The authors are thankful to Dr. Manjit Singh, Director TBRL, Chandigarh, India, for his encouragement and for permitting us to publish this work. We are grateful to Incharge CIL, Panjab University, Chandigarh, for NMR analyses and to the Director, NIPER, Mohali, for allowing the TGA and DSC analyses.

References

- [1] Cumming A.S., New Directions in Energetic Materials, *J. Def. Sci.*, **1996**, 1(3), 319.
- [2] Urbanski T., Vasudeva S. K., Heat Resistant Explosives, *J. Sci. Ind. Res.*, **1978**, 37(5), 250-255.
- [3] Schmid H., Coating of Explosives, *J. Hazard. Mater.*, **1986**, 13(1), 89-101.
- [4] Mattos E.C., Moreira E.D., Diniz M.F., Dutra R.C.L., Silva G., Iha K., Teipel U., Characterization of Polymer-coated RDX and HMX Particles, *Propellants Explos. Pyrotech.*, **2008**, 33(1), 44-50.
- [5] Daniel M.A., *Polyurethane Binder Systems for Polymer Bonded Explosives*, Report DSTO-GD-0492, Weapons Systems Division, Edinburgh, Australia, Dec, **2006**.
- [6] Talawar M.B., Agarwal A.P., Anniyappan M., Gore G.M., Asthana S.N., Venugopalan S., Method for Preparation of Fine TATB (2-5 μm) and Its Evaluation in Plastic Bonded Explosive (PBX) Formulations, *J. Hazard. Mater.*, **2006**, 137(3), 1848-1852.
- [7] Agrawal J.P., Some New High Energy Materials and Their Formulations for Specialized Applications, *Propellants Explos. Pyrotech.*, **2005**, 30(5), 316-328.
- [8] Kilmer E.E., *HNS/Teflon Explosive Charges for the Apollo 17 Seismic Experiments*, Report NOLTR 73-44, LSPE, Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland, USA, May 10, **1973**.
- [9] Boddu V.M., Viswanath D.S., Ghosh T.K., Damavarapu R., 2,4,6-Triamino-1,3,5-trinitrobenzene (TATB) and TATB-based Formulations – A Review, *J. Hazard. Mater.*, **2010**, 181(1), 1-8.
- [10] Kaur J., Arya V.P., Kaur G., Gupta Y.P., Verma M.M., Lata P., Determination of Solvent Contamination and Characterization of Ultrafine HNS Particles after Solvent Recrystallization, *Propellants Explos. Pyrotech.*, **2010**, 35(5), 487-493.
- [11] Schaffer C.L., *Compositional Analysis of PBX 9503- A TATB/HMX/Kel-F800 Formulation*, Report MHSMP-81-55, DE 82006183, Department of Energy, USA, November, **1981**.
- [12] *UN Recommendation on the Transport of Dangerous Goods, Manual of Tests and Criteria*, United Nations, 13.4.2 Test 3(a) (ii) BAM Fall Hammer, New York, USA, **2003**.
- [13] *UN Recommendation on the Transport of Dangerous Goods, Manual of Tests and Criteria*, United Nations, 13.5.1 Test 3(b) (i) BAM Friction Apparatus, New York, USA, **2003**.
- [14] Provas A., *Formulation and Performance Studies of Polymer Bonded Explosives (PBX) Containing Energetic Binder Systems. Part 1*, Report DSTO-TR-1397, Weapons Systems Division, Systems Sciences Laboratory, Edinburgh, Australia, March, **2003**.
- [15] Gautam P.C, Goel G., Khurana R., Sharma A.C., Singh M., Electrical Techniques for Measurement of Detonics Parameters of High Explosives, *8th International High Energy Materials Conference & Exhibit, HEMCE-11*, TBRL, Chandigarh, India, Nov 10-12, **2011**.

- [16] Urbanski J., *Handbook of Analysis of Synthetic Polymers and Plastics*, John Wiley & Sons, New York, USA, **1977**, p. 494.
- [17] Ameduri B., Boutevin B., Kostov G., Fluoroelastomers: Synthesis, Properties and Application, *Prog. Polym. Sci.*, **2005**, 26, 105-187.

Symbols and Abbreviations

$^1\text{H-NMR}$	Proton Nuclear Magnetic Resonance
Acetone- d_6	Acetone (deuterated)
DMSO- d_6	Dimethyl sulfoxide (deuterated)
DSC	Differential Scanning Calorimetry
FT-IR	Fourier Transform-Infrared Spectrometry
$h_{50\%}$	Height for 50% initiation
HNS	2,2',4,4',6,6'-hexanitrostilbene
HMX	1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane
IM	Insensitive Munitions
MEK	methyl ethyl ketone
PBX	Polymer Bonded Explosive
rpm	revolutions per minute
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analyser
UTM	Universal Testing Machine
VOD	Velocity of Detonation

