



Review / Przegląd

Polymer-bonded secondary explosives Kruszące materiały wybuchowe z lepiszczem polimerowym

Mateusz Szala

Military University of Technology, Faculty of Advanced Technologies and Chemistry, 2 gen. S. Kaliskiego Street, 00-908 Warsaw, Poland

E-mail: mateusz.szala@wat.edu.pl

Abstract. In this paper, a review of the available literature on physical and explosive properties of explosive compositions containing a secondary explosive and a polymer binder (PBX) is presented. The review focused on an analysis of the properties of compositions containing mostly synthetic polymers. The review showed that, at the moment, the most commonly used composition is a hexogen-based explosive bonded with a chemically cross-linked hydroxyl-terminated polybutadiene. The use of energetic polymers in PBX compositions was observed only in the experimental systems tested on a laboratory scale. The most popular methods of forming compositions include pressing a previously phlegmatized explosive or chemical cross-linking of the composition in the projectile shell. Compositions which can be formed and reloaded using injection machines are known, but due to many limitations, the method is not widely used.

Streszczenie. Wykonano przegląd literatury dotyczący właściwości fizycznych i parametrów detonacyjnych kompozycji składających się z kruszących materiałów wybuchowych oraz lepiszcza polimerowego (PBX). Skupiono się na analizie właściwości kompozycji zawierających głównie polimery syntetyczne. Zauważono, że współcześnie najczęściej stosowane są kompozycje na bazie heksogenu związanego za pomocą sieciowanego chemicznego polibutadienu z terminalnymi grupami hydroksylowymi. Zastosowanie polimerów energetycznych w kompozycjach PBX odnotowano tylko w układach doświadczalnych testowanych w skali nie większej niż laboratoryjna. Najpopularniejsze metody formowania kompozycji to prasowanie uprzednio sflegmatyzowanego materiału wybuchowego lub sieciowanie chemiczne kompozycji w skorupie pocisku. Znane są mieszaniny, które można formować i elaborować za pomocą wtryskarek, ale ze względu na liczne ograniczenia ta metoda nie zyskała większej popularności.

Keywords: secondary explosives, plastic-bonded explosives, applications of explosives

Słowa kluczowe: kruszące materiały wybuchowe, kompozycje wybuchowe z lepiszczem polimerowym, formy użytkowe materiałów wybuchowych

1. Introduction

Secondary explosives are the main class of energetic materials manufactured in large quantities both for military and mining applications by almost every single country in the world. Despite their acceptable sensitivity to initiation, the crystals in the final form of the blasting explosives are, in most cases, coated with polymer to reduce their sensitivity or to improve their mechanical properties. TNT, which in many applications is still used in its pure form, is an exception to this rule.

The acronym PBX, which stands for polymer-bonded explosive or plastic-bonded explosive, covers a broad range of blasting explosives containing polymer binders and applies not only to the plastic compositions with a consistency which allows the charges to be freely shaped by hand, but also to the loose compositions formed by pressing and to solid, chemically cross-linked compositions. C-4, developed in 1958 in the USA, containing hexogen bonded with plasticized polyisobutylene, is probably the best known PBX composition in the world [1].

Many different polymers can be used in PBX compositions, e.g. [2]:

- polyvinyl chloride (PVC),
- polyethylene (PE),
- polystyrene (PS),
- poly(methyl methacrylate) (PMMA),
- nylon 66,
- poly(ethylene terephthalate) (terylene),
- poly(ethylene oxide) (PEO),
- polytetrafluoroethylene (PTFE),
- copolymer of hexafluoropropylene (HFP) and vinylidene fluoride (Viton), and
- hydroxyl-terminated polybutadiene (HTPB).

A significant effect of the size and distribution of the explosive crystals on the sensitivity of hexogen and/or octogen-based PBX compositions has been observed [3]. The compositions with bimodal or trimodal particle size distribution show lower sensitivity compared to similar compositions containing unimodal explosives. In PBX compositions, blasting explosives, hexogen (RDX), octogen (HMX), 3-nitro-1,2,4-triazol-5-one (NTO), pentaerythritol tetranitrate (PETN), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) etc. [4] are used. However, RDX is the main component in the most common 120 and 155 mm calibre shells. To reduce environmental impact, the application of hydrolysis susceptible compounds containing a nitro-urea group e.g. 1,3,4,6-tetranitro glycoluril (TENGU), 2,4,6,8,10,12-hexanitrohexaazatricyclododecanedione (HHTDD) and 2,4,8,10-tetranitro-2,4,8,10-tetrazaspiroundecane-3,9-dione (TNSUK), was studied, however, their stability was too low to meet the latest safety standard for ammunition [5]. Due to insufficient biodegradability of HTPB (the most commonly used binder) new polymers showing lower toxicity or higher susceptibility to degradation in the natural environment, are studied. Cyclooctyne and isobenzofuran are considered to be potentially more environmentally-friendly binders [6].

2. Semi-synthetic polymers in PBX compositions

PBX compositions generally use synthetic polymers to make the production independent from any natural sources. Cellulose esters, particularly nitrocellulose (NC) with different degrees of esterification, can still be found in some PBX compositions. For example, HMX-based (94%) PBX-9404 composition contains a mixture of NC and tris(2-chloroethyl) phosphate (CEF) as a binder [7]. Another composition is EDC-37 containing 91% HMX, 8% di- and tri-nitroethylbenzene (K10 [8]) and 1% NC [9]. PBX-9007 composition (90% RDX), used in detonators, contains 0.4% rosin in its polystyrene and dioctyl phthalate-based binder [10].

3. PBX type compositions with synthetic polymer binders

The best known family of energetic compositions containing a high-strength blasting explosive and a synthetic binder is a US-developed series with an acronym beginning with PBX followed by a letter C, W, IH or N without a space, a dash and a number between 0 and 399. The letters C, W and IH after PXB indicate the experimental compositions developed and researched in the laboratories in China Lake, White Oak and Indian Head (USA), respectively. The letter N indicates that the composition has been classified for use in special weapon types. The numbers indicate [11]:

- 0 to 99 – compositions formed by pressing,
- 101 to 199 – compositions formed by casting and chemical cross-linking,
- 201 to 299 – compositions formed by extrusion, and
- 301 to 399 – compositions formed by injection.

PBXN-5, for example, means a composition implemented to production and approved for use in its end form obtained by pressing. Table 1 shows examples of PBXN compositions and the type of compatible weapon [12, 13]. It is the most popular PBX series composition in the world, however, the materials are classified by the elaboration method, and not chemical property criteria.

Table 1. Example weapons using PBXN compositions

Acronym	Chemical composition ^{*)} [%]	Weapon type
C-4	RDX/2-ethylhexyl sebacate/PIB/oil (91.0/5.3/2.1/1.6)	General-purpose blasting charges
PBXN-106	RDX/PEG (75/25)	AIM-54 Phoenix missile
PBXN-107	RDX/LMA (86/14)	BGM-109 Tomahawk, BLU-97 missile
PBXN-109	RDX/HTPB/Al/IPDI (64/15/20/1)	AGM-119 Penguin missile
PBXN-110	HMX/HTPB (88/12)	SCALP EG Storm Shadow missile
PBXN-111	RDX/AP/Al/HTPB	Mk 98 MNC

^{*)} PIB – polyisobutylene; PEG – poly(ethylene glycol); LMA – lauryl methacrylate

Pressing is a commonly used method for compacting and shaping explosives. A wide range of phlegmatized explosives which can be shaped by pressing is known from acquired expertise. The family of pressed PBXs includes compositions with various applications. Table 2 shows the main compositions of this type. Depending on the function of the PBX in its end form, different blasting explosives and different binders are used. The most commonly used binders include fluorocarbon polymers: PTFE, Viton, poly(1-chloro-1,2,2-trifluoroethylene) (Kel-F), chemically inert, showing high density and good adhesion to the crystals of most explosives. In most cases, the fluorocarbon polymers do not require plasticizers, which significantly increases the physical durability of the binder and the composition itself.

Table 2. PBX compositions formed by pressing

Acronym	Chemical composition ^{*)} [%]
PBXN-1	RDX/Al/nylon (68/20/12)
PBXN-2	HMX/nylon (95/5)
PBXN-3	HMX/nylon (86/14)
PBXN-4	DATB/nylon (94/6)
PBXN-5	HMX/Viton A (95/5)
PBXN-6	RDX/Viton A (95/5)
PBXN-201	RDX/Al/Viton A/PTFE (83/12/5)
PBX-9010	RDX/Kel F (90/10)
PBX-9011	HMX/Estane (90/10)

Table 2. continuation

Acronym	Chemical composition ^{*)} [%]
PBX-9404-03	HMX/NC/chloroethyl phosphate (94/3/3)
PBX-9205	RDX/PS/ethylhexyl phthalate (92/6/2)
PBX-9501	HMX/dinitropropyl acrylate/fumarate (95.0/2.5/2.5)
PBX-9502	TATB/Kel-F 800 (95/5)
PBX-9503	TATB/HMX/Kel-F 800 (80/15/5)
LX-16	PETN/FPC461 (96/4)
LX-15	HNS/Kel-F 800 (95/5)
LX-14-0	HMX/Estane 5702-F1 (95.5/4.5)
LX-10-0	HMX/Viton A (95/5)

^{*)} DATB – 1,3-diamino-2,4,6-trinitrobenzene; Estane – thermoplastic polyurethane; FPC461 – copolymer of chloroethylene and chlorotrifluoroethylene

3.1. Compositions with butadiene derivative binders

For many years, HTPB or hydroxyl-terminated polybutadiene has been the most commonly used synthetic polymer in blasting compositions. The compositions most often include a liquid prepolymer, cross-linked using a suitable diisocyanate. The prepolymers discussed in the literature show different average molar mass, viscosity, glass transition temperature etc. Table 3 shows the properties of the main HTPB prepolymers used in the explosive compositions.

Table 3. Properties of HTPB prepolymers used in the blasting explosive compositions [14]

Properties	HTPB type		
	R45 HTLO	R-20LM	LBH2000
Density [g/cm ³]	0.90	0.91	0.89
Molar mass, M_n [g/mol]	2800	1200	2100
Viscosity at 30 °C [cPa]	5000	1400	13000
Glass transition temperature, T_g [°C]	ca. -75	ca. -70	ca. -35

Many diisocyanates used for cross-linking the HTPB-based compositions are discussed in literature, including: 2,4- and 2,6-toluene diisocyanate (2,4-; 2,6-TDI), methylene diphenyl diisocyanate (2,2'-; 2,4'-MDI), 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI), isophorone diisocyanate (IPDI), dimeryl diisocyanate (DDI). A suitable plasticizer is usually added to the prepolymer and the cross-linking agent. The most common plasticizers referred in literature include: dibutyl, dioctyl, di(ethylhexyl) 1,2-benzenedicarboxylates (phthalates); 1,8-octanedicarboxylates (sebacates), 1-octanedicarboxylates (pelargonates) and citrates. Polymerization initiators, e.g. dibutyltin dilaurate (DBTDL) or iron(III) acetylacetonate ($\text{Fe}(\text{AcAc})_3$) are used in trace amounts [15].

Table 4 shows the main PBX compositions including HTPBs. The explosives are characterized by high detonation parameters (velocity of detonation (VOD) and pressure of detonation (P_{CJ})) and acceptable densities. The critical diameter of B2238 is 2 mm and it is used in small calibre ammunition and grenades. PBXN-109 composition is classified as a high blasting material used in US-made anti-ship missiles. PBXW-126, containing NTO and a suitable polyurethane binder, is considered the least sensitive to accidental detonation.

Table 4. Chemical constitution and basic properties of PBX type compositions

Acronym	Chemical composition ^{*)} [%]	Density [g/cm ³]	VOD [km/s]	P_{CJ} [GPa]	Ref.
PBXN-109	RDX/HTPB/Al/IPDI (64/15/20/1)	1.66	7.58	23.7	[13]
PBXN-110	HMX/HTPB (88/12)	1.68	8.39	24.9	[16]
LX-14	HMX/HTPB (95.5/4.5)	1.83	8.84	34.4	
DLE-C038	HNIW/HTPB (90/10)	1.82	9.04	33.0	
B 2238	RDX/HTPB (85/15)	1.57	8.04	25.4	[17]
PBXW-126	NTO/RDX/AP/Al/PU (22/20/20/26/12)	1.80	6.47	16.0	[18]

^{*)} PU – polyurethane

Elbeih [19] has analysed different explosive compositions based on high-energetic poly(nitramine) and HTPB. The compositions included 82% of energetic nitramine and 18% binder including HTPB, dioctyl adipate and a phase modifier (tris(1-(2-methyl)aziridinyl)phosphine oxide (MAPO)). Table 5 shows the main energetic properties. The highest detonation parameters have been observed for the HNIW-based composition due to its highest density among the analysed nitramines.

Table 5. Properties of experimental PBX compositions based on high-explosives

Composition ^{*)}	Density [g/cm ³]	VOD [km/s]	P_{CJ} [GPa]
RDX-HTPB	1.52	7.53	20.1
HMX-HTPB	1.57	7.81	21.3
BCHMX-HTPB	1.56	7.75	21.2
HNIW-HTPB	1.63	8.17	23.7

^{*)} BCHMX – bicyclo-HMX

A systematic analysis of HNIW-based compositions has been carried out by Wang *et al.* [20]. Four compositions with HNIW content between 88% and 92% were analysed (Table 6). The highest composition density (1.73 g/cm³) has been achieved at 91% HNIW. The composition also showed the highest detonation velocity and an acceptable level of sensitivity to mechanical stimuli. The relatively low density of compositions containing HNIW is due to the use of material with non-optimised shape and grain size.

Table 6. Chemical composition of experimental HNIW-based compositions

HNIW/HTPB composition [%]	Density [g/cm ³]	VOD [km/s]	Impact sensitivity H_{50} [cm]	Friction sensitivity [N]
88/12	1.63	7.61	–	–
90/10	1.72	8.23	–	–
91/9	1.73	8.27	36.88	160
92/8	1.64	7.86	–	–

Vadhe *et al.* [21] studied standard PBX compositions modified with tungsten powder (<45 μ m). The compositions were formed by casting in a standard vacuum planetary mixer using bimodal RDX or HMX (150 μ m/5 μ m, 3:1). Table 7 shows the detailed characteristics of obtained compositions. The analysed compositions show lower sensitivity compared to the reference composition without added tungsten. A decrease in the detonation velocity with an increase in tungsten content was also observed in the compositions. The authors suggested that these compositions are suitable for use in shaped charges.

Table 7. Physical and chemical properties of PBX compositions containing tungsten

Composition [%]	Oxygen balance [%]	Density [g/cm ³]	Impact sensitivity [J]	VOD [km/s]
RDX/HTPB (85/15)	-61.1	1.56	6.3	7.9
RDX/W/HTPB (70/15/15)	-60.5	1.76	8.2	7.3
RDX/W/HTPB (65/20/15)	-60.3	1.83		
RDX/W/HTPB (60/25/15)	-60.1	1.94	8.6	6.8
HMX/HTPB (80/20)	-73.9	1.55	8.4	8.0
HMX/W/HTPB (65/15/20)	-73.1	1.73	9.4	7.3
HMX/W/HTPB (60/20/20)		1.82	10.0	7.1
HMX/W/HTPB (55/25/20)		1.90	10.4	6.9

Similarly popular are the compositions with enhanced blast properties, also referred as thermobaric explosives (TBX). The compositions can be classified as high explosives and can be formed using methods typical to cast PBXs [22]. Apart from a high-strength explosive they usually contain additives, including metallic powders and an oxidiser, usually NH₄ClO₄ (AP). Due to the requirement to extend the positive phase duration of the overpressure impulse in relation to pure blast explosive, TBX compositions usually contain a large amount of high-strength explosive and a mixture used as a pyrotechnic composition e.g. PBXN-105 includes 7% RDX, whereas PBXN-103 does not include any nitramines and the energetic composition components include alcohol nitrates (Table 8).

Table 8. PBX type thermobaric compositions

Acronym	Chemical composition ^{*)} [%]	Density [g/cm ³]	VOD [km/s]	P _{CJ} [GPa]	Ref.
PBXN-103	AP/Al/TMETN/TEGDN/NC/EC/Res. (40/27/23/2.5/6/1.3/0.2)	1.88	7.66	13.3	[23]
PBXN-105	AP/Al/BDNPA/RDX/PEG (49.8/25.8/12.9/7/4.5)	1.65	6.3	12.8	
PBX-1	HMX/Al/AP/HTPB (55/0/25/20)	1.67	7.4	14.1	[24]
PBX-2	HMX/Al/AP/HTPB (35/20/25/20)	1.71	6.4	11.5	
PBX-3	HMX/Al/AP/HTPB (25/30/25/20)	1.72	5.9	8.7	

^{*)} TMETN – trimethylethane trinitrate; TEGDN – triethylene glycol dinitrate; EC – ethyl cellulose; BDNPA – bis(2,2-dinitropropyl)acetal; Res. – synthetic resin

Aluminized PBX type compositions are also being developed for underwater applications. Due to the specificity of underwater applications, the compositions were compared using a detonation test of same mass charges at a fixed distance from a 550×450×5 mm steel plate. After the test, the depth of the dent in the plate was measured with the best results being obtained for PBX-25 [25]. The effect was improved compared to the reference hexogen/trinitrotoluene (RDX/TNT) composition, i.e. HBX-3 (Table 9).

Table 9. Chemical composition and capability to form experimental PBX compositions for underwater applications

Acronym	Chemical composition [%]	Dent in the plate [mm]
PBX-35	RDX/Al/HTPB (50/35/15)	30.2
PBX-30	RDX/Al/HTPB (55/30/15)	31.7
PBX-25	RDX/Al/HTPB (60/25/15)	35.1
PBX-20	RDX/Al/HTPB (65/20/15)	31.8
PBX-15	RDX/Al/HTPB (70/15/15)	30.7
PBX-0	RDX/HTPB (85/15)	28.2
HBX-3	RDX/TNT/Al/wax (31.3/29.0/34.8/4.9)	34.4

A series of PBX compositions with TATB and aluminium with detonation parameters similar to the composition B, but with improved thermal resistance, was produced [26]. Due to the different response of its components to thermal stimuli, the cook-off test was selected as the most reliable. For TATB/Al/ZF (60/35/5), the system reaction temperature was 100 °C higher than for the reference HMX system and 77 °C higher than for the similar composition with fluorine resin substituted with PVB (Table 10).

Table 10. PBX compositions with improved thermal resistance and blast wave parameters

Chemical composition ^{*)} [%]	Density [g/cm ³]	VOD [km/s]	P_{CJ} [GPa]	Reaction temperature during the cook-off test [°C]
TATB/Al/PVB (75/20/5)	2.025-2.031	–	–	257
TATB/Al/ZF (75/20/5)		7.33	–	311
TATB/Al/ZF (75/20/5)		7.30	24.3	314
TATB/Al/ZF (60/35/5)		7.16	23.5	334
TATB/HMX/Al/ZF (55/20/20/5)		7.67	–	230

^{*)} PVB – polyvinyl butyral; ZF – fluorine resin (the content was not disclosed by the authors)

3.2. PBX compositions with energetic binder

Even at the maximum explosive content in the PBX composition, in practice it is difficult to exceed 90-95% content of the energetic component, since it either dramatically increases the sensitivity of the composition or makes it impossible to scale up production. The use of synthetic energetic polymers plasticized using energetic plasticizers may be the solution to this problem. The most commonly studied energetic polymers include:

- poly(3-azidomethyl-3-methyl oxetane) (polyAMMO),
- poly(bis-azidomethyl oxetane) (polyBAMMO),
- glycidyl azide polymer (GAP),
- poly(glycidyl azide) (polyGLYN),
- poly(3-nitro methyl-3-methyl oxetane) (polyNIMMO),
- polyphosphazene.

Not all of them have been used in PBX compositions at a larger than micro-laboratory scale. Mostly GAP, polyGLYN and polyNIMMO have been used at a larger laboratory scale. The most commonly used energetic plasticizers include bis-(2,2-dinitropropyl)acetal and bis(dinitropropyl) formal (BDNPA/BDNPF, 1/1). Table 11 shows the selected thermobaric compositions with energetic polymers [27]. Despite using a relatively small amount of blasting explosive at 27-60%, the addition of energetic binders provides a detonation velocity similar to that observed for TNT.

Table 11. Selected PBX compositions with energetic binders

Acronym	Explosive composition ^{*)} [%]	Density [g/cm ³]	VOD [m/s]
GHX 82	RDX/AP/Al/GAP-BDNPAF (27/25/30/18)	1.91	6810
GHX 117	RDX/AP/Al/GAP-BDNPAF (27/30/25/12)	1.87	7080
CPX 458	NTO/HMX/Al/poliNIMMO/K-10 (30/30/20/10/10)	1.85	7680
CPX 460	NTO/HMX/Al/poliNIMMO/K-10 (27.5/27.5/25/10/10)	1.88	6420

^{*)} K-10 – 2,4-dinitroethyl benzene/2,4,6-trinitroethyl benzene (plasticizer)

Provtas [28] analysed PBX compositions containing PolyGLYN-based energetic binders with RDX as the main energetic component. Table 12 shows the basic physical, chemical and energetic properties. The chemical composition was modified by up to 4% to maintain the density of the composition at a similar level. The decomposition temperature increased with an increase in RDX content.

Sensitivity to friction decreased with an increase in RDX content. The differences in the detonation velocity and pressure were minor at 120 m/s and 1.3 GPa, respectively.

Table 12. Properties of the experimental RDX-based PBX compositions with energetic binder

Acronym	Chemical composition	Density [g/cm ³]	Decomposition temperature [°C]	Friction sensitivity [N]	VOD [km/s]	P _{CJ} [GPa]
ARX-3001-M5	RDX/PolyGLYN (75/25)	1.67	201	96	8.04	27.1
ARX-3001-M6	RDX/PolyGLYN (77/23)	1.68	208	112	8.08	27.5
ARX-3005-M1	RDX/PolyGLYN (77/23)	1.68	208	112	8.15	27.9
ARX-3006-M1	RDX/PolyGLYN (79/21)	1.68	209	120	8.16	28.4

3.3. PBX compositions with siloxane binder

The high popularity of polysiloxanes, used mainly in PBX compositions, is due to their high chemical and thermal resistance. PBXC-303 is an interesting example of an explosive composition which can be freely shaped into complex geometries [29]. This composition shows good detonation parameters and a critical diameter below 1 mm (Table 13). The injected material undergoes cross-linking and shows good shape stability. Due to its low critical diameter and ability to form complex shapes and high detonation parameters, the material has been considered for use in nuclear weapon detonators.

Other popular compositions: H-TBX and A-TBX [30-33] patented by Bulgarian scientists, include hexogen, ammonium perchlorate (AP), aluminium and chemically cross-linked siloxane (Table 13). Due to patent confidentiality, the chemical composition has not been disclosed. According to the authors and the press release, its TNT equivalent is over 2.5.

Chyłek *et al.* [34] analysed the production process and the properties of hexogen-based PBX composition with silicone paste binder (Table 13). The components were homogenized with a paddle mixer. The obtained PBX detonates at a 2 mm thick layer with a velocity similar to TNT [34].

Table 13. Properties of explosive compositions with siloxane binders

Acronym	Chemical composition ^{*)} [%]	Forming method	Density [g/cm ³]	VOD [km/s]
PBXC-303 or XTX-8003	PETN/Sylgard 183 (80/20)	Injection/extrusion	1.40	7.20
H-TBX	RDX/KClO ₄ /Al/siloxane	Casting/chemical cross-linking	1.75	7.20
A-TBX	RDX/KClO ₄ /Al/siloxane		1.95	8.00
RDXSil1	RDX/Silpaste (73/27)	Extrusion	1.45	6.95

^{*)} Sylgard – a family of silicone elastomers

Elbeih *et al.* [35] achieved some interesting sensitivity test results for siloxane-bonded PBXs. A series of PBX compositions were formed using the same explosive and binder content, with the only variable being the binder type. Extrusions with a diameter of 40 mm were formed using a dual-screw extruder. The sensitivity and explosive power were tested using a ballistic pendulum. Table 14 shows the results. Replacing PMMA with siloxane in all cases resulted in a 2 to 3 time decrease in sensitivity to impact and a slight decrease in sensitivity to friction. The explosive strength of the composition including siloxane binder measured using the ballistic pendulum was approx. 1% lower than that for a similar composition including PMMA [35].

Table 14. The results of comparative test of PBX compositions with different binders

Chemical composition	Impact sensitivity [J]	Friction sensitivity [N]	Relative explosive power (compared to TNT) [%]
RDX-PMMA (91/9)	11.8	240	137.8
RDX-Silicone (88/12)	31.9	254	136.0
HMX-PMMA (91/9)	12.7	211	137.6
HMX-Silicone (88/12)	27.6	228	136.4
BCHMX-PMMA (91/9)	6.1	192	139.2
BCHMX-silicone (88/12)	24.3	232	137.5
HNIW-PMMA (91/9)	8.2	164	142.6
HNIW-silicone (88/12)	26.0	192	141.1

3.4. PBX composition formed by injection or extrusion

Extrusion, as a method of forming explosives is relatively unpopular and most often applies to PBXC-303 (Table 15). Flexible sheets with a thickness of several millimetres, commonly referred to as *primasheet* (from the trade name of the product manufactured by *North American Explosives* (NAX)), are more and more often used in blasting operations. Since a low critical diameter of the explosive material is required, the sheets are usually based on PETN. For example, P1-P2 compositions are extruded and then formed into 5 mm sheets by calendaring [36]. P3-P5 compositions show reduced sensitivity to shaped charge impact and are used in explosive reactive armours (ERA).

Table 15. Example PBX compositions developed for extrusion and injection

Acronym	Chemical composition*) [%]	Forming method	Density [g/cm ³]	VOD [km/s]	Ref.
PBXC-303	PETN/Sylgard 183 (80/20)	Injection/extrusion	1.4	7.2	[29]
P1	RDX/PU/Viton (90/6/4)	Extrusion	1.52	7.90	[36]
P2	RDX/PU/Viton (90/4/6)		1.54	7.90	
P3	RDX/TATB/HTPB (75/10/15)		1.45	1.15	[37]
P4	RDX/TATB/HTPB (70/15/15)		1.47	7.12	
P5	RDX/TATB/HTPB (65/20/15)		1.49	7.10	
P6	RDX/crepe rubber (80/20)		1.13	5.86	[38]
P7	RDX/EVA (80/20)		1.28	6.50	
P8	RDX/Estane (80/20)		1.20	6.29	
P9	RDX/HTPB (85/15)		1.43	7.20	

*) PU – polyurethane; Crepe rubber – type of latex; EVA – a copolymer of polyethylene and poly(vinyl acetate)

4. Chemical stability of PBX composition

Along with their detonation parameters, the chemical and physical stability of explosives are one of the most important properties. The compositions which include synthetic binders show higher stability compared to their natural counterparts. Pre-implementation evaluation and periodical inspections of stored ammunition involves the use of advanced analytical instruments. The main techniques include:

- calorimetry and microcalorimetry (DTA, DSC),
- chromatography (gas chromatography (GC), high-performance liquid chromatography (HPLC), size exclusion chromatography (GPC)),
- spectroscopy (ultraviolet–visible spectroscopy (UV-VIS), infrared spectroscopy (IR) and nuclear magnetic resonance (NMR)).

For compositions containing HTPB based binders, the stability depends on the ratio of the isocyanate group to hydroxy group in the substrates (NCO/OH). The susceptibility to degradation related to oxidation increases with the polymer's NCO/OH ratio of the polymer [39].

An important phenomenon affecting the stability and physical properties of PBX compositions is plasticizer evaporation. The experiments on HTPB/Bu-NENA (*n*-butyl-*n*-nitrateethylnitramine) showed that within the range of plasticizer-polymer ratio from 0.8 to 1.5, a loss of mass can be observed above 1.2 due to premature ageing, which may affect the properties of the composition [40].

5 Summary and conclusions

A review of chemical constitution, physical and explosive properties of approximately 100 different PBX compositions was carried out. The explosive compositions with synthetic polymer binders can be formed using reactive casting, pressing or injection techniques. The most popular method of forming charges for medium calibre ammunition charges and various rockets is the reactive casting of the composition with an HTPB binder. In PBX compositions, approx. 10 different blasting explosives are used, with hexogen used most often, since it shows both high detonation parameters and moderate sensitivity to mechanical stimuli and shock wave. A trend to replace TNT-based cast composition with PBX compositions has been observed for many years, and the analysis of literature shows that this trend will most likely continue.

References

- [1] *Military Explosives, Department of the Army Technical Manual*. Headquarters, Department of the Army, TM9-1300-214, USA, **1984**.
- [2] Ahmad S.R., Cartwright M. *Laser Ignition of Energetic Materials*. John Wiley & Sons, **2015**.
- [3] van der Steen A., Verbeek R. Initiation and Detonation of RDX and HMX HTPB-Based Plastic-Bonded Explosives. *Propellants Explos. Pyrotech.* **1990**, *15*: 19-21.
- [4] Nouguez B., Mahe B., Vignaud P.O. Cast PBX Related Technologies for IM Shells and Warheads. *Sci. Tech. Energ. Mater.* **2009**, *70*(6): 135-139.
- [5] Chapman R., Young K., Baldwin L., Nelson A., Hoang H., Merritt A., Carter J. *Self-Remediating Energetic Fills Based on Cyclic Dinitroureas*. Report WP2147, China Lake, USA, **2017**.
- [6] Dube P. *Development of Novel Environmentally Sustainable Binders for Energetic Formulations*. Report WP-2407, Centerbrook, USA, **2015**.
- [7] Burnham A.K., Fried L.E., Richardson B. *Kinetics of PBX9404 Aging*. Report W-7405-Eng-48, LLNL, USA, **2006**.
- [8] Willcox W., Padfield J., McAteer D. Demonstration of 1-Nitramino-2,3-dinitroxypropane as an Energetic Plasticiser Component in an HMX-based PBX. *Insensitive Munitions and Energetic Materials Technology Symp.* Las Vegas, USA, **2012**.
- [9] Millett J.C.F., Taylor P., Roberts A., Appleby-Thomas G. The Strength of Two HMX Based Plastic Bonded Explosives During One Dimensional Shock Loading. *J. Dyn. Behav. Mater.* **2017**, *3*(1): 100-109.
- [10] James E. *The Development of Plastic Bonded Explosives*. Report UCRL-12438-T, Lawrence Radiation Livermore Laboratory, CL, USA, **1965**.
- [11] Hamshere B.L., Lochert I.J., Dexter R.M. *Evaluation of PBXN-109: the Explosive Fill for the Penguin Anti-Ship Missile Warhead*. Defence Science and Technology Organisation, Technical Report DSTO-TR-1471, Australia, **2003**.
- [12] Castiglia M. Application of PBX Technology to Improve IM Response. *Explosive Safety Management and Risk Analysis Symp. Ammunition Technology*, Rome, Italy, **2016**.
- [13] Sandusky H.W. *Shock Sensitivity of PBXN-109 When Containing Different RDX Fills without and with Aging*. Naval Surface Warfare Center, Indian Head, Report IHTR 3217, **2010**.

- [14] *Hydroxyl-Terminated Polybutadiene Resins and Derivatives – Poly bd[®] and Krasol[®]*. Product Bulletin, Total Cray Valley, **2016**, https://www.crayvalley.com/docs/technical-paper/cray_valley_poly-bd-krasol-prod-bulletin.pdf [retrieved 18.05.2021].
- [15] Lima V., Pelissoli N., Dullius J., Ligabue R., Einloft S. Kinetic Study of Polyurethane Synthesis using Different Catalytic Systems of Fe, Cu, Sn, and Cr. *J. Appl. Polym. Sci.* **2010**, *115*: 1797-1802.
- [16] Hatch R., Mileham M., Braithwaite P., Lee K.E. *Characterization and Comparison of a High Performance CL-20 Explosive*. Report ARDEC 2010-361, INIT233, **2010**.
- [17] Kent R. Cast PBX B2238 for Small-Calibre High Performance Insensitive Munitions. *Propellants Explos. Pyrotech.* **1997**, *22*: 65-70.
- [18] Hall S., Knowlton G.D. Development, Characterization and Testing of High Blast Thermobaric Compositions. *Proc. 31st Int. Pyrotechnic Seminar*, Fort Collins, USA, **2004**, 663-678.
- [19] Elbeih A., Wafy T.Z., Elshenawy T. Performance and Detonation Characteristics of Polyurethane Matrix Bonded Attractive Nitramines. *Cent. Eur. J. Energ. Mater.* **2017**, *14*(1): 77-89.
- [20] Wang J., An Ch., Li G., Liang L., Xu W., Wen K. Preparation and Performances of Castable HTPB/CL-20 Booster Explosives. *Propellants Explos. Pyrotech.* **2011**, *36*: 34-41.
- [21] Vadhe P.P., Manickam S., Rahujade N., Kondra A., Prasad U., Sinha R. Studies on Tungsten Based High Density Cast Polymer Bonded Explosive (PBX) Formulations. *Cent. Eur. J. Energ. Mater.* **2015**, *12*(3): 497-506.
- [22] Baker J.J. *Thermobaric Explosives, Articles of Manufacture, and Methods Comprising the Same*. Patent US 7807000, **2010**.
- [23] Bocksteiner G., Whelan D. *The Effect of Ageing on PBXW-115, PBXN-103 (Aust.) and 105*. Defence Science and Technology Organisation, Report DSTO-TR-0228, Australia, **1995**.
- [24] Antić G., Džingalašević V., Stanković M., Borković Z. Explosive Characteristics of Cast PBX Based on HMX, Ammonium Perchlorate and Aluminium. *Sci. Tech. Rev.* **2004**, *54*(3-4): 38-43.
- [25] Kumar A., Rao V.B., Sinha R.K., Rao A.S. Evaluation of Plastic Bonded Explosive (PBX) Formulations Based on RDX, Aluminium, and HTPB for Underwater Applications. *Propellants Explos. Pyrotech.* **2010**, *35*: 359-364.
- [26] Gong F., Guo H., Zhang J., Shen Ch., Lin C., Zeng Ch., Liu S. Highly Thermal Stable TATB-based Aluminized Explosives Realizing Optimized Balance between Thermal Stability and Detonation Performance. *Propellants Explos. Pyrotech.* **2017**, *42*: 1424-1430.
- [27] Vadhe P., Pawar R., Sinha R., Asthana S., Rao S.A. Cast Aluminized Explosives (Review). *Combust. Explos. Shock Waves* **2008**, *44*(4): 461-477.
- [28] Provatas A. *Formulation and Performance Studies of Polymer Bonded Explosives (PBX) Containing Energetic Binder Systems. Part.1*. Defence Science and Technology Organisation, Report DSTO-TR-1397, Australia, **2003**.
- [29] Lind C.D. *Techniques for Injection Loading of PBXC-303 Explosive*. Naval Weapons Center, Report AD/A-001 678, China Lake, CL, USA, **1974**.
- [30] Kovlev S., Tsonev T. Solid State Fuel-air Explosives with Enhanced Power and Stability. *Proc. 46th Int. Annual Conf. of ICT*, Karlsruhe, Germany, **2015**.
- [31] Tsonev T., Kovlev S. *Thermobaric Composition Based on Polyoxane Polymers*. (in Bulgarian) Patent BG 111270(A) **2013**.
- [32] Tsonev T., Kovlev S. *Thermo-barium Composition Based on Polysilicon Polymer Matrix Included in the Composition of Explosive Substances*. (in Bulgarian) Patent BG 111636(A), **2015**.
- [33] Tsonev T., Kovlev S. *Underwater Explosive Based on Aryl/Alkyl Polysiloxane Polymer Matrix with Explosive Substances in the Composition*. (in Bulgarian) Patent BG 111985(A), **2016**.
- [34] Zalewski K., Chyłek Z., Trzcíński W. Studies on the Properties of a Putty-like Explosive with a Silicone Binder. *Cent. Eur. J. Energ. Mater.* **2021**, *18*(1): 112-123.
- [35] Elbeih A., Zeman S., Jungova M., Akstein Z. Effect of Different Polymeric Matrices on the Sensitivity and Performance of Interesting Cyclic Nitramines. *Cent. Eur. J. Energ. Mater.* **2012**, *9*(2): 131-138.

- [36] Jangid S., Singh M., Solanki V., Talawar M., Nath T., Sinha R., Asthana S. 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX)-Based Sheet Explosive Formulation with a Hybrid Binder System. *Propellants Explos. Pyrotech.* **2016**, *41*: 377-382.
- [37] Joseph M.D., Jangid S.K., Satpute R.S., Polke B.G., Nath T., Asthana S.N., Rao A.S. Studies on Advanced RDX/TATB Based Low Vulnerable Sheet Explosives with HTPB Binder. *Propellants Explos. Pyrotech.* **2009**, *34*: 326-330.
- [38] Nath T., Asthana S.N., Gharia J.S. Studies on RDX Based Sheet Explosives with EVA and Estane Binders. *Theory and Practices of Energetic Materials* Vol. II, Shenzhen, Guangdong, China, **1997**, 87-90.
- [39] Villar L., Cicaglioni T., Diniza M., Takahashi M., Rezende L. Thermal Aging of HTPB/IPDI-based Polyurethane as a Function of NCO/OH Ratio. *Mater. Res.* **2011**, *14*(3): 372-375.
- [40] Yuan S., Luo Y. Mechanical Properties of HTPE/Bu-NENA Binder and the Kinetics of Bu-NENA Evaporation. *Cent. Eur. J. Energ. Mater.* **2020**, *17*(1): 119-141.

Received: May 25, 2021

Revised: October 7, 2021

First published online: October 29, 2021