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Study of Advanced Plastic Bonded Explosives

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Abstract:

Thermochemical Properties of selected types of PBXs, based on mixtures of explosives, either classical or advanced, (RDX, HMX, PETN, CL-20 or Bicyclo-HMX) and either inert or energetic binder (HTPB or GAP), were evaluated by EXPLO5 program. PBX based on CL-20 gave the higher performance when compared with those based on RDX, HMX, PETN or Bicyclo-HMX and the compositions based on GAP have higher performance than those based on HTPB.
According to the results of thermochemical calculations, PBXs samples, based on RDX and Bicyclo-HMX as energetic fillers and PU binders based on either HTPB or GAP, were selected and successfully prepared by casting technique. PBX formulations based on RDX and Bicyclo-HMX showed ignition temperature less than of pure RDX and pure Bicyclo-HMX. Furthermore, the activation energy needed for PBXs initiation decreased in presence of PU binders when compared with that of pure RDX and pure Bicyclo-HMX. The measured sensitivity characteristics proved that PBX formulation based on PU/HTPB has lower sensitivity to mechanical stimulus (impact, friction) than that of pure Bicyclo-HMX and pure RDX. The heat of combustion for PBX formulations based on PU/HTPB was higher than that based on PU/GAP. The brisance value for PBX based on PU/GAP was higher than that based on HTPB.

Key words

Thermochemical calculations, Plastic bonded explosives, EXPLO5, RDX, HMX, PETN, Biyclo-HMX, CL-20, GAP, HTPB

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1. Introduction

By the end of the first world war, the explosives development took the direction to improve the explosive performance, and as a result the sensitivity of explosives has been increased. Over the years, many accidents happened during handling, transporting, testing, and even manufacturing of explosives at which explosive chemists have always paid attention to increase performance without considering safety aspect. In July 1968 the aircraft carrier USS Forrestal on station in the gulf of tonkin, was conducting normal flight operations when a rocket inadvertently fired from an aircraft on the flight deck. The resulting fire and explosion cost the lives of 134 seamen, 74 million dollars in material damage to the carrier alone and operational loss of vessel for an extended period. In January 1969, a similar incident occurred aboard the USS enterprise, numerous deaths and severe damage occurred as a result of violent reaction of ammunition explosives. These accidents were results of what was termed "cook-off", at which confined explosives in ammunition were exposed to extreme heat such as a fuel fire. As a result, a violent reaction may occur leading to a high order detonation [1].

The demand for increased safety in explosives handling, storage and transportation has led to the development of Insensitive Munitions (IM). The design of these explosives and weapons decreases the probability of unexpected detonation from external stimuli such as shock, weapon fragments, and heat. This can be achieved by modification of the external weapons system, explosive formulation or a combination of both [2].

The new trend in the field of explosives is to develop plastic bonded explosives with a significantly lower vulnerability to various stimuli than conventional high explosives that suffer from various disadvantages [3]. A plastic bonded explosive (PBX) is a term applied to various explosive mixtures where the crystals of high explosives are coated with a thin layer of polymeric material. PBXs have many advantages including; lower vulnerability and sensitivity to mechanical and thermal stimuli, improved mechanical properties, higher performance and detonation velocity due to safe-pressing to high densities, simplicity of the manufacturing technique (most of them produced by casting technique) and excellent chemical stability and resistance to humidity, so they have increased shelf life. Moreover, PBXs overcome the problems encountered with casted TNT. The first actually castable PBXs were developed in the early 1960s.These formulations were RDX or HMX dispersed in polyester or polyether prepolymers. These formulations were of relatively low viscosity and were processed in conventional mixing kettles. The virtues of these systems were the simplicity of mixing, ease of pouring, relative minor shrinkage during curing and resistance to elevated temperatures after curing [4]. This kind of PBXs was not problem-free. Their first problem was their considerable sensitivity to vibrations, shocks and other such impulses that in turn was directly attributable to the hard, brittle, and friable nature of the fully polymerized end products. During the 1960s, polyurethanes were introduced as binders for RDX or HMX-based explosives. These materials resulted in more rubbery and less shock sensitive explosives. Several energetic binders and plasticizers were also developed to compensate performance loss upon using inert binders [5].

In this work the performance of different types of PBXs was evaluated by both thermochemical calculations and experimental results of prepared selected PBX compositions that use a mixture of either classical or advanced explosives and different types of either inert or energetic binders to choose explosive formulations which satisfy the required performance parameters needed for the application of PBXs.

2. Thermochemical Calculations

EXPLO5 program was used for calculation of the detonation parameters shown in Table (1), while the explosion force (F) and brisance (B) were then calculated according to the following equations [6]

$$\mathbf{F = n\,R\,T_v} \qquad (1)$$

F Explosion force [J/kg].
n Number of moles of gaseous products / 1kg of explosive.
R Universal gas constant.
T_v Explosion temperature [K].

And $\mathbf{B = f\,\rho}$ (2)

B Brisance [N/m.s)].
ρ Density [kg/m^3].
D Detonation velocity [m/s].

Table 1: Detonation parameters calculated by EXPLO5

Property	Units
Explosion heat (Q_v)	[kJ/kg]
Explosion temperature (T)	[K]
Explosion pressure (P)	[kbar]
Detonation velocity (D)	[m/s]
Moles of explosion products (n)	[per mole of explosive]
Specific volume (V_o)	l/kg

Samples abbreviations of used PBX formulations are shown in Table (2). Results of thermochemical calculations were very important for explosive compositions that are candidate for preparation and expected to give the required performance of the needed application.

Table (2) Samples abbreviation of PBX formulations

PBXs abbreviation	RDX (Wt%)	HMX (Wt%)	PETN (Wt %)	Bicyclo-HMX (Wt%)	CL-20 (Wt%)	PU based on HTPB (Wt %)	PU based on GAP (Wt %)
PBXRT3	86	-	-	-	-	14	-
PBXHT3	-	86	-	-	-	14	-
PBXPT3	-	-	86	-	-	14	-
PBXBT3	-	-	-	86	-	14	-
PBXCT3	-	-	-	-	86	14	-
PBXRG3	86	-	-	-	-	-	14
PBXHG3	-	86	-	-	-	-	14
PBXPG3	-	-	86	-	-	-	14
PBXBG3	-	-		86	-	-	14
PBXCG3	-	-		-	86	-	14

2.1 *Explosion heat (Q_v)*

The explosion heat is one of the most important characteristics of the explosive because it determines its efficiency.
The explosion heat of the PBX formulations decreases as the weight percent of PU binder increases. Comparing the values of explosion heat of the PBX formulations containing PU binder based on (HTPB or GAP), it is clear that formulations based on GAP have higher explosion heat than those formulations based on HTPB due to higher oxygen balance. The formulation PBXCG3 gives the highest explosion heat among other formulations.

2.2 Detonation velocity (D)

Detonation velocity is an essential characteristic of high explosives. It represents the rate of energy delivery through explosive conversion.
The detonation velocity of the PBX formulations decreases as the weight percent of PU binder increases, which confirms the fact that PU binder will not directly represent a reaction partner in the detonation zone; therefore PU reduces the reacting molecules in the detonation front. From technological point of view,14% binder is the minimum percentage that could be casted. Therefore, the comparison will be held between the formulations based on 14% binder.
Explosive formulations containing PU/GAP give higher results than those containing PU/HTPB, e.g. for PBXCT3, detonation velocity decreased by approximately 7.8% but for PBXCG3 the decrease is approximately 3.7% compared with that of pure CL-20. This may be due to the higher density and energetic groups of GAP (Azide group and oxygen atoms), hence its higher conversion rate than that of HTPB, which contains only carbon and hydrogen atoms. The formulation PBXCG3 gives the highest detonation velocity among other formulations containing 14% binder.

2.3 Explosion force (F)

Explosion force involves the total work output of the explosive charge over the full period of the explosion. It is also an important term in the calculation of brisance. The explosion force is calculated by equation (1).
The explosion force of PBX formulations decreases as the weight percent of PU binder increases. The explosive formulation PBXBG3 exhibits the highest explosion force because Bicyclo-HMX has more specific volume of gaseous products (V_o) and explosion temperature (T_v) than other explosives.

2.4 Brisance (B)

Brisance represent the shattering effect of the explosion on the objects lying in the near vicinity of the explosive charge. It depends on explosive density, detonation velocity, amount of gaseous products, and explosion temperature.
The brisance of the PBX formulations decreases as the weight percent of PU binder increases. Such behavior is mainly due to the decrease in detonation velocity as the binder weight percent increases.
Explosive formulations containing HTPB-based binder produce values of brisance much less than that of pure explosive, e.g for PBXCT3, the brisance decreased by about 25% compared with that of pure CL-20. This may be due to the decrease of the

brisant high explosive (CL-20) content and hence the decrease of oxygen balance (more negative), number of moles of gaseous products and detonation velocity of the PBX formulations. A better situation is obtained for the formulations containing GAP-based binder, where values of brisance are not much decreased, e.g for PBXCG3, the brisance decreases by about 13% compared with that of pure CL-20. The values of brisance for formulations based on GAP are higher than those of corresponding compositions based on HTPB. The formulation PBXCG3 has the highest brisance among other formulations.

3. Experimental work

The explosive properties of many types of PBX formulations that use a mixture of either classical or advanced explosive and different types of either inert or energetic binder were invstigated through thermochemical calculations, to choose the plastic bonded explosive formulations (PBXs) suitable for the required applications. It was decided to prepare and test PBX formulations containing PU (based on HTPB/GAP) as binder and BCHMX/RDX as high explosive (filler).

The procedure of the exprimental work was carried out in the following steps:

- Dewaxing of high explosive, which was essential to obtain pure explosive crystals.
- Characterization of the obtained pure RDX crystals by scanning electron microscope (SEM) and ignition temperature measurement.
- Preparation of PBX samples based on RDX and BCHMX as energetic fillers and PU binders based on either HTPB or GAP by casting technique.
- Characterization of the prepared PBX formulations by sensitivity and preformance tests..
- Determination of the PBX compositions having the required performance and sensitivity for application as low-sensitive, brisant main charge of warheads or air bombs.

3.1 Dewaxing of RDX

3.1.1 *Convetional method using DMSO solvent*

Conventional dewaxing method using DMSO solvent was applied sucessfully for dewaxing of waxed HMX with good yield results, but it was not efficent for dewaxing of waxed RDX as showen in Figure (1) due to the following:

- DMSO solvent dissolves RDX crystals but not the wax.
- Difficulties of separation of RDX crystals from wax traces.
- Necessity of using large quantities of expensive DMSO solvent.
- Low yield, around 30%.

3.1.2 Novel method using TCE and DMSO solvents

Due to the conventional dewaxing process disadvantages, a novel method of dewaxing was applied using both DMSO and TCE solvents, as shown in Figure (2).

3.1 Preparation of PBX containing RDX, Bicyclo-HMX and PU based on HTPB or GAP

These formulations (PBXRT3, PBXRG3, PBXBT3 and PBXBG3) were prepared by casting technique. Prepolymers used in this work were HTPB and GAP (HTPB of 0.85 and GAP of 1.43 measured mg equivalent OH/g HTPB and GAP respectively) the plasticizer (DOZ) and bonding agent (MAPO) were used with HTPB and GAP. The prepolymer, bonding agent and the plasticizer were mixed together at 50-60 ^{o}C then explosives was added thorough mixing. The curing agent (HMDI) of 11.89 mg equivalent NCO/g HMDI was added and mixing was carried out for relatively short time. The explosive mixture was then poured in PVC mould tubes.

3.2 Determination of explosive characteristics of PBXs

Sensitivity tests

Sensitivity to impact was carried out using IKa Maschinenbau apparatus, using 5 Kg falling weight. Upper sensitivity limit was used to identify the minimal height at which 100% initiation was achieved. Sensitivity to friction was determined using BAM friction test apparatus. The frictions test was determined by the percentage of initiation by changing the loading of the pistil. The sensitivity to heat was obtained in two steps; measuring the ignition temperature for the prepared PBX samples and determining the ignition temperature at constant delay period (2 seconds) of ignition using Chilworth deflagration test apparatus. To determine the ignition temperature, the temperature was uniformly increased [20^{o}C/min] until the explosion conversion occurred.

3.3 Determination of explosive performance of PBXs

3.3.1 Brisance

This test was carried out using the brisance testing unit according to Kast technique [7], where 2.5 g of the explosive charge was pressed to a density of 1.6 g/cm3 into an aluminum tube of 30 mm height, 12 mm inside diameter and 4 mm wall thickness. Electric detonator is used to initiate the explosive charge. The copper crusher used is of 9.8 mm height and 6 mm diameter. The deformation (final lengths) of copper crusher was determined after the explosion of the charges and converted into force units according to the calibration table of the copper crusher static compression force test [8].

3.3.2 Determination of the heat of combustion

The measurement of the combustion heat is analogous to the determination of the heat exchange in various chemical or physical processes. The experiment is performed in an adiabatic calorimeter assembly and is based on the observation of the temperature increase in the calorimetric vessel during the process. The combustion of the samples was carried out in atmosphere of oxygen at a pressure of approximately 20 bar. The heat capacity of the calorimeter assembly is determined by a calibration run during which a substance of known combustion heat as benzoic acid is used. Consequently, the combustion heat of the sample under test is determined by a similar run, using the equation:

$$Q = K_w \ \Delta T \qquad (3.2)$$

Where

K_w Heat capacity of the calorimeter (water value) [kJ/kg].

Δ T Temperature difference of the water bath [^{o}K].

4. Results and Discussions

4.1 Dewaxing of RDX

4.1.1 *Conventional method using DMSO solvent*

Conventional dewaxing method using DMSO solvent was not efficient for dewaxing of waxed RDX because DMSO solvent dissolved RDX crystals but not the wax. As a result, the produced RDX (still contaminated by wax) was not accepted for prepration of PBX formulations based on pure RDX.

Some experiments were carried out for characterization of produced dewaxed RDX, namely, ignition temperature and impact senstivity. Obtained results are shown in Table (3) and SEM photo of waxed is RDX shown in Fig (3).

Table (3). Sensitivity parameters of RDX separated by conventional method

Expriment	Literature values	Experimental values
Ignition temperature (K)	495 [9]	522
Impact sensitivity (J)	7.4 [10]	10.5

The remarked deviation of experimental results from the reported values [9,10] shown in Table (3) confirms that RDX produced by this conventional method is not totally wax-free.

4.1.2 Novel method using TCE and DMSO solvents

A novel method of dewaxing was applied using both DMSO and TCE solvents to enhance the complete removal of wax from RDX crystals.

Same sensitivity parameters, namely, ignition temperature and impact senstivity were measured again to identify produced dewaxed RDX. Obtained results are shown in Table (4) and SEM photo of dewaxed RDX is shown in Fig (4).

Table (4). Sensitivity parameters of RDX separated by novel method

Expriment	Literature values	Experimental values
Ignition temperature (K)	495 [9]	514
Impact sensitivity (J)	7.4 [10]	7.5

The impact sensitivity and SEM photo results confirm the production of almost wax-free RDX. The agreement of ignition temperature values is better than before. The remaining deviation my be attributed to different heating rates.

4.1 Sensitivity results of prepared PBX formulations

For pure RDX, pure Bicyclo-HMX and prepared PBX formulations (PBXRT3, PBXRG3, PBXBT3, PBXBG3), the sensitivity results are listed in table (5). It is clear that for all prepared PBXs, the of sensitivity to impact decrease when compared with pure RDX and pure Bicyclo-HMX as shown in Figure (5). However, PBX formulations used polyurethane binder based on HTPB have lower sensitivity to impact than those formulations based on GAP. These results reveal high degree of safety of these formulations towards impact impulses which is an important criteria required for explosive formulations used for airplanes bombs and rocket warheads.

PBXRT4, PBXRG3, PBXBT3 and PBXBG3 showed no initiation even when applying the maximum friction force (360 N) of the test apparatus. PBXs showed ignition temperature slightly lower than RDX and Bicyclo-HMX as shown in Figure (6). This can be attributed to the fact that the coating of polyurethane based on GAP or HTPB acts as heat sensitizing medium because its softening temperature is less than 152^{o}C [10]. The values of ignition temperature corresponding to constant delay periods (2 seconds), for the prepared PBX formulations are listed in Table (5).

4.2 Performance characteristics of the prepared PBX formulations

4.2.1 Combustion heat

The measured combustion heat of RDX was 9902 (kJ/kg) while it was 9124 (kJ/kg) for pure Bicyclo-HMX. For all the prepared PBX formulations containing RDX or Bicyclo-HMX and PU binder (based on HTPB or GAP) the calorific values (heat of combustion) were determined at 1 atm. using the apparatus shown in Chapter three. The results, given in kj/kg, are listed in Table (5) and illustrated in Figure (7).

The calorific value of explosives (heat of combustion) may be employed as a general indication of the energy content and energy output of these explosives. For positive oxygen balance explosives, the value of heat of combustion should be the same as that for the heat of explosion, but for negative oxygen balance explosives the calorific value will be higher than the heat of explosion. From Table (5) and Figure (7) it is clear that the type and content of binder have significant effect on the calorific values of the prepared PBX formulations. The heat of combustion for PBX formulations containing PU based on HTPB is higher than that containing PU based on GAP. This may be explained by the higher mean molar mass (M_{Wav}.) of HTPB pre-polymer than that of GAP which means large structure of HTPB compared with GAP. Moreover, HTPB contains higher number of elements which produce more heat during combustion than that of GAP.

4.2.2 Brisance

From Table (5) and Figure (8), it is clear that the brisance value for PBX formulations containing PU based on GAP is higher than that of PU based on HTPB. This may be explained by the presence of more energetic groups (azide groups, oxygen atoms) and high density of GAP which is expected to increase the oxygen content, number of moles of gaseous products and detonation velocity of the prepared PBX formulations containing PU based on GAP. We can conclude that PBXs based on GAP, which have high values of brisance, are recommended to be used as main explosive charge of low sensitive warheads and demolition charges.

Table (5). Sensitivity and performance results of RDX and Bicyclo-HMX and PBX formulations based on RDX, Bicyclo-HMX and PU (HTPB, GAP)

	Sensitivity results				Performance results	
	Impact (J)	Friction (N)	Ignition temp (K)	Ignition temp. (oC) (after 2 sec delay)	Combustion heat (Kj/kg)	Brisance (MPa)
RDX	7.2	120	514	320	9902	--
PBXRT3	22	> 360	503	310	14391	115.7
PBXRG3	19.6	> 360	505	320	11574	121.8
Biyclo-HMX	2.98	88	503	--	9124	--
PBXBT3	12.25	> 360	489	290	13860	108.9
PBXBG3	9.8	> 360	502	320	11327	117

5. Conclusions

From thermochemical calculation results, it can be concluded that PBX formulations based on 10% binder have the best performance parameters, but from technological point of view, 14% binder content is the minimum percentage that could be casted. Theoretical calculations obtained from EXPLO5 program showed that PBXs formulations containing PU based on GAP have the highest performance characteristics among other formulations containing PU based on HTPB because GAP is denser and more energetic since it has higher calorific value than HTPB. Formulations based on GAP have the highest values of heat of explosion, detonation velocity and brisance than those based on HTPB. Moreover, since CL-20 has high of formation and density (its performance is approximately 20% higher than standard explosives).

The measured sensitivity characteristics proved that PBX formulation based on PU/GAP has lower sensitivity to mechanical stimulus (impact, friction) than that of pure Bicyclo-HMX and RDX. However, PBXs formulations used polyurethane binder based on HTPB have lower sensitivity to impact than those formulations based on GAP. These results reveal high degree of safety of these formulations towards impact impulses which is an important criteria required for explosive formulations used for airplanes bombs and rocket warheads.

For all the prepared PBX formulations based on RDX and Bicyclo-HMX as chosen energetic fillers and PU binders based on either HTPB or GAP, the ignition for PBXs formulations based on PU (GAP or HTPB) are less than that of pure RDX and pure Bicyclo-HMX which can be attributed to the coating of PU (GAP or HTPB) that acts as a heat sensitizing medium because its softening temperature which is less than 152 ^{o}C. It can be concluded that the activation energy needed for the initiation of the prepared PBXs formulations decreased in presence of PU binders when compared with that of RDX and Bicyclo-HMX, which resulted in increasing the sensitivity of PBXs formulations to heat after a 2 second delay time due to the presence of such binder content as a coating layer.

For all the prepared PBX formulations based on RDX and (HTPB, GAP) and all the prepared PBX formulations based on Bicyclo-HMX and (HTPB, GAP), the calorific values (heat of combustion) were determined as a general indication of the energy content and energy output of these explosives. It is clear that the type and content of binder have significant effect on the calorific values of the prepared PBXs formulations. The heat of combustion for PBX formulations based on PU/HTPB is higher than that based on PU/GAP. This may be explained by the higher mean molecular mass (M_{Wav}.) of HTPB pre-polymer than that of GAP which means large structure of HTPB compared with GAP. In addition, HTPB contains more number of elements which produce more heat during combustion than that of GAP.

The brisance value for PBX based on PU/GAP was higher than that based on HTPB. This may be explained by the presence of more energetic groups (azide groups, oxygen atoms) and high density of GAP which is expected to increase the oxygen content, number of moles of gaseous products and detonation velocity of the prepared PBXs formulations based of GAP. We can conclude that PBXs based on GAP, which have high values of brisance, are candidate to be used as main explosive charge of low sensitive warheads and demolition charges.

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