Concerning the Shock Sensitivity of Cyclic Nitramines Incorporated into a Polyisobutylene Matrix[*)]

Vojtěch PELIKÁN[1*], Svatopluk ZEMAN[1], Qi Long YAN[1],
Milan ERBEN[2], Ahmed ELBEIH[3] and Zbyněk AKŠTEIN[4]

*[1]Institute of Energetic Materials, Faculty of Chemical Technology,
University of Pardubice, CZ-532 10 Pardubice, Czech Republic
[2]Deptartment of General & Inorganic Chemistry,
Faculty of Chemical Technology,
University of Pardubice, CZ-532 10 Pardubice, Czech Republic
[3]Military Technical College, Kobry Elkobbah, Cairo, Egypt
[4]Research Institute of Industrial Chemistry, Explosia Co.,
CZ-532 17 Pardubice, Czech Republic
E-mail: vojtech.pelikan@upce.cz

Abstract: Two types of plastic bonded explosives (PBXs) based on ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (ε-HNIW, CL-20), and PBXs based on 1,3,5-trinitro-1,3,5-triazinane (RDX), β-1,3,4,7-tetranitro-1,3,5,7-tetrazocane (β-HMX) and cis-1,3,4,6-tetranitro-octahydroimidazo-[4,5-d]imidazole (bicyclo-HMX, BCHMX) were prepared using a polyisobutylene binder with dioctylsebacate (DOS) as plasticizer, *i.e.* a C4 matrix. One version of the ε-HNIW PBX is a product with reduced sensitivity (RS-ε-HNIW). All these PBXs, referenced respectively as RS-ε-HNIW-C4, ε-HNIW-C4, RDX-C4, HMX-C4 and BCHMX-C4, were tested using the Small Scale Gap Test according to STANAG 4488. The results of the gap test on the PBXs with RDX, β-HMX and BCHMX correspond to the impact sensitivities of the original crystalline nitramines. This is not entirely valid for ε-HNIW. In other words, PBXs with RS-ε-HNIW cannot achieve as low a shock sensitivity as would be expected from the differences obtained from the impact sensitivities between RDX, β-HMX and BCHMX, on the one hand, and RS-ε-HNIW on the other. It is shown that the morphological stability of RS-ε-HNIW in the C4 matrix is insufficient. However, further development and use of RS-ε-HNIW

as a filler of PBXs would seem to be both desirable and beneficial. Despite the relatively high impact sensitivity of crystalline BCHMX, the shock sensitivity of its analogous C4 PBX is already good, and comparable with that of RS-ε-HNIW.

Keywords: BCHMX, β-HMX, RDX, ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, CL-20, gap test, impact

1   Introduction

The synthesis of the attractive bicyclic nitramine, *cis*-1,3,4,6-tetranitro-octahydroimidazo-[4,5-d]imidazole (bicyclo-HMX, BCHMX) has recently been developed [1, 2]. In order to evaluate the application possibilities of this particular nitramine (BCHMX), 1,3,5-trinitro-1,3,5-triazinane (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, ε-CL-20) have been used for comparison [3]. Some plastic bonded explosives (PBXs) based on these nitramines were included in this evaluation [3]; softened polyisobutylene (PIB – *C4 matrix*) was used as one of the binders [3, 4]. HNIW is still considered as a very powerful, but also very sensitive, explosive (impact sensitivity 2.0-4.5 J [5, 6]). Impact sensitivities of the pure polymorphic forms of HNIW were determined in the 1990s and published as follows [7]: 13.2 J for ε-, 10.1 J for α-, 11.9 J for β- and 12.2 J for γ-form; all of these values are still mostly ignored in the literature. In the last five years, however, the sensitivity of technical grade HNIW has been the main area for crystal engineering of this nitramine [8, 9]. The most widespread method for crystallization of HNIW uses the "solvent-antisolvent" system [9-13]; by the addition of some compound-promoters into a saturated solution before adding the antisolvent, and by using a suitable method for HNIW precipitation from the resulting solution, ε-HNIW crystals can be obtained with rounded edges and with minimal defects and impurities [10-14]. Its impact sensitivity can be close to the values which are published for its pure polymorphs [10-14] and such a version is referred to as RS-ε-HNIW (*i.e.* reduced sensitivity HNIW) [14]. As for the nature of the promoters, all compounds which are able of forming non-bonding interactions with the HNIW molecules [11] (*i.e.* compounds based on polyalcohols, carboxylic acids, amino acids and/or their esters, but also pyridine [13]), may be used. A relatively well-known alternative for HNIW crystallization involves the use of an ultrasonic operation in the precipitation of the nitramine from its solution [9, 15]. RS-ε-HNIW is also a topic of research at our Institute [3, 11]. So far no information has been published concerning

practical applications of this version of HNIW. In this regard, this paper is mainly focused on the shock sensitivity of C4 matrix bonded explosives (PBXs), not only for BCHMX but also for "normal" and the RS types of ε-HNIW.

2 Experimental

2.1 ε-2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (ε-HNIW, CL-20)
HNIW was obtained in the α-form from the pilot plant of Explosia Company, Pardubice, Czech Republic. Different kinds of solvent (ethyl acetate, methyl ethyl ketone, acetone) and antisolvent (n-heptane, toluene, xylene, chloroform) were used for the crystallization process described in a recent paper [11]; for the purposes of the current paper a system using "ethyl acetate – n-heptane" was used. Table 1 presents the particle size characteristics of this HNIW and a Scanning Electron Microscope photograph is shown in Figure 1 [11]; its impact sensitivity [11] is shown in Table 2.
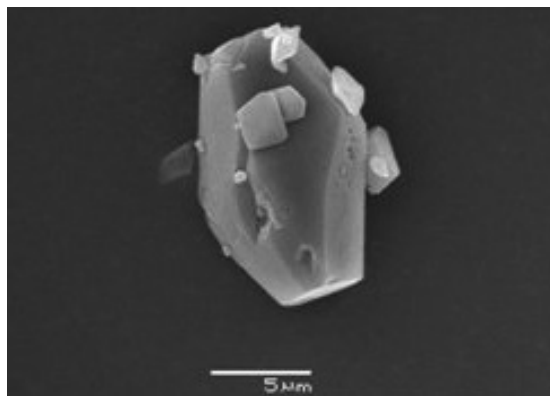

Figure 1. Scanning Electron Microscope photograph of the normal ε-HNIW crystals used [11].

RS-ε-HNIW was prepared by the new method, which is based on removing the impurities and the water content from a solution of HNIW by adding a promoter to the solution before precipitation. Then, RS-ε-HNIW crystals were obtained by the normal crystallization process [11]; their particle size characteristics are summarized in Table 1 (Scanning Electron Microscope photograph in Figure 2 [11]). The impact sensitivity of the RS-HNIW prepared [11] is shown in Table 2.
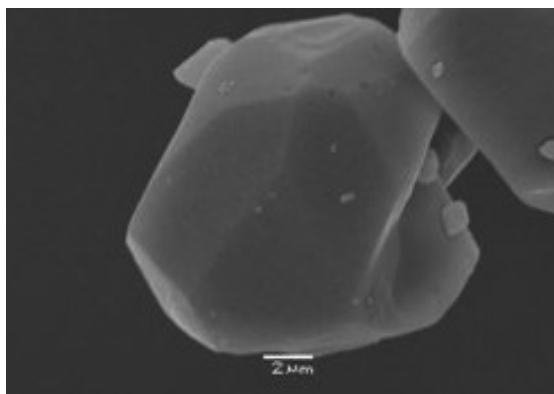
Figure 2.   Scanning Electron Microscope photograph of the RS-ε-HNIW crystals used [11].

2.2 Nitramines BCHMX, RDX and *β*-HMX

The cis-1,3,4,6-tetranitro-octahydroimidazo-[4,5-d]imidazole (BCHMX) used here was prepared in this laboratory [1, 2]. Its particle size characteristics are shown in Table 1. A Scanning Electron Microscope photograph of its crystals is shown in Figure 3. The 1,3,5-trinitro-1,3,5-triazinane (RDX) sample used was a product of Dyno Nobel (a mixture with a mass ratio of 2:1 of Classes 2 and 5 according to the standard [16]). The *β*-1,3,5,7-tetranitro-1,3,5,7-tetraazocane (*β*-HMX) was imported from Russia and its particle size was close to Class 3 according to the standard [17]. A summary of the particle size distributions of these nitramines is presented in Table 1.
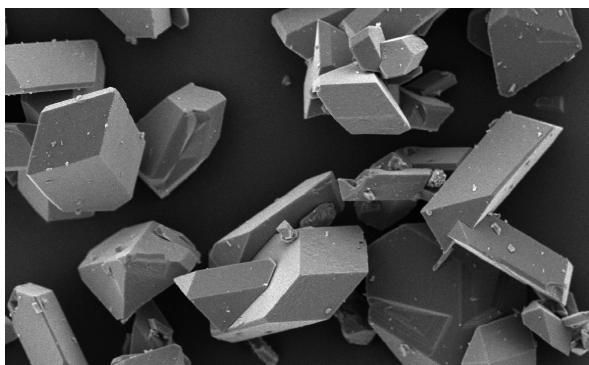

Figure 3.   Scanning Electron Microscope photograph of the BCHMX crystals used.

Table 1. Summary of particle size distribution[*]

Nitramine	Median particle size [mm]	Diameter on cumulative 10% [mm]	Diameter on cumulative 90% [mm]
ε-HNIW	13.2	7.3	22.1
RS-ε-HNIW	7.8	2.6	16.5
BCHMX	14.7	8.0	25.9
RDX (grade 2)	143.8	26.2	282.3
RDX (grade 5)	12.6	7.2	20.1
β-HMX	144.3	67.6	426.3

Note: [*] Determined by using a Horiba LA-950 particle size distribution analyzer.

2.3 Preparation of plastic explosives (PBXs) with a C4 matrix

A C4 matrix refers to a non-energetic binder containing 25 wt.% polyisobutylene, 59 wt.% dioctylsebacate and 16 wt.% of the oil HM46. The preparation of the binder involved mixing small pieces of two types of polyisobutylene (disintegrated by rolling) with the sebacate and the HM46 oil. The plastic explosives themselves were prepared by mixing 91 wt.% of the particular nitramine with 9 wt.% of the binder. The formulations were mixed in a computer controlled Brabender Plastograph at 70 °C under vacuum for 70 min. The samples of the final plastic explosives were then extruded using a 40 mm single screw, extrusion machine to obtain long charges of plastic explosive with a diameter of 21 mm. The impact sensitivities of the nitramine-C4 mixtures, including RS-HNIW-C4 [4] are presented in Table 2. The PBXs prepared were stored for 3 months at laboratory temperature to allow the mass to "settle down" before measurements were taken.

2.4 Thermal stability

Table 2 contains results from the study of the thermal reactivity of the C4 explosives using the Czech vacuum stability test STABIL [19]; Figure 4, taken from paper [19], shows that the production of gaseous products in this test is a zero-order reaction, which means that this reactivity can be represented by the specific rate constants (Eyring equation) of its decomposition [19].
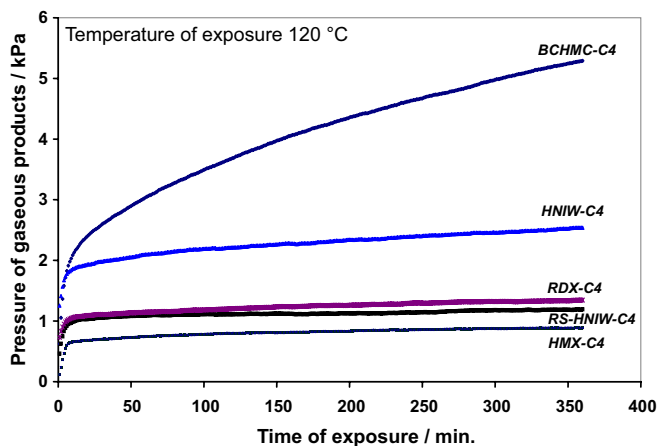
Figure 4.   Recordings from the vacuum stability test of the studied PBXs, taken from paper [19]. It implies that the formation of gaseous products is a zero-order reaction. Thus the rate of the thermal decomposition is equal to the specific rate constant, k_r, of the reaction expressed by the Eyring equation $\{k_r = T(k/h) \exp\text{-}(\Delta G^{\#}/RT)\}$.

RS-ε-HNIW was also exposed to a temperature of 70 °C for 70 min in a mixture containing 5 wt.% dioctylsebacate (DOS) using Thermogravimetry (TG, Netzsch 209F3 instrument, Al_2O_3 crucible). This exposure simulates the thermal conditions of the incorporation of ε-HNIW into the C4 matrix. This TG technique was also used for the nitramine crystals mentioned, with 30 min exposure at 190 °C [18] − see Figure 11.

2.5 IR spectroscopy

IR spectra were recorded in the 4000-100 cm^{-1} region on a Nicolet 6700 FTIR spectrometer purged with dry air using the ATR technique (single bounce diamond crystal, 128 scans, resolution 1 cm^{-1}). FTIR spectroscopy has been shown to be a very sensitive tool for differentiating HNIW polymorphs in formulations [20, 21]. Thus, the IR spectra of crystalline samples of β-HNIW, γ-HNIW, ε-HNIW and RS-ε-HNIW in both the MIR and FAR regions were collected and compared with those obtained for their corresponding C4 formulations – see Figures 9 and 10. The crystalline sample of ε-HNIW, as well as its formulations with the C4 matrix, showed IR bands characteristic of the pure ε-HNIW polymorph. All of the samples studied have no absorption bands in the region 3,600-3,100 cm^{-1}, which would indicate that the ε-HNIW is entirely anhydrous [21]. The formulation prepared from RS-ε-HNIW has an IR pattern typical of contamination with the

β- and γ-HNIW polymorphs, respectively [20, 21]. The most striking differences are in the regions 1,590-1,525 cm^{-1} (asymmetric NO$_2$ stretching), 1,430-1,180 cm^{-1} (symmetric NO$_2$ stretch and C–H deformation), 940-890 cm^{-1} (C–N stretching), and 760-730 cm^{-1} (NO$_2$ deformation), see Figure 9. The presence of other HNIW polymorphs in the HNIW-C4 formulation was unambiguously proved by the collapse of the quartet typical of pure samples of ε-HNIW (757-737 cm^{-1}) [20]. The doublet at 589-581 cm^{-1} present in the spectrum of ε-HNIW was also missing and new bands at 513, 478, 409, 322 and 285 cm^{-1}, attributable to the β- and γ-HNIW polymorphs, appeared. A transformation was also apparent from the decrease in the IR bands of ε-HNIW at 565 and 524 cm^{-1}. Thus, FTIR spectroscopy unambiguously proves that, during the incorporation of RS-ε-HNIW into the C4 matrix, this polymorphic form transforms into different polymorphs (demonstrably into γ-HNIW – trace G in Figures 9 and 10), whereas the C4 formulation prepared from ε-HNIW contains exclusively the pure ε-polymorphic form (trace F in Figures 9 and 10). The RS-ε-HNIW, in its mixture with 5 wt.% DOS, after 70 min at 70 °C, is roughly 30% transformed (based on PLS analysis of the IR spectra in both the MIR and FAR regions) into γ-HNIW, see trace E in Figures 9 and 10.

2.6 Gap test

The Small Scale Water Gap Test (SCWT) [22] was used to determine the shock sensitivity of the PBX samples prepared − all experimental procedures and methods were conducted according to the NATO STANAG 4488 [22]. This method is suitable for materials having a critical diameter less than 20 mm. The arrangement of the SCWT is presented in Scheme 1; here the procedure was slightly modified: an O-ring seal for the donor charge, which is not part of the bottom of the arrangement in the original version, was used, and the witness metal sheet was a sturdier version. The O-ring seal, and the fact that the kit was configured differently compared with the original standard, should eliminate the formation of an air bubble in the water gap during the assembly of the kit. The 50% initiation probability point (in mm) of the water column and the standard deviation for the test sample initiation were calculated using Bruceton statistical analysis of the Up and Down test sequence, performed with 25 consecutive trials. The results of the SCWT are then presented as the water column height and pressure corresponding to a 50% probability of sample activation. The data obtained for the various PBXs studied here are presented in Table 2.
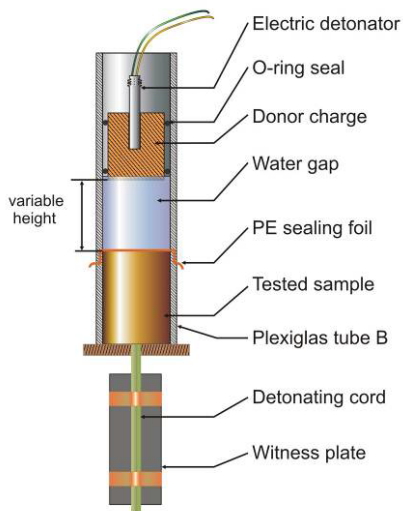
Scheme 1. An arrangement of the Small Scale Water Gap Test (SCWT) with small improvements over the original standard STANAG 4488: the donor charge is sealed by an O-ring and the whole kit is configured in a manner contrary to the original version.

Table 2. Summary of shock sensitivity data in this paper, and both impact sensitivity and thermal decomposition data from paper [19]

Type of crystalline nitramine	Impact sensitivity in [J], taken from [19][*]		Gap test sensitivity of the C4 PBX		Specific rate constants[**] [kPa·g⁻¹·min⁻¹]
	crystalline	C4 PBX	water gap [mm]	pressure [GPa]	
ε-HNIW	4.1	14.8	19.72 ±0.69	1.87	0.0012 0.0015
RS-ε-HNIW	10.8	17.0	16.33 ±0.81	2.38	0.0004 0.0003
BCHMX	3.2	11.6	16.67 ±1.08	2.33	0.0076 0.0078
RDX	5.6	21.1	14.95 ±0.45	2.64	0.0006 0.0007
β-HMX	6.4	20.2	14.10 ±1.08	2.81	0.0004 0.0005

Note: [*] Data obtained from bam drop hammer at the iem [19].
       [**] This represents a reaction rate of zero order, thermal decomposition in vacuum, taken from paper [19].

3   Results and Discussion

Recently, attention has been paid to the impact sensitivity [3, 19], friction sensitivity [3] and thermal reactivity [19] of PBXs filled with cyclic nitramines, including mixtures with a C4 binder. The relationship between the impact sensitivity and thermal reactivity of the C4 explosives has been described [19], and relationships have also been found between the impact sensitivity and the PBXs' performance [3]. However, the shock sensitivity of these PBXs has not been studied until now, but such a study is clearly desirable, mainly for the cases of BCHMX and HNIW.

The determination of the shock sensitivity of explosives based on RS-RDX and on RS-HMX by means of the Small Scale Water Gap Test (SCWT) [22] is the subject of a paper by Johansen *et al*. [23]: these authors presented shock sensitivity in the form of the two threshold levels (safe level "No-Go", initiation threshold level "Go"). Because of the different kinds of PBXs that they have tested using the original version of the SCWT, their results differ from the results obtained in the work described here (from 3.88 to 4.58 GPa for RS-RDX PBXs) [23]. The results obtained here using "standard" RDX and HMX are given in Table 2. They present higher sensitivities compared with the pressable RS-RDX analogue mentioned in paper [23]. On the other hand, when comparing these data, one has to bear in mind certain other differences: 1) a mean value is used in this study for the water column; 2) the explosive materials used here are incorporated in a plastic matrix; and 3) the granularity is different. The credibility of the present results can be verified by studying Figures 7 and 8 (see the clear evidence of the data trend).

Figure 5 shows a logarithmic relationship between impact sensitivity and the specific rate constant, according to which set the C4 PBXs studied are divided into the group with monocyclic nitramines and the group of polycyclic nitramines with crowded molecules − here the heightened impact sensitivity corresponds to an increased thermal reactivity for BCHMX. Figure 5 is consistent with the fact that only low-temperature decomposition data, which are not influenced by autocatalysis, can be extrapolated and/or compared with the conditions of detonation [24-26].
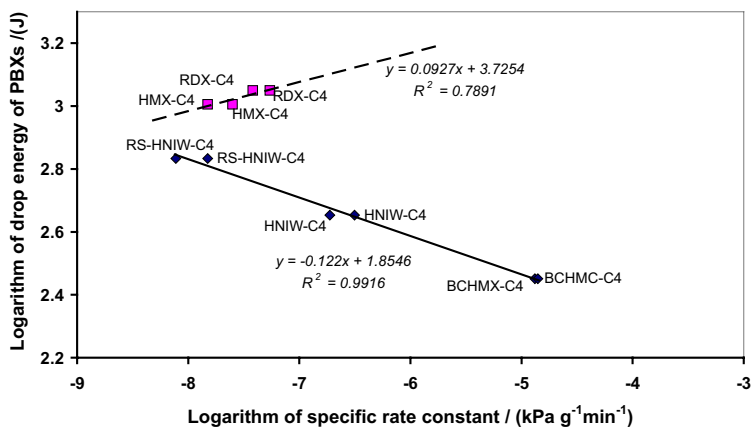
Figure 5. Logarithmic relationship between impact sensitivity and specific rate constant of the C4 PBXs studied, taken from paper [19].

Figure 6 represents an approximate logical relationship between the zero order iso-thermal decomposition velocity of the C4 PBXs studied [19] and their shock sensitivities. Here the data for BCHMX-C4 are situated outside the data for the rest of the C4 PBXs due to the relatively high initiation reactivity of BCHMX by itself [1, 4].
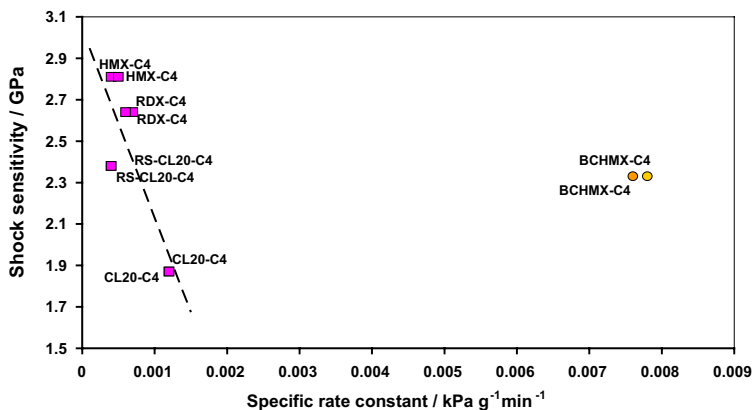

Figure 6. Approximate relationship between shock sensitivity of the C4 explosives studied and specific reaction constants of their thermal decomposition at 120 °C in vacuum [19]; data for BCHMX do not correlate due to the relatively high thermal reactivity of BCHMX.

According to Table 1 the granularity of the nitramines is very different, therefore, it needs to be explained why a relationship exists between the impact sensitivities of the original crystalline nitramines and the shock sensitivities of

the corresponding C4 PBXs. This relationship is given in Figure 7. Data for the HNIW mixtures form a separate group, mainly due to the distinctive molecular structure of HNIW (globular crowded molecule), but also partially due to the influence of the C4 matrix on the initiation reactivity of the corresponding HNIW PBXs (see below). The C4 PBX with RS-ε-HNIW cannot achieve as high a shock sensitivity as would be expected from the difference in impact sensitivities of RDX, β-HMX and BCHMX, on the one hand, and RS-ε-HNIW, on the other.
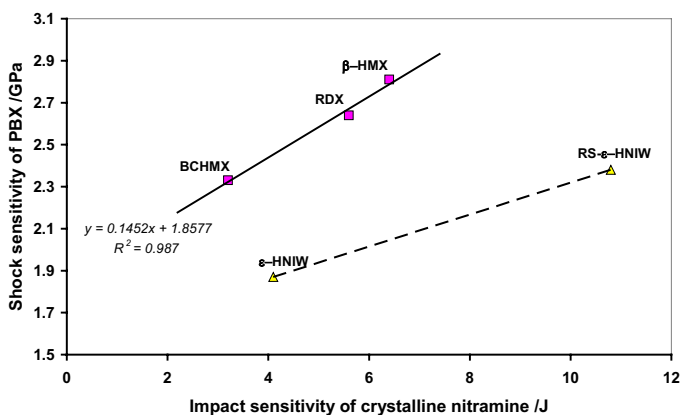

Figure 7.   Relationship between shock sensitivity and impact sensitivity of the pure nitramine fillers.

Figure 8 shows a comparison of the shock and impact sensitivities of the PBXs studied. Due to the higher impact sensitivity of BCHMC-C4, its data lie outside the other PBXs' data.

It was found by TG and DSC techniques [27] that the thermal decomposition of ε-HNIW-C4 and RS-ε-HNIW-C4 follows a two-step mechanism, where the initial step is partly influenced by crystal structure. Crystal structure also influences sensitivity to mechanical stimuli. In this regard, the question arises as to why the difference between the impact sensitivities of crystalline ε-HNIW and RS-ε-HNIW does not correspond to the same difference between ε-HNIW-C4 and RS-ε-HNIW-C4, and is also not fully reflected in the shock sensitivity, based on the trends in shock sensitivity shown for all of the PBXs studied. From the FTIR measurements (see Figures 9 and 10) it has been shown that RS-ε-HNIW changes completely into the γ-form during its incorporation into a C4 matrix, while ε-HNIW does not change during this process; this is documented by Figures 9 and 10. Under static conditions, *i.e.* during thermal exposure of the mixture of RS-ε-HNIW with 5 wt.% of DOS to 70 °C for 70 min, roughly only 30% of the ε-modification is converted into γ-HNIW. This transition into γ-HNIW

is associated with a change of density from 2.044 to 1.916 g·cm⁻³ [28], which corresponds to a theoretical crystal volume increase of 6.3%.
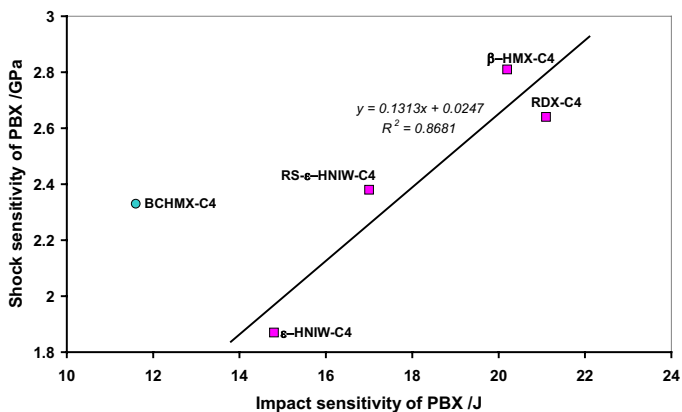

Figure 8. A comparison of the trends of shock and impact sensitivities of the PBXs studied.
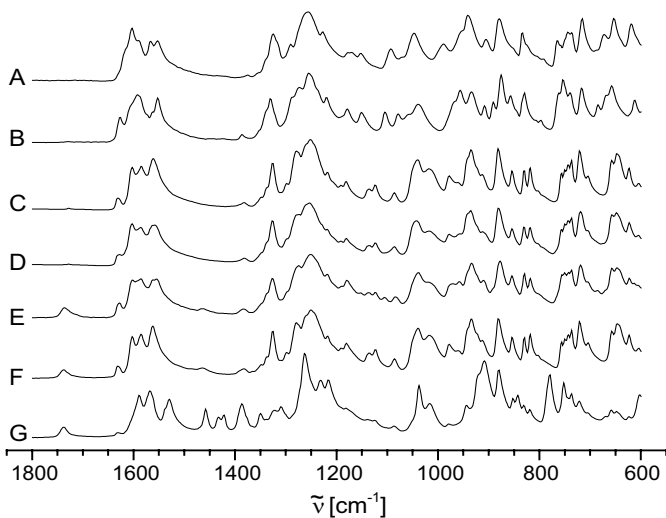

Figure 9. MIR-FTIR spectra in the region 1,800-600 cm⁻¹. A) *β*-HNIW, B) *γ*-HNIW, C) RS-*ε*-HNIW, D) *ε*-HNIW, E) RS-*ε*-HNIW with 5 wt.% of DOS after heating 70 minutes at 70 °C, F) *ε*-HNIW in C4 formulation, G) RS-*ε*-HNIW in C4 formulation (probably slightly contaminated by other binders from the heavy-duty mixer during semi-plant production) should represent *γ*-HNIW. (Vertical axis represents relative absorbance.)
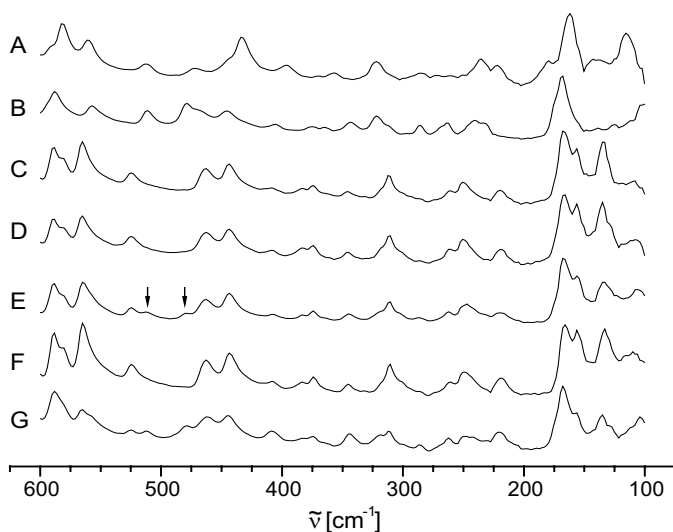
Figure 10. FAR-FTIR spectra in the region 600-100 cm^{-1}. Labelling of IR traces is identical to that used in Figure 9. Arrows in trace E highlight the bands of γ-HNIW, a contaminant present in the sample. (Vertical axis represents relative absorbance.)

Isothermal exposure of RS-ε-HNIW shows that its crystals crack during heating for 30 min at 190 °C due to the $\varepsilon \rightarrow \gamma$ transition (Figure 11). During this transition, microregions with gradients of mechanical stresses are formed because of the movement of the dislocations – the subsequent process is then controlled by microstresses that arise at the front of this $\varepsilon \rightarrow \gamma$ transition [29]. It is clear that the presence of admixtures with a type of lubricant might eliminate these stresses and thus facilitate the $\varepsilon \rightarrow \gamma$ transition in the HNIW crystals; also the influence of pressure during kneading of the HNIW-C4 mixture should have a supportive effect here. This might lead to the formation of fresh disruptions, as Figure 11 shows. A more detailed study of a wave-like process, an abrupt volume expansion, movement, and fragmentation of the HNIW particles during phase transition, is represented by paper [30].

The ε-HNIW phase was identified as being stable at ambient pressure up to a temperature of 120 °C [31]. A phase transition $\varepsilon \rightarrow \gamma$ was observed at 125 °C and the γ-HNIW then remained stable until thermal decomposition above 150 °C [31]. However, Torry and Cunliffe have found the $\varepsilon \rightarrow \gamma$ transition occurs at 56.5 ± 1.5 °C for γ-HNIW incorporated into polar plasticizers and/or polar polymeric binders (polyGLYN, polyNIMMO, *etc*.) [32].
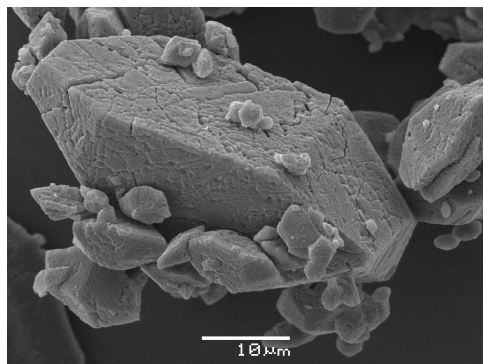
Figure 11. Scanning Electron Microscopy photograph of the γ-HNIW crystals, obtained by heating RS-ε-HNIW for 30 minutes at 190 °C by means of isothermal TG in the sense of the method described in paper [18].

Results from the gap tests correspond to expectations; logically they are affected by the impact sensitivities of the original ε-HNIW and BCHMX crystals (see comparisons in Table 2). While the relatively high shock sensitivity of the C4 mixture with the "normal" kind of ε-HNIW should be connected with cracks and other defects in its crystals (see Figure 1), in the case of BCHMX-C4 this sensitivity is already at a satisfactory level.

Concerning BCHMX and its C4-explosives, their relative high initiation reactivity is due to this nitramine's rigid and crowded molecule [1]. The N–N bonds in the BCHMX molecule are not equivalent – the longest of them (141.2 nm) corresponds to the smallest mutual distance of oxygen atoms in the respective nitro group (216.1 nm) [1]. The longest N–N bond in ε-HNIW is that of the nitramino group at position 2 [7] (143.6 nm). Whereas BCHMX does not have any polymorphic forms, the HNIW molecule has a certain freedom in its molecular conformation. This fact, together with higher intermolecular forces in the HNIW molecular crystals (see heats of fusion of the nitramines studied [18]), should make this nitramine more stable towards mechanical initiation compared with BCHMX. This stabilizing effect of the crystal lattice in HNIW, however, can be easily disrupted by polar additives (plasticizers, energetic binders, *etc*.) as this paper and also paper [31] document. However, further development and uses for RS-ε-HNIW are desirable and should be beneficial.

4   Conclusion

The results of gap tests on PBXs based on nitramines RDX, β-HMX and BCHMX with the polyisobutylene binder (C4 matrix), correspond to the impact sensitivities of the original crystalline nitramines. This statement, however, is not entirely valid for ε-HNIW. Its globular and crowded molecules can form perfect crystals of the ε-form (RS-ε-HNIW), whose morphological stability in the C4 matrix, however, is not the best, even at the temperatures used for preparing this PBX. This might be a major reason why a PBX with RS-ε-HNIW cannot achieve as high a shock insensitivity as would be expected from the difference in the impact sensitivities of RDX, β-HMX and BCHMX, on the one hand, and RS-ε-HNIW on the other. While the impact sensitivity of crystalline BCHMX is relatively high due to its molecular structure, the shock sensitivity of its C4 PBX is already good, and comparable with that of RS-ε-HNIW-C4. The results obtained show that development and use of RS-ε-HNIW as a filler for PBXs should be both desirable and beneficial.

5   References

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