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Preliminary Study of Several Plastic Bonded Explosives Based on Cyclic Nitramines

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Abstract: A series of plastic explosives have been prepared with binders based on polyisobutylene (PIB), acrylonitrile-butadiene rubber (ABR), Viton A and using four nitramines, namely RDX (1,3,5-trinitro-1,3,5-triazinane), ε-HMX(ε-1,3,5,7-tetranitro-1,3,5,7-tetrazocane), BCHMX (*cis*-1,3,4,6-tetranitro-octahydroimidazo-[4,5-*d*]imidazole) and ε-HNIW (ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane). Pentaerythritol tetranitrate (PETN) and three putty – plastic explosives based on PETN were used for comparison. Detonation velocities, *D*, impact and friction sensitivities of these explosives were determined. The relations of the friction sensitivity to impact sensitivity, and of both these sensitivities to the D^2 term indicate that the mechanism of transfer of the friction force to the reaction centre of nitramine molecule should be different from that of impact energy transfer. Mutual comparison of the friction and impact reactivities of technical-grade and of "reduced sensitivity" grade of ε-HNIW led to the finding that the impact sensitivity distinctly depends on the crystal quality of nitramines, while in the case of friction sensitivity this dependence should not so pronounced. From the relationship between the determined *D* values and the loading densities of PBX containing the PIB and ABR binders, the *D* value of 9.800 mm · μs^{-1} at 2.04 g · cm^{-3} for ε-HNIW was found.

Key words: explosion mechanics; plastic bonded explosive; friction sensitivity; impact sensitivity; detonation velocity

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1 Introduction

Recently, information about new polycyclic nitramines has been published[1]. Out of them, *cis*-1,3,4,6-tetranitrooctahydroimidazo-[4,5-*d*] imidazole (bicyclo-HMX or BCHMX), a relatively accessible explosive, attracted our attention[2]. Qui and Xiao published a molecular dynamic study of the plastic bonded explosives (PBXs) containing BCHMX[3]. As we have developed an original method of BCHMX synthesis[4], we can practically deal with testing of this nitramine in real PBX mixtures. Therefore, this paper represents a preliminary study of PBXs on the basis of BCHMX in comparison with those of technically attractive explosives based on 1,3,5-trinitro-1,3,5-tiazinane (RDX), β-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (β-HMX), and ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (ε-HNIW); all these nitramines were studied in crystalline state as well as in the form of PBXs bonded with different kinds of binders; polyisobutylene (PIB), acrylonitrile-butadiene rubber (ABR) and fluorinated polymers Viton were used for this purpose. PETN (penterythritol tetranitrate) and three well-known putty-plastic explosives based on PETN were used for comparison.

2 Experimental

2.1 Materials

2.1.1 Nitramines

The RDX sample used was a product of Dyno Nobel (mixture of Classes 2 and 5 according to the standard[5]), β-HMX was imported from Russia and its particle size was close to Class 3 according to the standard[6]), technical-grade ε-HNIW was a product of Explosia pilot plant, and BCHMX was prepared by a two step laboratory synthesis at the Institute of Energetic Materials (IEM)[4], and the detonation velocity measurements were performed with a mixture based on it[2] combined with binder 3% addition of Viton B (in Table 1 called BCHMX-Viton B). Also ε-HNIW with reduced sensitivity (RS-ε-HNIW) and 1% content of impurities was used, and this nitramine is an R&D product from IEM. However, for the PBX preparation in this research we adopted a technical-grade sample of ε-HNIW containing 2.6% of impurities. The used PETN, quality D, was a product of Explosia Comp.

2.1.2 Plastic bonded explosives

The plastic explosives with C4 matrix were prepared in Explosia Comp. Pardubice (Research Institute of Industrial Chemistry). The C4 matrix is a mixture of 25% polyisobutylene (PIB), 59% dioctyl sebacate (DOS), and 16% oily material (HM46). The binder was prepared by mixing small pieces of polyisobutylene with sebacate and the oil under specific conditions. The explosive (91% wt.) was mixed with the binder matrix (9% wt.) at the temperature of 70 ℃ for 70 min. in vacuum using a computerized mixer Plastograph BRABENDER. The prepared samples were extruded by means of a 40 mm screw extruder to obtain long charges of plastic explosive with 16 mm diameter. In Table 1 the products have the following codes: RDX-C4, HMX-C4, BCHMX-C4 and HNIW-C4. The same procedure was used for preparation of putty-plastic PBX bonded with acrylonitrile-butadiene rubber binder softened with non energetic plasticizer. The corresponding products have the code designations Semtex-RDX, Semtex-HMX, Semtex-BCHMX and Semtex-HNIW in Table 1 and Figures.

All the samples bonded with Viton A 200 were prepared by a modified water-solvent slurry method[7]. Viton A 200 (obtained from DuPont Performance Elastomers) is an elastomer with the fluorine content of 66%, the density of 1.82 g · cm^{-3} and Mooney viscosity of 22. This fluorine content corresponds to a 60/40 weight ratio of vinylidene fluoride to hexafluoropro-

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pene monomers or approximately 77.83 mole% vinylidene fluoride[8]. The nitramine was dispersed in water (aqueous phase), and Viton A was dissolved in an organic solvent with low boiling point, immiscible with water, which was added during the process. This process was carried out with vigorous stirring (500 －600 rpm). The solvent was then removed by distillation with continuous stirring, and the polymer precipitated on the surface of the crystals of the explosive at the end of the solvent elimination. One part of the samples prepared contained 91% wt. of explosive and 9% wt. of Viton A, and in Table 1 these explosives have code designations RDX-Viton A9%, HMX-Viton A9%, BCHMX-Viton A9% and HNIW-Viton A9%. The other part of the samples contained 95% wt. of nitramine and 5% wt. of Viton A, and their codes in Table 1 and Figures are RDX-Viton A5%, HMX-Viton A5%, BCHMX-Viton A5% and HNIW-Viton A5%.

For a comparison, the following PETN-based putty-plastic explosives were used: Semtex 1A (83% PETN and 17% of binder composed of polystyrene-butadiene rubber and mineral oil) and former Czech military explosives Semtex 10 (85% PETN and 15% of acrylonitrile-butadiene rubber softened with non energetic plasticizer), both products from Explosia Comp. Pardubice, and Swedish military explosive Sprängdeg m/46 from NeXplo Bofors AB (86% PETN and 14% highly viscid mineral oil).

2.1.3 Pressing of the samples

The plastic bonded explosives based on Viton A were pressed in Explosia Comp. Pardubice using a hydraulic pressing machine (PYE 100). All the samples were pressed by the pressure of 486 MPa in vacuum for 10 seconds to obtain cylinders with 16 mm diameter and 20 mm height. Eighteen cylinders were made from each sample and glued together to obtain three charges, each containing six cylinders.

2.2 Friction sensitivity measurements

A BAM friction test apparatus was used to determine the sensitivity to friction (FS) by applying the standard test conditions[9]. The sensitivity to friction was determined by spreading about 0.01 g of the dry explosive on the surface of a porcelain plate in the form of a thin layer. Different loads were used to change the normal force between the porcelain pistil and the plate. The sample initiation was evaluated according to characteristic symptoms: sound, smoke appearance, or characteristic smell of the decomposition products. Using the probit analysis[10], only the normal force at which 50% of initiations occurred is reported as the friction sensitivity in Table 1.

Table 1 The loading densities, detonation velocities, impact and friction sensitivities of the studied explosives

No.	explosive	ρ/g · cm^{-3}	D/mm · μs^{-1}	impact sensitivity/J	friction sensitivity/N
1	RDX	1.76	8.750	5.58	120
2	β-HMX	1.90	9.100	6.37	95
3	BCHMX	1.79	8.800*	2.98	88
4	ε-HNIW	1.96	9.440	1.81	64
5	RS-ε-HNIW	1.96	9.440	10.8	69
6	RDX-C4	1.61	8.055	21.10	214
7	HMX-C4	1.67	8.318	20.25	193
8	BCHMX-C4	1.66	8.266	11.56	181
9	HNIW-C4	1.77	8.594	6.4	148
10	RDX-Viton A 9%	1.76	8.285	10.6	326
11	HMX-Viton A 9%	1.84	8.602	10.3	304
12	BCHMX-VitonA 9%	1.81	8.474	5.3	283
13	HNIW-VitonA 9%	1.94	9.023	6.9	252
14	RDX-Viton A 5%	1.76	8.424	9.2	271
15	HMX-Viton A 5%	1.84	8.730	9.2	243
16	BCHMX-VitonA 5%	1.81	8.612	4.8	230
17	HNIW-VitonA 5%	1.95	9.194	6.4	186
18	BCHMX-Viton B3%	1.79	8.650	4.0	156
19	Semtex-RDX	1.54	7.621	23.6	278
20	Semtex-HMX	1.59	7.910	21.9	269
21	Semtex-BCHMX	1.57	7.824	16.8	253
22	Semtex-HNIW	1.64	8.228	17.9	216
23	Semtex 10	1.53	7.486	15.7	204
24	PETN	1.70	8.400	2.90	44
25	Semtex 1A	1.47	7.418	13.70	187
26	Sprängdeg m/46	1.52	7.520	14.02	183

Note: * calculated for 96% of TMD by Kamlet & Jacobs method.

2.3 Impact sensitivity measurements

A standard impact tester (Julius Peters[9]) was used with exchangeable anvil, the amount of tested substance being 50 mm^3; drop hammers of 2 kg and 5 kg weight were used. The probit analysis[10] was used to determine the probability levels of the initiation. The obtained sensitivity was expressed as the drop energy, E_{dr}, versus the initiation percentage. Only the 50% probability of initiation is used in this article and is reported in Table 1.

2.4 Detonation velocity measurements

The detonation velocity, D, of all prepared mixtures was measured by the ionization copper probe method[9] where the data were reported on the oscilloscope (Tektronix TDS 3012). The plastic samples were prepared in cylindrical form of 16 mm diameter and 200 mm length. The copper probes were inserted in the charge. The first probe was inserted at the distance of 50 mm from the booster and the second probe was inserted at 100 mm distance from the first probe. In the case of the pressed charges, the first probe was inserted between the first and the second prepared cylinder, while the second probe was inserted between the fifth and the last cylinder where the distance between the two probes was 80 mm. Both probes were connected to the oscilloscope *via* a coaxial cable. Charges were set off using a booster charge (Semtex 1A with the mass of 6 g and diameter of 16 mm) adjusted with electric detonator. For each sample, three measurements were performed and the mean value (max. 60) for each is reported in Table 1. In this Table, the D values for RDX and HMX were taken from Ref. [11] and those for HNIW from Ref. [12]. The D value for crystalline BCHMX was calculated according to Kamlet & Jacobs[13], and it corresponds to 96% of its theoretical maximum density (TMD); the theoretical D value at TMD ($1.86\ g \cdot cm^{-3}$) of BCHMX is $9.050\ mm \cdot \mu s^{-1}$[2].

3 Results and discussion

Figure 1 represents a well-known dependence of detonation velocity on loading density. The PBX samples with Viton A binder stand outside of the studied set of explosives. This fact is due to the effect of this binder upon (i) the loading density and (ii) the thermochemistry of detonations of PBX samples containing Viton binder; the formation of hydrogen fluoride during detonation of the fluorine-containing explosives[14] is a most favorable influence on detonation compared with the oxygen consumption by C4 or Semtex matrices at enhanced formation of elemental carbon or CO in the detonation wave. Using the dependence represented by solid line in Fig. 1, we can obtain the value $D = 9.800\ mm \cdot \mu s^{-1}$ for theoretical maximal density (monocrystal) of ε-HNIW; this value is identical with those given by Bogdanova et al.[15].

Figure 2 points out the difference between initiation by impact (uniaxial compression) and initiation by friction (shear slide with a fixed volume). The difference might be due to a different transfer mode of the initiation impulse into reaction center of the given nitramine molecule (force in the case of FS, and drop energy in the case of impact sensitivity). Figure 2 shows that from the standpoint of lowering of both these sensitivities the optimum binder is the Semtex 10 matrix – it significantly lowers the sensitivity of nitramines possessing the highest initiation reactivity, i.e. technical-grade ε-HNIW and BCHMX; however, Fig. 1 shows that this matrix provides PBXs with relatively low loading density. The group comprising RS-ε-HNIW, HMX-C4, RDX-C4, Semtex-HMX and Semtex-RDX represents explosives with considerably lowered initiation reactivity as compared with pure RDX, HMX and technical-grade ε-HNIW. Significantly differing types of ε-HNIW (technical-grade versus RS-grade) possess approximately the same FS characteristic but differ particularly in their impact sensitivity values, which could be connected with relatively smaller influence of crystal lattice defects (crystal quality) on the FS of this nitramine. Szczygielska et al.[16] studied crystallization of ε-HNIW; they tested the products obtained only for their friction sensitivities, while their purity and impact sensitivity remained unnoticed. The FS values of their products varied in the interval from 55.2 to 110.4 N[16]. The highest values were found for the crystals with rounded shapes which were mostly single[16]. However, our findings also in the present work show that the crystallization procedure of HNIW and its purity affect far more strongly its impact sensitivity than its FS (see Table 1, but in part also[17]); the crystals of RS-ε-HNIW have higher density and very low porosity as compared with the original ε-HNIW[17].

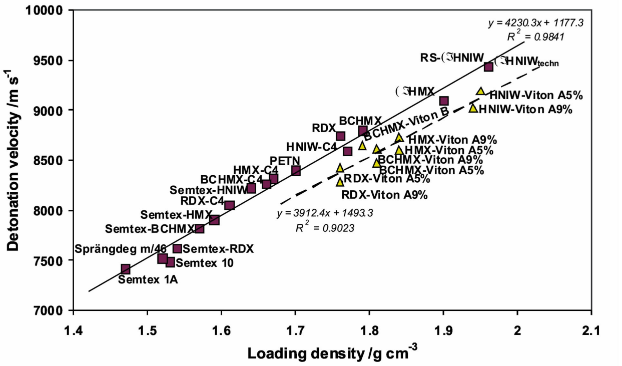

Fig. 1 Dependence of detonation velocity on loading density of the studied explosives. For fluorinated binders only one "averaged" line is presented

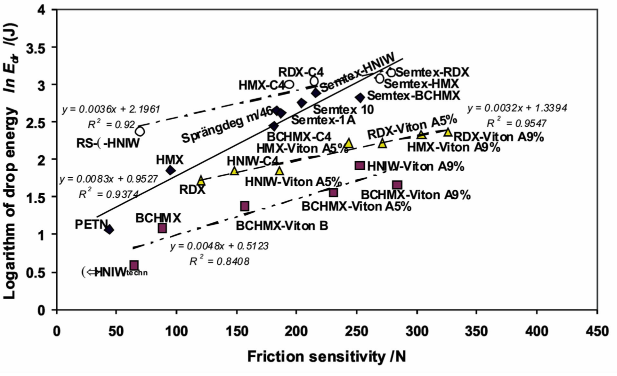

Fig. 2 Mutual relationships between friction and impact sensitivities of the studied explosives

The relationship between impact sensitivity (expressed as drop energy) and detonation pressure of the studied explosives (expressed by the term ρD^2 – see Fig. 3) corresponds with our expectations. Since the square of detonation velocity approximately corresponds with the heat of explosion, the classification of PBXs given in Fig. 3 is due to thermochemical aspects of their detonation; it is logical that here the data for RS-ε-HNIW correlate again with those of the least sensitive PBXs, i. e. RDX-C4, HMX-C4, Semtex-HMX and Semtex-RDX. The relationship of the type presented in Fig. 3 might be viewed as another form of modified Evans-Polanyi-Semenov equation (for more details about this equation, see [18 -19]).

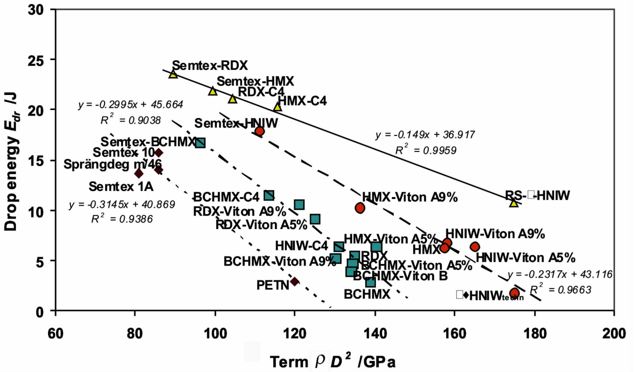

Fig. 3 Relationship between the drop energy E_{dr} and ρD^2 of the studied explosives

Analogous relationship for FS should be semi-logarithmic (see Fig. 4). A good correlation in the sense mentioned exists in the case of the PBXs containing binders based on polyisobutylene and acrylonitrile-butadiene rubber. The variation observed in the case of PBXs with polyfluorinated binders is connected with inclusion of two qualities of these explosives into a single correlation (PBXs with 5% wt. and 9% wt. of Viton A). Comparison of Fig. 3 and Fig. 4 again indicates different mechanisms of transfer of initiation impulse into reaction centre of the given nitramine molecule during impact and during friction.

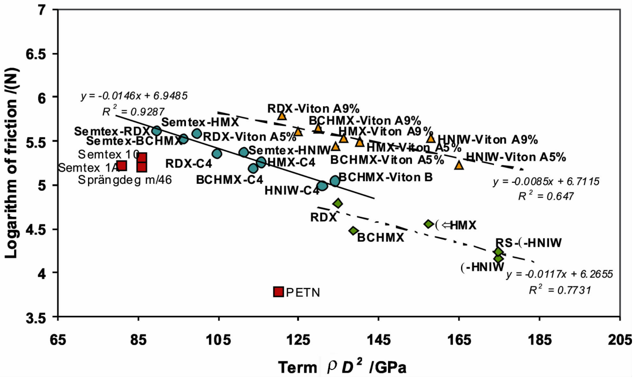

Fig. 4 Semi-logarithmic relationship between the friction sensitivity and ρD^2 of the studied explosives. For fluorinated binders only one "averaged" line is presented.

From the point of view of sensitivity, BCHMX approaches PETN[2], but it is an explosive of higher performance[2]; it provides the putty-plastic Semtex-BCHMX whose sensitivity is somewhat lower than that of Semtex 10. In contrast to that, BCHMX-C4 possesses somewhat worse sensitivity characteristics than the studied putty-plastic PBXs based on PETN. The phlegmatization with Viton more distinctly lowers the friction sensitivity of BCHMX, but very slightly lowers its impact sensitivity.

4 Conclusions

The dependence of detonation velocity upon the loading density of plastic bonded explosives containing the PIB and ABR binders differs from that for PBXs containing polyfluorinated binders. The reason lies in different effects of these binders on loading density and thermochemistry of detonation of the respective PBXs. By means of the first mentioned dependence the D value of 9.800 mm · μs^{-1} for theoretical maximal density of ε-HNIW was found. From among of the binders studied, the matrix based on acrylonitrile-butadiene rubber most effectively lowers the impact and friction sensitivities of nitramines, but it provides putty-plastic PBXs with relatively low loading density. From mutual comparison of these sensitivities and from their relationship to the performance of PBXs it is obvious that the mechanisms of transfer of initiation impulse into reaction centre of nitramine molecule are different for impact and for friction. As far as BCHMX is concerned, the impact sensitivity of BCHMX-C4 is higher than that of Semtex 1A, its performance being close to that of HMX-C4. Semtex-BCHMX has somewhat lower impact and friction sensitivities than Semtex 10, but its performance should be lower than that of RDX-C4. The example of ε-HNIW indicates that while the impact sensitivity markedly depends on the crystal quality of nitramine, an analogous dependence of the friction sensitivity appears to be less pronounced and deserves additional investigation.

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以环状硝胺为基的几种塑料黏结炸药的初步研究

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摘　要：用聚异丁烯(PIB),丙烯腈-聚丁橡胶(ABR),维通 A 黏结剂和 RDX,HMX,BCHMX 和 ε-HNIW 四种硝胺炸药制备了一系列塑性炸药。PETN 和以 PETN 为基的三种塑性炸药用于比较。测试了这些炸药的爆速,撞击和摩擦感度。摩擦感度与撞击感度的关系以及两种感度与 D^2 的关系表明摩擦力向硝胺炸药分子反应中心的转移机理不同于撞击能的转移机理。从摩擦和撞击反应的相互比较以及降低 ε-HNIW 感度等级中发现撞击感度依赖于硝铵炸药的晶体品质,而摩擦感度的依赖却不明显。测试爆速 D 与含 PIB 和 ABR 黏结剂的 PBX 装药密度之间的关系表明,ε-HNIW 的密度为 2.04 g·cm^{-3}时,爆速 D 为 9.800 mm·μs^{-1}。

关键词：爆炸力学；塑料黏结炸药；摩擦感度；撞击感度；爆速

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