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Investigation of the Properties of Polymer Bonded Explosives Based on 1,1-Diamino-2,2-dinitroethene (FOX-7) and 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX)

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Abstract: The influence of polymeric matrices on the physical properties and stability of polymer bonded explosives based on FOX-7 (1,1-diamino-2,2-dinitroethene) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) was investigated. Samples of explosives were prepared with different polymeric additives *e.g.* nonylphenylpolyoxyethyleneglycol ethers (ROKAFENOL), silicone greases and poly(3-methyl-3-nitroxymethyloxetane) (Poly(NIMMO)). The mass ratio of polymeric matrices to explosives was determined experimentally in order to obtain plastic samples stable at room temperature. The most promising products were tested for sensitivity to mechanical and thermal stimuli. Determinations of the critical diameter and detonation velocity were also performed. The use of silicone grease in the mixture containing Poly(NIMMO) gave the most desirable results, that is to say a combination of high performance and high stability.

Keywords: FOX-7, HMX, Poly(NIMMO), plasticity, silicone

1 Introduction

1,1-diamino-2,2-dinitroethene (2,2-dinitroethylene-1,1-diamine (IUPAC) also known as FOX-7 or DADNE), described for the first time by Latypov *et al.* in 1998 [1], is still a quite new and prospective explosive that combines low sensitivity with high performance. The unique characteristics of FOX-7 originate from the compound's structure in which many inter- and intra-molecular hydrogen bonds occur. These have a major influence on the high stability of FOX-7 crystal's structure [2]. For these reasons, FOX-7 has been extensively studied recently and the results presented in many research papers [3-19]. Usable forms

of explosives containing FOX-7 as the main component have been predominantly prepared and studied as pressed charges (as a mixture with other explosives and phlegmatizing agents) [20-22] as well as charges made of castable compositions (containing, for example, energetic polymers) [23, 24].

Elbeih *et al.* [25] presented the results of a study of polymer bonded explosives made from high energy materials (Nitroamines) (~90%) and several polymeric matrices (~10%) based on polydimethyl-siloxane (PDMS, silicone matrix), for example. They showed that the addition of silicone was crucial for decreasing the impact sensitivity of the explosives studied [25].

In the present work the influence of polymeric matrices on the physical properties and stability of polymer bonded explosives based on FOX-7 and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (1,3,5,7-tetranitro-1,3,5,7-tetrazoocane (IUPAC) also known as HMX) was investigated. Samples of explosives were prepared using different polymeric additives *e.g.* nonylphenylpolyoxyethyleneglycol ethers (ROKAFENOL), silicone greases and poly(3-methyl-3-nitroxymethyloxetane) (Poly(NIMMO)). The main assumptions were that: small samples of the compositions should be homogenous, able to be formed by hand into stable and desirable shapes, and also stick firmly to various vertical surfaces. Two sensitivity and output parameters (the critical diameter and velocity of detonation) were determined for the most promising samples.

2 Experimental

2.1 Explosives and energetic polymer

HMX (designated by us as HMX_{LC}) was delivered by NITRO-CHEM S.A. Bydgoszcz. FOX-7 and Poly(NIMMO) (an energetic polymeric additive) were synthesized in our laboratory according to methods we described previously [17, 26]. At the start of our study the crystal sizes of both explosives were in the range 250-400 μm denoted as *LC* (*large crystals*). Subsequently explosives with smaller crystals were used. In order to reduce the size of the crystals to the size range 5-50 μm, recrystallization was performed. The material so obtained was denoted by us as *SM (small crystals)*.

2.1.1 Recrystallization of FOX-7 (250-400 μm, FOX_{LC})

26 g (0.18 mol) of FOX-7 and a mixture of solvents (900 g water and 300 g N-methyl-2-pyrrolidone from Sigma-Aldrich) were stirred while heating to boiling temperature. Next, the yellow transparent solution obtained was cooled at a rate of 0.3 K/min to a temperature of about 5 °C. After filtration and drying,

about 25.5 g (98%) of recrystallized FOX_{LC} was obtained.

2.1.2 Recrystallization of FOX-7 (5-50 μm, FOX_{SC})

A hot (above 85 °C) transparent solution of 25 g of FOX-7 (0.17 mol) in 160 g of N-methyl-2-pyrrolidone was poured into 1120 g of ambient-temperature water, stirred for a while, filtrated and then washed with cold water. After drying, about 24.5 g (98%) of recrystallized FOX_{SC} was obtained.

2.1.3 Recrystallization of HMX (5-50 μm, HMX_{SC})

A hot solution of 7.5 g HMX (0.02 mol) in 500 g of acetone was poured into 2000 g of water at ambient temperature, stirred for a while and filtrated. After drying, about 7.2 g (96%) of recrystallized HMX_{SC} was obtained.

2.2 Non-energetic additives

ROKAFENOL and Sorbitan monooleate (ROKWIN 80) were supplied by PCC Rokita SA. Silicone greases (Silicone MV and Silicone HV, where MV and HV stand for medium and high viscosity, respectively) were supplied by Merck Millipore. Polyisobutylene (PIB) and vaseline were supplied by Sigma Aldrich.

2.3 Preparation of the polymer bonded explosives

All of the samples were prepared by mixing the powdered explosives with polymer additives. The mass ratio of FOX-7 to HMX was constant and equal to 70/30. Small portions of the polymer were added to the dry mixture of explosives and mixed until a homogenous plastic consistency was obtained. Compositions containing materials with smaller crystals (*SC*) were found to be mechanically more stable and also can more easily be formed into any charge shape.

2.4 Thermal stability of mixture consistency

In order to verify the stability of the prepared compositions to changing temperature conditions, samples were refrigerated at −20 °C. After 2 h the samples were warmed to room temperature, their plasticity was controlled and the testing procedure was repeated after 4 h of freezing. No differences were observed in the behavior of compositions tested before and after periods of freezing: the samples retained their original consistency and plasticity. Next, new samples of the same compositions were heated for 2 h and 4 h at 50 °C. After these periods of time, samples were cooled to room temperature and their plasticity and the intensity of “the effect of perspiration” (shown in Figure 1) were controlled.

2.5 The adhesion to various vertical surfaces

Samples of about 5 g were applied with constant force to flat glass, metal, wood, PVC and ceramic surfaces. Next the resulting specimens were mounted vertically. If the sample did not fall off from the surface after 10 min, the adhesion test was passed.

2.6 Sensitivity to mechanical stimuli

The impact sensitivity was studied using a BAM Apparatus with a 5 kg hammer [27]. The minimum drop height was determined at which initiation was observed at least once in six trials. The friction sensitivities of FOX-7, HMX, Poly(NIMMO) and prepared mixtures were measured using a Julius-Peters machine according to the method described in reference [27]. The smallest loading of pistil was determined at which initiation was observed at least once in six trials.

2.7 Thermal analysis

The thermal properties of selected samples were measured using a simultaneous TG/DTA analyzer LabSys TG/DTA-DSC manufactured by SETARAM. The analyses were conducted in open Al_2O_3 crucibles (100 μL capacity) under an argon atmosphere (flow rate of 50 mL/min). About 3-mg samples were heated to 400 °C at a rate of 5 K/min.

2.8 Critical diameter of detonation

Charges with diameters ranging from 6 mm to 20 mm (2 mm step) and 6 mm to 12 mm (1 mm step) were prepared by inserting plastic material into paper tubes and then placing the tubes on a metal plate as a reference (shown in Figure 4). Detonation was initiated directly using electric detonators.

2.9 Velocity of detonation

Velocity of detonation was measured by the electrocontact method. An explosive charge (10 mm in diameter) was put into a PVC tube cut lengthwise (shown in Figure 5). The cleavage of the tube enables precise positioning of four sensors, which were made of two twisted insulated copper wires. The sensors were placed at 25 mm distances from each other. Time measurement was initiated and recorded by the short-circuiting of the sensor wires. The detonation velocity was obtained as a ratio between the distance travelled and the corresponding time interval.

3 Results and Discussion

The mass ratio of components for the selected samples is shown in Table 1. The designation (1:1) is the ratio of the masses of both polymer additives relative to each other in the final mixture. The density of the prepared compositions was determined from their dimensions and masses. The values of density were in the range of 1.45-1.65 g/cm^3.

Table 1. Mass ratio of the components for selected samples

No.	Composition	Percentage of polymer [wt.%]	Density [g/cm^3]
1	FOX_{LC}/HMX_{LC} + ROKWIN 80	19.3	1.57
2	FOX_{SC}/HMX_{SC} + ROKWIN 80	21.9	1.51
3	FOX_{LC}/HMX_{LC} + Silicone HV	21.9	1.57
4	FOX_{SC}/HMX_{SC} + Silicone HV	26.6	1.66
5	FOX_{LC}/HMX_{LC} + Silicone MV	26.6	1.57
6	FOX_{SC}/HMX_{SC} + Silicone MV	30.5	1.61
7	FOX_{LC}/HMX_{LC} + PIB	20.6	1.55
8	FOX_{SC}/HMX_{SC} + PIB	18.0	1.66
9	FOX_{SC}/HMX_{SC} + Vaseline	23.1	1.47
10	FOX_{SC}/HMX_{SC} + PIB/Vaseline (1:1)	21.9	1.56
11	FOX_{SC}/HMX_{SC} + PIB/Silicone HV (1:1)	23.1	1.49
12	FOX_{SC}/HMX_{SC} + Poly(NIMMO)	24.8	1.56
13	FOX_{SC}/HMX_{SC} + Poly(NIMMO)/PIB (1:1)	23.1	1.53
14	FOX_{SC}/HMX_{SC} + Poly(NIMMO)/Silicone HV (1:1)	27.0	1.54
15	FOX_{SC}/HMX_{SC} + Poly(NIMMO)/Silicone MV (1:1)	28.6	1.55

The use of silicone greases allowed us to obtain mixtures characterized by the highest consistency in thermal stability. Later in the study, Poly(NIMMO) and PIB were also used. The observed behavior (shown in Figure 1), that is "the effect of perspiration", can occur as a result of a reduction in the viscosity of the polymer additives during heating.

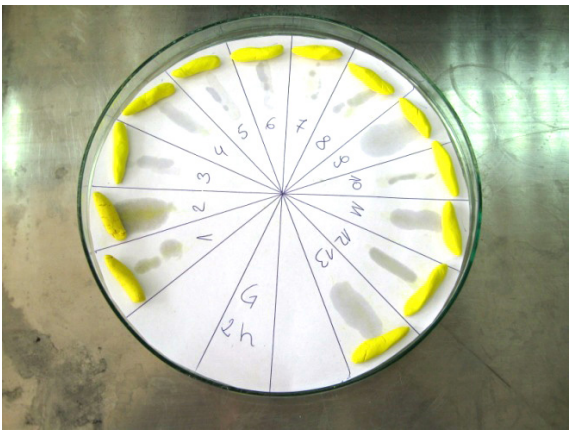

Figure 1. The effect of perspiration: the polymer separates from the mixture during the heat treatment. The markings on the image correspond to the numbers in Table 1.

All of the mixtures tested gave a positive result irrespective of the type of surface. However, compositions containing silicone greases remained on all surfaces much longer than others, thus exhibiting the best adhesion.

Results of the impact sensitivity expressed as the impact energy are presented in Table 2. For all the mixtures tested (with the exception of the more sensitive composition of FOX_{SC}/HMX_{SC} + Poly(NIMMO)) the impact sensitivity was very low (impact energy equal to 20 J or more). No friction sensitivity was observed up to a loading of 360 N for all the compositions tested (Table 2).

The DTA and TG thermograms obtained under these conditions are shown in Figures 2 and 3, respectively. A clear difference in the behavior during heating of the various compositions can be seen. Decomposition of samples containing Poly(NIMMO) began at lower temperatures, the exact value depending directly on the average molecular mass of the NIMMO. Usually the onset point of the exothermic decomposition of Poly(NIMMO) occurred between 150 °C and 200 °C. The sample without energetic polymer was more thermally stable and decomposed at temperatures corresponding to values obtained for pure FOX-7.

The influence of Poly(NIMMO) additive can be seen by comparing the mass loss of samples. The greatest amount of gaseous decomposition products (about 80% of mass lost) occurred when the mixture containing only energetic polymer additive was tested. As expected, the addition of silicone grease resulted in the smallest amount of gaseous products being formed. The mass losses of samples FOX_{SC}/HMX_{SC} + Poly(NIMMO)/Silicone MV and FOX_{SC}/HMX_{SC} + Silicone MV were 63% and 57%, respectively.

Table 2. Results of friction and impact sensitivity determination

Sample	Friction sensitivity [N]	Impact sensitivity [J]
HMX_{LC}	150	5.0
HMX_{SC}	185	4.0
FOX_{LC}	> 360	11.5
FOX_{SC}		19.5
Poly(NIMMO)		8.0
FOX_{LC}/HMX_{LC} + Silicone HV		20.5
FOX_{SC}/HMX_{SC} + Silicone MV		24.0
FOX_{SC}/HMX_{SC} + Poly(NIMMO)		14.0
FOX_{SC}/HMX_{SC} + Poly(NIMMO)/PIB		20.0
FOX_{SC}/HMX_{SC} + Poly(NIMMO)/Silicone HV		21.5
FOX_{SC}/HMX_{SC} + Poly(NIMMO)/Silicone MV		20.5

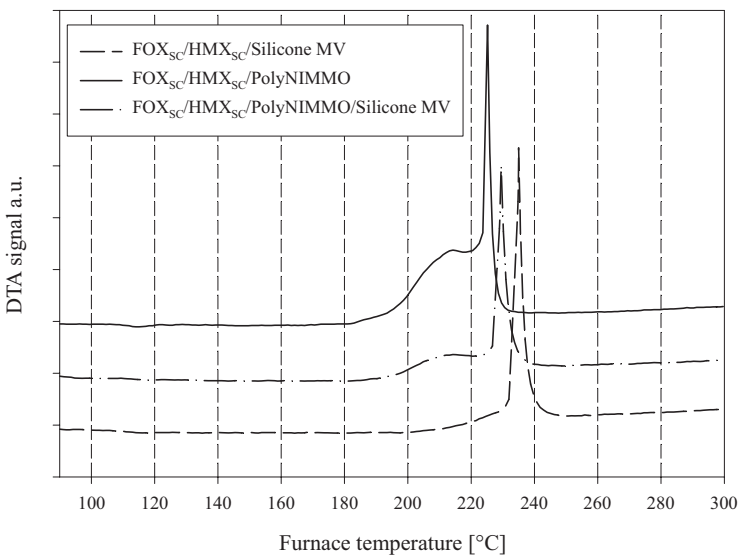

Figure 2. DTA thermograms for compositions containing silicone grease and/or Poly(NIMMO).

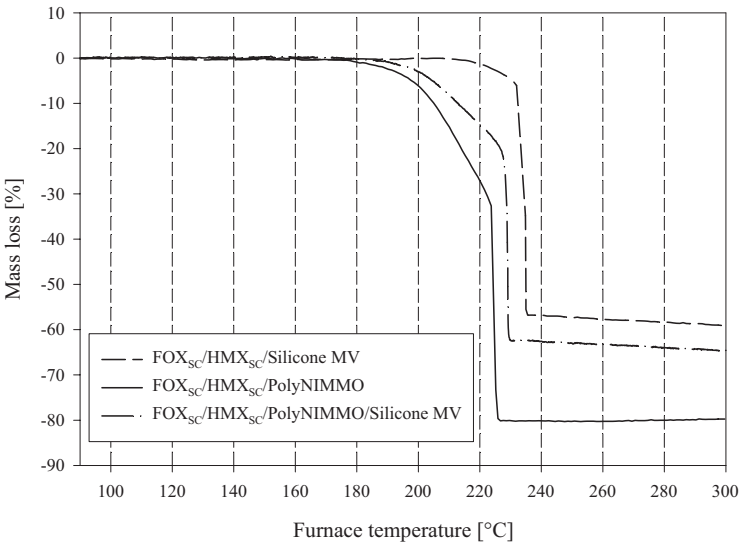

Figure 3. TG curves for compositions containing silicone grease and/or Poly(NIMMO).

The critical diameter of two selected compositions was determined. Samples containing only non-energetic silicone grease (FOX_{SC}/HMX_{SC} + Silicone MV) (No. 6) did not detonate up to the largest diameter (20 mm) used. For the mixture also containing energetic polymer (FOX_{SC}/HMX_{SC} + Poly(NIMMO)/ Silicone MV) (No. 15) the propagation of the detonation wave stopped after passing through the charge with a diameter of 7 mm.

We assumed that the preferred value for the critical diameter of a practically usable polymer bonded composition should be less than 10 mm. Only the mixture FOX_{SC}/HMX_{SC} + Poly(NIMMO)/Silicone MV satisfied this assumption.

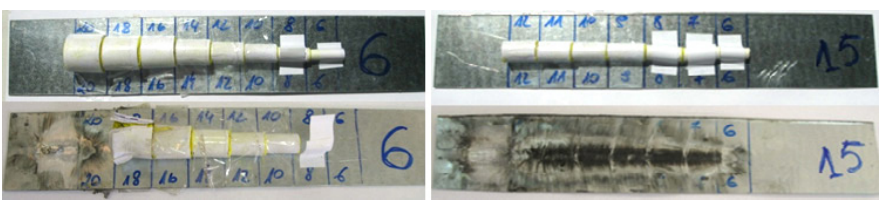

Figure 4. Examples of explosive charges prepared for critical diameter determination and traces on the plates formed after tests.

Velocity of detonation (VOD) was measured only for the most promising polymer bonded high-energetic material, that is the composition $FOX_{SC}/$

HMX_{SC} + Poly(NIMMO)/Silicone. The detonation velocity was determined to be 6960 ± 70 m/s (sample density of 1.55 g/cm^3). Table 3 contains theoretical values of detonation velocity (VOD_t), detonation pressure (PCJ_t) and temperature (T_t) calculated using the thermochemical code CHEETAH (parametrization − BKWC library) [28]. We found that the addition of PolyNIMMO as a high-energetic component had considerable influence on the explosive performance of the compositions investigated. However, the compositions FOX_{SC}/HMX_{SC} + Poly(NIMMO)/Silicone MV have the lowest density, which effectively reduced their VOD. Despite the non-ideal, heterogeneous nature of the mixture, experimental results corresponded satisfactorily with the calculated value.

Table 3. Calculated detonation properties of selected polymer compositions

Sample	Density [g/cm^3]	VOD_t [m/s]	PCJ_t [GPa]	T_t [K]
FOX_{SC}/HMX_{SC} + Silicone MV	1.61	6835	20.0	3730
FOX_{SC}/HMX_{SC} + Poly(NIMMO)	1.56	7585	22.2	3710
FOX_{SC}/HMX_{SC} + Poly(NIMMO)/Silicone MV	1.55	6830	19.5	3750

Figure 5. Explosive charge prepared for detonation velocity determination.

4 Conclusions

During the study, a group of over 30 different polymer bonded samples based on mixtures of FOX-7/HMX were investigated. After systematic study, samples which did not meet the pre-determined requirements (such as plasticity, homogeneity, mechanical and/or thermal stability) were excluded. The most promising compositions were subjected to thermal analyses, critical diameter and detonation velocity determination.

In the present paper we tried to answer the following question: Is it possible to obtain elastic polymer explosive charges with very low sensitivity to mechanical stimuli that are also characterized by high usable parameters? As we have shown,

the addition of silicone greases and the use of explosives such as FOX-7 and HMX with small crystals were important in obtaining the composition with desirable physical properties and stability. PolyNIMMO, as a typical compound contains nitric acid ester groups, is thermally more sensitive than others used in explosive compositions containing FOX-7 and HMX. Increasing the quantity in the compositions was found to have an influence on decreasing the stability but allows improvements in other usable parameters (*e.g*. detonation velocity and critical diameter).

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