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Studies on Tungsten Based High Density Cast Polymer Bonded Explosive (PBX) Formulations

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Abstract: Aluminized melt-cast TNT and PBX (cast/pressed) based compositions have been widely studied and used in different warheads for various applications,such as air blast, underwater blast, thermobaric effects, *etc*. Tungsten (W) based cast PBX formulations are the least reported in the literature. We have partially replaced RDX or HMX in the control PBX formulation with 15 to 25% W powder and investigated the effect of this on the ease of processing, density, sensitivity, mechanical properties and explosive performance. The viscosity was improved from 9 to 3 kPoise, and the density by about 12 to 25% on the addition of W powder to the PBX formulations. The sensitivity to impact for the RDX/Wand HMX/W based PBX formulations was improved by 12 to 37%. The reinforcing effect of the W powder caused an increase in hardness (Shore A) by 16 to 45%. A decreasing trend in the velocity of detonation (VOD) was observed because of the replacement of the nitramine content (RDX/HMX) with W powder. The approximate detonation pressure of RDX/W/HTPB (65/20/15), roughly calculated by the Kamlet-Jacobs method, is better than the other tungsten based formulations investigated.

Keywords: tungsten, RDX, HMX, HTPB, PBX

1 Introduction

Metal particles are commonly added to explosives to increase the density and improve the blast performance of the explosive formulation. The metal particles typically react over a much longer timescale than the explosive itself and primarily contribute to the work done by the expanding detonation products, and hence the blast impulse and duration get enhanced. High explosive formulations incorporating aluminium (Al) powder have been extensively studied and reviewed for their enhanced blast performance characteristics [1-7]. Metal powders such as lead (Pb) [8], silicon (Si) [8-9], titanium (Ti) [10], boron (B) [11-12] *etc.* have also been used as fuels in explosive formulations. The use of W powder in TNT-based melt-cast explosive compositions has been investigated mainly for its massiveness and transfer of momentum and impulse to surrounding bodies [13-17]. The HMX based PBX formulations with different percent of W powder has been studied for overdriven detonation in coaxial double layer cylindrical charges to improve jet performance [18].

W powder incorporated in the RDX and HMX based control PBX formulations [(RDX/HTPB, 85/15) and (HMX/HTPB, 80/20)], and its effect on the ease of processing, density, sensitivity (impact/friction), velocity of detonation and mechanical properties has been studied and is reported in the present paper.

2 Experimental

2.1 Materials

W powder (<45 μm, purity 99%) was obtained from a local source. Its particle size distributionwas measured on a Sympatec particle size analyzer (model: HELOS) using distilled water as the liquid dispersant. Some characteristic values are shown in Table 1.

Table 1. Particle size distribution of W powder

Tungsten powder	X_{10}, [μm]	X_{50}, [μm]	X_{90}, [μm]
< 45 μm	2.68	10.29	23.33

RDX (average particle size 150 μm), DOP (dioctyl phthalate) coated RDX (5-6 μm), HMX (average particle size 150 μm) and fine HMX (average particle size 10-12 μm) were obtained from our production units. The pre-polymer hydroxyl terminated polybutadiene, HTPB (Mn ~2700), dioctyl adipate (DOA) and butyl stearate (BS) were obtained from local sources. The curing agent 4,4’-methylene diphenyl diisocyanate (MDI) was obtained from Merck. All of the chemicals were used as received, without further treatment.

2.2 Processing

Processing was carried out in a 15 L planetary mixer at batch size 6 kg. The pre-polymer HTPB, DOA and BS were mixed under vacuum for complete deaeration.

Bimodal RDX (coarse particles of average size 150 μm and fine particles (DOP coated RDX) of average size 5-6 μm in the ratio (3:1)) was selected for a better packing density and processing of the PBX formulations. For processing of HMX based PBXs, bimodal HMX (coarse particles of average size 150 μm and fine particles of average size 10-12 μm in the ratio (3:1)) was selected. Mixing was carried out at room temperature. MDI as the curing agent was also added to the mix at room temperature. The slurry was then cast into split moulds of diameter 50 mm and length 400 mm. The filled moulds were kept overnight at room temperature during curing/hardening. The PBX charges were then extracted from the moulds and machined to the required dimensions.

The percentage of each ingredient for the various PBX formulations are shown in Table 2.

Table 2. PBX formulations

Formulation	RDX/ HMX	DOP coated RDX/ fine HMX	W	HTPB	DOA	BS	MDI	% Oxygen Balance
RDX/HTPB (85/15)	63.75	22.61	0	8.23	3.71	0.93	0.77	–61.1
RDX/W/HTPB (70/15/15)	48.75	22.61	15	8.23	3.71	0.93	0.77	–60.5
RDX/W/HTPB (65/20/15)	43.75	22.61	20	8.23	3.71	0.93	0.77	–60.3
RDX/W/HTPB (60/25/15)	38.75	22.61	25	8.23	3.71	0.93	0.77	–60.1
HMX/HTPB (80/20)	60	20	0	9.14	8	2	0.86	–73.9
HMX/W/HTPB (65/15/20)	45	20	15	9.14	8	2	0.86	–73.1
HMX/W/HTPB (60/20/20)	40	20	20	9.14	8	2	0.86	–73.1
HMX/W/HTPB (55/25/20)	35	20	25	9.14	8	2	0.86	–72.9

2.3 Testing

The sample for impact and friction sensitivity is prepared as per procedure given in Military Specification (MIL-E-82902(OS)). The impact sensitivity of the PBX formulations was determined using the fall hammer method, using a 2 kg drop weight. A minimum of 25 tests are run to determine height of 50% explosion using Bruceton procedure. The friction sensitivity was determined on a Julius Peters apparatus. The frictional load for consecutive 6 trials with no explosions was considered to be limit for friction sensitivity. The End of Mix (EOM) viscosity of the mixes was measured using a Brookfield Viscometer (Model No. RVDV II+) with T bar spindle (spindle no. S-93). The density was measured using a weighing balance (Mettler Toledo, Model No. MS204S, repeatability 0.1 mg) having the extended facility to measure density (based on Archimedes' Principle). The theoretical maximum density (TMD) is the sum of the relative volume of each component as determined from their relative mass within the formulation and known density [19]. The percent TMD is estimated by taking ratio of experimental density and theoretical maximum density multiply by 100. The velocity of detonation (VOD) was measured by the pin oscilloscopic technique (POT) with an accuracy of ±3%. The hardness (Shore A) was measured with a Durometer (model No. SHR-A-Gold, BSE Testing Machine).

3 Theoretical Prediction

The gaseous detonation products of the metallised PBX formulations were calculated according to the Spring all Robert rules [20]. Using this thermo-chemical parameters like the heat of detonation (Q, kJ/g), the specific volume per gram of explosive occupied by the gaseous detonation products (V, cm^3/g), the number of moles of gaseous detonation products per gram of high explosive (N, moles) and the mean average molecular weight of the gaseous products (M) were calculated. The VOD of PBX formulations were predicted by the Kamlet-Jacobs (K-J) method [21], while the detonation pressures (P) were calculated by both the K-J method and Cook's method [22]. Thermo-chemical properties are presented in Table 4.

4 Results and Discussion

From the control PBX formulation, RDX or HMX were partially replaced with 15 to 25% W powder. The oxygen balance of the RDX and HMX based control formulations decreases slightly with addition of W powder (Table 2). The effects of the addition of W powder on EOM viscosity, density, sensitivity, mechanical properties and explosive performance were investigated (Table 3). The friction sensitivity (insensitive up to 36 kg) was unaffected by the addition of W powder to the RDX and HMX based PBX formulations.

Table 3. Properties of the metallised PBX formulations

Composition	Exptl. density [g/cm^3]/ (% TMD)	EOM viscosity at 27 °C [kPoise]	Impact sensitivity [J]	Hardness (Shore A)	Exptl. VOD [m/s]
RDX/HTPB (85/15)	1.56 / (98.1)	8.07	6.28	45	7900
RDX/W/HTPB (70/15/15)	1.76 / (97.3)	3.27	8.24	68	7340
RDX/W/HTPB (65/20/15)	1.83 / (97.0)	2.80	8.24	69	7280
RDX/W/HTPB (60/25/15)	1.94 / (97.5)	2.58	8.63	67	6820
HMX/HTPB (80/20)	1.55 / (98.1)	9.07	8.44	45	8020
HMX/W/HTPB (65/15/20)	1.73 / (97.3)	5.56	9.42	55	7320
HMX/W/HTPB (60/20/20)	1.82 / (98.3)	3.63	10.01	52	7050
HMX/W/HTPB (55/25/20)	1.90 / (97.9)	2.51	10.39	52	6900

The EOM viscosity improved from 8 to 2.6 kPoise (~68% improvement) on addition of W powder to the RDX based PBX formulation, while the HMX based PBX formulation showed an improvement in the EOM viscosity from 9.07 to 2.5 kPoise (~72% improvement). The improvement in the viscosity of the W based formulations was due to the fine particle size and higher density (19.35 g/cm^3) of the W powder.

There was about 12 to 25% improvement in the density on addition of W to the RDX and HMX based PBX formulations. The better packing efficiency, homogeneity of the mix and also the higher density of the W powder is responsible for the increased density. The experimental densities of the W based PBX formulations were greater than 97% of TMD.

The RDX based metallised PBX formulations were insensitive to impact up to 8.24 J as compared to 6.28 J for the control PBX formulation RDX/HTPB (85/15). Similarly, the HMX based metallised PBX formulations were insensitive up to 9.42 J as compared to 8.44 J for the control PBX formulation HMX/HTPB (80/20).

The partial replacement of sensitive nitramine particles (RDX or HMX) with W powder causes an increase in insensitivity to impact of W based PBX formulations. The better wetting of the W particles by the HTPB binder, due to the high surface energy of the W metal powder (4.3 J/m^2), is also responsible for the lower sensitivity. The impact energy of the fall hammer gets dissipated by the polymer matrix leading to lower sensitivity of the formulation. An overall increase in hardness (Shore A) by 16-45% in the RDX and HMX based metallised PBX formulations was observed due to the reinforcing effect of the W powder.

The VOD of the RDX and HMX based PBX formulations decreased on addition of W. The decreasing trend in VOD was observed for the W based formulations because of the partial replacement of nitramine (RDX/HMX) with W powder. The VOD of the W based PBX formulations, as predicted by the Kamlet-Jacobs method [21], is given in Table 4.

Table 4. Thermo-chemical parameters and predicted VOD of the PBX formulations

Composition	W remains inert					W takes part in reaction				
	N	M	V	Q	Calc. VOD	N	M	V	Q	Calc. VOD
RDX/HTPB (85/15)	0.046	19.9	1026	4.02	7805	0.046	19.9	1026	4.02	7805
RDX/W/ HTPB (70/15/15)	0.040	14.3	905	3.17	6933	0.041	18.5	923	3.26	7533
RDX/W/ HTPB (65/20/15)	0.038	14.1	857	2.92	6810	0.039	19.6	878	3.05	7573
RDX/W/ HTPB (60/25/15)	0.036	13.9	806	2.69	6673	0.037	18.9	818	2.89	7399
HMX/HTPB (80/20)	0.048	21.5	1078	3.53	7862	0.048	21.5	1078	3.53	7862
HMX/W/ HTPB (65/15/20)	0.041	13.3	927	2.85	6643	0.042	17.5	945	2.94	7244
HMX/W/ HTPB (60/20/20)	0.039	13.1	876	2.62	6488	0.038	18.3	890	2.75	7205
HMX/W/ HTPB (55/25/20)	0.037	12.7	826	2.38	6320	0.036	17.9	814	2.59	6968

The possible reactions of W powder with detonation products like H_2O, CO and CO_2 are shown below.

(i) $W_{(s)} + 3H_2O_{(g)} \longrightarrow WO_{3(g)} + 3H_{2(g)} + 116.9$ kJ/mol
(ii) $W_{(s)} + 2CO_{(g)} \longrightarrow WC_{(s)} + CO_{2(g)} + 207.6$ kJ/mol
(iii) $W_{(s)} + 3CO_{2(g)} \longrightarrow WO_{3(g)} + 3CO_{(g)} - 6.13$ kJ/mol

Tungsten trioxide (WO_3) is the most favoured oxidation product of the W powder. Water has great reactivity with W powder at all temperatures [23]. It is an exothermic reaction with an increase in the number of gaseous products. The reaction between W powder and carbon monoxide is also an exothermic reaction,but with a decrease in gaseous products. The W powder gets carbonised to solid tungsten carbide ($WC_{(s)}$) while $CO_{(g)}$ gets oxidized to $CO_{2(g)}$. The endothermic reaction of W powder with $CO_{2(g)}$ results in the formation of $WO_{3(g)}$ and $CO_{(g)}$. However, the possibility of reaction of W powder with $CO_{2(g)}$ is ruled out since it is endothermic in nature.

The heat of detonation, the number of moles of gaseous products and the average molecular weight of the gaseous products were calculated on the basis of the reaction of W powder with $H_2O_{(g)}$ and $CO_{(g)}$. Here, $WO_{3(g)}$ was considered as a gaseous product at the detonation temperature, since it sublimes at 900 °C [24].

The VODs, calculated with the assumption that W remains inert in the detonation zone, were lower than the experimental values. This indicates that W does not remain inert in the detonation zone. The reaction of W with the detonation products results in an increase in the heat of detonation (Q), specific volume (V) and mean average molecular weight of gaseous products (M). The VODs, calculated with the assumption that W reacts in the detonation zone agree well with the experimental values (the overall deviation is $\leq 8.5\%$) in the RDX/W based PBX formulations. The VODs, calculated with the assumption that W remains inert in the detonation zone are lower than the experimental values (the overall deviation is $\leq 6.5\%$) of RDX/W based PBX formulations. The calculated VOD of HMX/W based PBX formulations agree well with the experimental values (the overall deviation is $\leq 2\%$) with the assumption of W powder reacts in detonation zone. The calculated VOD of HMX/W based formulations with the assumption of W remains inert in the detonation zone are lower than the experimental values (the overall deviation is $\leq 9\%$).

Detonation pressure is an important performance parameter. Two approaches are used to estimate the detonation pressure of C-H-N-O explosives, namely the Kamlet-Jacobs empirical formula (K-J method) [21] and Cook's method [22].

(i) K-J method:

$P = 15.58\ Ø\cdot\rho^2$

where $Ø = N\ (MQ)^{1/2}$ and ρ is TMD.

(ii) Cook's method:

$P\ (GPa) = \rho\cdot D^2/(\gamma+1)$

where ρ is the loading density (g/cm^3), D is the experimental VOD (km/s) and γ is the polytrop exponent (=3).

However, application of these methods gives only a rough approximation of the detonation pressure of metallised non-ideal explosives [1, 25, 26]. The detonation pressures of the PBX formulations calculated by these methods are tabulated in Table 5.

Table 5. Calculated detonation pressure (P) by different methods

Composition	P, [kbar] (K-J method)	P, [kbar] (Cook's method)
RDX/HTPB (85/15)	241	243
RDX/W/HTPB (70/15/15)	238	237
RDX/W/HTPB (65/20/15)	243	243
RDX/W/HTPB (60/25/15)	245	224
HMX/HTPB (80/20)	242	249
HMX/W/HTPB (65/15/20)	217	232
HMX/W/HTPB (60/20/20)	215	226
HMX/W/HTPB (55/25/20)	213	229

The detonation pressures of the RDX/W based formulations with 20% and 25% W, computed by the K-J method, are comparable to the detonation pressure of the control PBX formulation. However, when the detonation pressure was calculated by Cook's method, the RDX/W based formulation RDX/W/HTPB (65/20/15) has a higher approximate detonation pressure compared to the other W based PBX formulations.

6 Conclusions

The W based PBX formulations were found to be more impact insensitive compared to the control PBX formulations [(RDX/HTPB, 85/15) and (HMX/HTPB, 80/20)]. The decrease in VOD on incorporation of W in the PBX formulations is due to partial replacement of the nitramine. The increase in hardness (Shore A) is due to better packing and the reinforcing effect of W powder.

As a rough approximation, the values of the detonation pressure calculated by the K-J method and Cook's method indicate that the PBX formulation RDX/W/HTPB (65/20/15) can be better than the other W based formulations developed and it may have potential for application in the warheads of hard target penetrator missiles, shaped charges based on over driven detonation phenomena and in future insensitive munitions.

7 References

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