Features of the incorporation of single and double based powders within emulsion explosives

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Features of the incorporation of single and double based powders within emulsion explosives

J B Ribeiro[1], R Mendes[1], B Tavares[1] and C Louro[2]

[1]ADAI/LEDAP - Assoc. for Dev. of Ind. Aerodynamics / LEDAP - Lab. Energetics and Detonics, Department of Mechanical Engineering, University of Coimbra, Rua Luis Reis Santos, Polo II, 3030-788 Coimbra, Portugal

[2]CEMUC - Centro de Engenharia Mecânica da Universidade de Coimbra, Department of Mechanical Engineering, University of Coimbra, Rua Luis Reis Santos, 3030-788 Coimbra, Portugal

jose.baranda@dem.uc.pt

Abstract. In this work, features of the thermal and detonation behaviour of compositions resulting from the mixture of single and double based powders within ammonium nitrate based emulsion explosives are shown. Those features are portrayed through results of thermodynamic-equilibrium calculations of the detonation velocity, the chemical compatibility assessment through differential thermal analysis [DTA] and thermo gravimetric analysis [TGA], the experimental determination of the detonation velocity and a comparative evaluation of the shock sensitivity using a modified version of the "gap-test". DTA/TGA results for the compositions and for the individual components overlap until the beginning of the thermal decomposition which is an indication of the absence of formation of any new chemical species and so of the compatibility of the components of the compositions. After the beginning of the thermal decomposition it can be seen that the rate of mass loss is much higher for the compositions with powder than for the one with sole emulsion explosive. Both, theoretical and experimental, values of the detonation velocity have been shown to be higher for the powdered compositions than for the sole emulsion explosive. Shock sensitivity assessments have ended-up with a slightly bigger sensitivity for the compositions with double based powder when compared to the single based compositions or to the sole emulsion.

1. Introduction

The problem that the possible re-use of demilitarized energetic material poses is significant, due to both technical and environmental reasons [1-2]. Among possible disposal alternatives for such materials, the solution of recycling for incorporation within commercial explosives has emerged in the last decade as an environmentally friendly and economically interesting possibility [3-5]. The economic benefits are due to both the amount of commercial explosive that is replaced by the demilitarized energetic material, and the reduction in the amount of material necessary to be incinerated.

The main purpose of this study is to evaluate the detonation features of the compositions resulting from the mixing of single and double base powders with Emulsion Explosives (EX). We are especially interested in the performance of the composition, evaluated with the theoretical and the experimental detonation velocity values, the shock sensitivity, evaluated using a modified version of the well-known Gap Test method, and the chemical compatibility of the mixtures, assessed by DTA/TGA tests and performed on mixtures and on their individual components.

2. Materials and methods

2.1 Materials

The studied compositions were: a standard EX, a mixture of a standard EX with 20% (w/w) of single base powder (SBP) which was previously ground and sieve cut at 500 μm (see figure 1), and a mixture of a standard EX with 20% (w/w) double base gun powder (DBP).

The AN-based emulsion used in this work was comprised of: AN, water, and a mixture of oil and emulsifiers with the mass percentages of 84/10/6. Such an emulsion presents an effective density of 1.38 g/cm^3 and an equivalence ratio of 1.01. The standard EX was sensitized with 5% (w/w) dicapearl microballoons (DMB) with a mean particle diameter of 70 μm. The sensitized EX presents an effective density of 1.18 g/cm^3.

The powder-EX samples were prepared by gradually adding and gently mixing the DMB with the pre-prepared powder-EX mixtures. The density of the sample obtained by this preparation method was evaluated by gravimetric methods with a maximum error of 1% (see table 1).

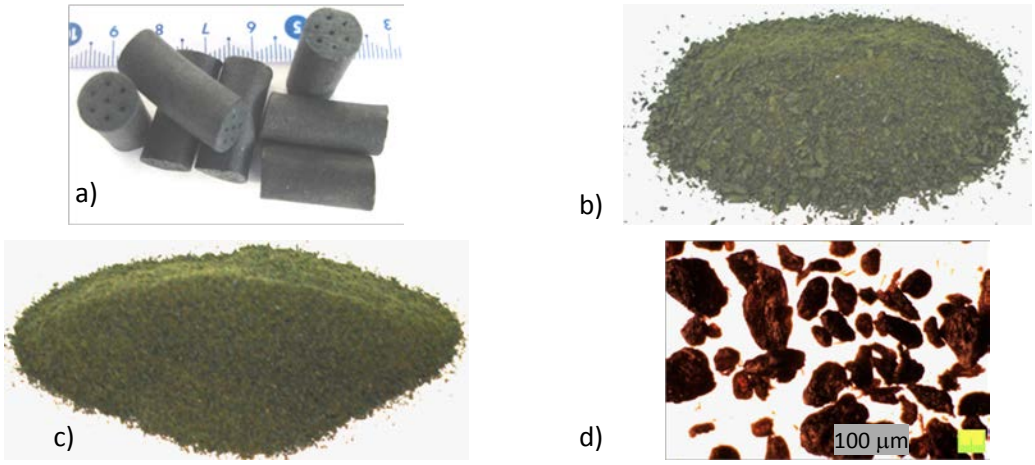

Figure 1. Single base powder: a) as received; b) grinded; c) sieve cut and d) optical microscope photo**.**

2.2 Experimental methods

The experimental determination of the detonation velocity, aiming to assess the compositions' performance and shock sensitivity, was conducted using 8 to 10 ionization pins positioned in a row, spaced 10 mm apart from one another. In these experiments, the compositions were confined within PVC tubes with an internal diameter of 25 mm and a wall thickness of 5 mm. Charges were initiated using a number 8 detonator.

Shock sensitivity was evaluated using a modified version of the Gap-Test which, for this specific assessment, uses the spatial evolution of the shock/detonation velocity on the acceptor charge, D = D(x). The ability of the detonation wave to more quickly reach its normal detonation velocity reflects the greater shock sensitivity of the charge.

The chemical compatibility between the gun powders and the emulsion explosive was assessed by both the differential thermal analysis, and the thermogravimetric analysis (DTA/TGA – Scientific Rheometrics 1500) of the individual components of the mixtures (EX, SBP and DBP) and of the mixtures themselves. The possible existence of chemical incompatibilities, which may result in the formation of new components, would appear as new pikes in the DTA/TGA data. The DTA/TGA tests were carried out using nitrogen as purge gas and a heating rate of 10 ºC/min. The mass of the samples tested ranged from 1 to 2 mg for the gun powders to 4 to 5 mg for the other samples.

Table 1. Calculated detonation velocity of prepared samples.

	Sample	ρ [g.cm^{-3}]	AN inert [%]	NC [%]	NG [%]	D_{cal} [m.s^{-1}]	D_{exp} [m.s^{-1}]
#1	EX	1.173	0	0	0	6047	4645
#1a	EX	1.173	17.6	0	0	4645	-
#3	EX+20% SBP	1.203	17.6	20	0	4885	4970
#4	EX+20% DBP	1.186	17.6	15	5	5019	5100

2.3 Theoretical calculations of the detonation velocity

The theoretical calculations of the detonation velocity of the different compositions that were experimentally tested in this study were performed using the CHEETAH code [6]. CHEETAH is a physics- and chemistry-based computational tool that can reliably predict the performance (e.g. detonation velocity, detonation pressure, and the detonation products' composition) of ideal and non-ideal high explosives and explosive formulations. In the version used in this work, CHEETAH calculations were based on traditional Chapman-Jouguet thermodynamic theory, which assumes that the thermodynamic equilibrium of the detonation products is reached at the sonic plane bounding the end of the exothermic reaction where all the reactants are consumed completely. For the standard EX, two kinds of calculations were performed. In one, the ammonium nitrate (AN) was considered to be fully reacting within the chemical reaction zone as an ideal explosive composition. In the other, as done by several authors (see, for example, [7, 8]), part of the AN was considered inert, or at least releasing its energy far away from the chemical reaction zone. In this last case the amount of AN considered inert was adjusted so that the value of the theoretical detonation velocity was equal to the value measured experimentally.

3. Results and discussion

3.1 Detonation process characterization

For the ideal situation, in which all the AN was considered to be reacting (sample #1) and releasing its energy within the chemical reaction zone as seen in ideal explosives, the calculated detonation velocity for an infinite diameter charge was found to be 6047 ms^{-1}, well beyond the value experimentally measured, which was 4645 ms^{-1} (see table 1). For sample #1a, in order to adjust the calculated value of the detonation velocity to that experimentally measured, a value as high as 17.6% of AN was considered inert. If part of the AN did not react within the detonation front, less energy is available to support the propagation of the detonation front and this would be reflected as a reduction of the detonation velocity. For samples #3 and #4, which incorporated 20% (w/w) of SBP and DBP respectively, it was found that the calculated detonation velocity was in both cases above (5.2% for the #3 and 8.1% for #4) the calculated value of sample #1a (see table 1). It should be mentioned that, in these calculations, the SBP was considered to be 100% nitrocellulose (NC), and the DBP was considered to be a mixture of 75% (w/w) NC and 25% (w/w) nitroglycerine (NG). The experimentally measured values of detonation velocity for samples #3 and #4 were higher than the calculated values (see table 1). The differences observed between the calculated and measured detonation velocity values can only be explained based on the presence of the powder. The reaction of the powder is believed to substantially enhance the reactivity of the AN. This means that a greater amount of AN will react within the chemical reaction zone when compared with a simple emulsion explosive, increasing the propagation velocity of the detonation front.

As referred, the shock sensitivity was evaluated through a modified version of the Gap-Test experiment. As a donor charge, a standard emulsion explosive (sensitized with 5% DMB), confined within a 150 mm long and 25 mm internal diameter tube with a 5 mm wall thickness, was used. The acceptor charge was confined within a 120 mm long PVC tube with the same internal diameter and the same wall thickness. This tube was filled with the composition being tested (the standard emulsion

explosive or the emulsion explosive mixed with single or the double base powders). The spacer used between the donor and acceptor was a 15 mm thick Polymethyl metacrylate (PMMA) disk.

The results obtained from the experiments performed as described above (presented in figure 2) allow us to identify in the acceptor charge the distance at which the normal detonation velocity is attained. Through the analysis of these results, is possible to state that the composition with DBP is the more sensitive one. The sensitivity of the other two compositions seems to be very similar.

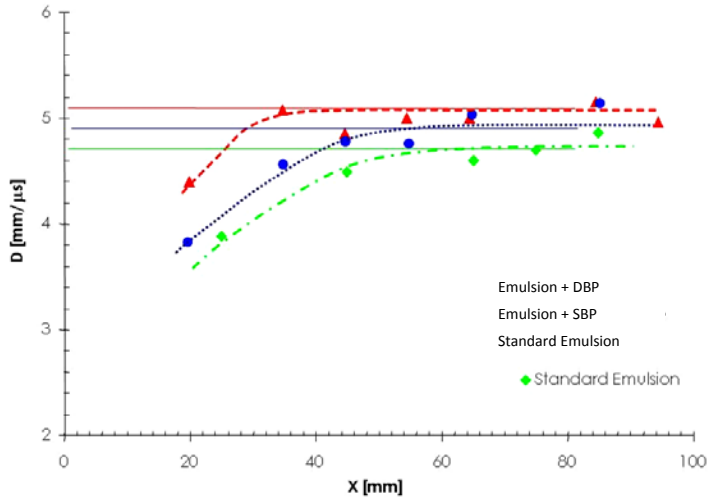

Figure 2. Evolution of the shock/detonation velocity in the acceptor charges as a function of the DF run propagation. The horizontal lines represent the detonation velocity for steady state DF propagation conditions.

3.3 Thermal analysis (DTA/TGA)

The DTA and TGA tests were first performed for individual components of the mixtures: the standard emulsion explosive, and the single based powders (results for the double based powders are not yet available). For use as a reference, a DTA/TGA test was also performed for pure ammonium nitrate.

The DTA and TGA curves for the AN are presented in figure 3a. The results obtained are typical, and are in agreement with the literature [9], showing three phase transitions. Almost no residue was found for this test. For the emulsion explosive, the same type of data is presented in figure 3b. Two of the AN phase transitions, as well as the melting endothermic peak, can clearly be seen at the same temperatures as those found for the AN. The onset of the thermal decomposition agreed with the value found for the AN. For the emulsion however, the mass loss at this point was greater than that which was found for the AN. This difference is believed to correspond with the evaporation of the emulsion water. A slightly larger amount of residue can be observed at the end of the thermal decomposition. The results for the SBP are shown in figure 3c. No phase transitions have been observed up to the onset of the abrupt and marked exothermic thermal decomposition at 185 ºC. The thermal decomposition ends up at 200 ºC, however it leaves a relatively high residue of about 30% of the initial mass.

The DTA/TGA results for the mixture of the emulsion explosive with the SBP powder are shown in figure 3d. All features of the thermal decomposition of the AN up to its melting point are identifiable. No other endothermic or exothermic peaks beyond the ones found for the emulsion and the AN are visible. The onset temperature of the thermal decomposition of the powder is kept at approximately 185 ºC. These results clearly indicate that no new chemical compound was formed upon the mixing of the emulsion explosive with the SBP. At the end of the thermal decomposition of the SBP (within the emulsion), is possible to observe an enhanced thermal decomposition of the AN. The mass loss at 185 ºC, about 40%, cannot be attributed only to the SBP. When compared to the results obtained for the emulsion (see figure 3b), an enhanced AN energy release due to the reaction of the SBP can be stipulated. This conclusion is in accordance with the observed increase of the

detonation velocity of the emulsion explosive mixed with the SBP when compared with the values of the standard emulsion explosive.

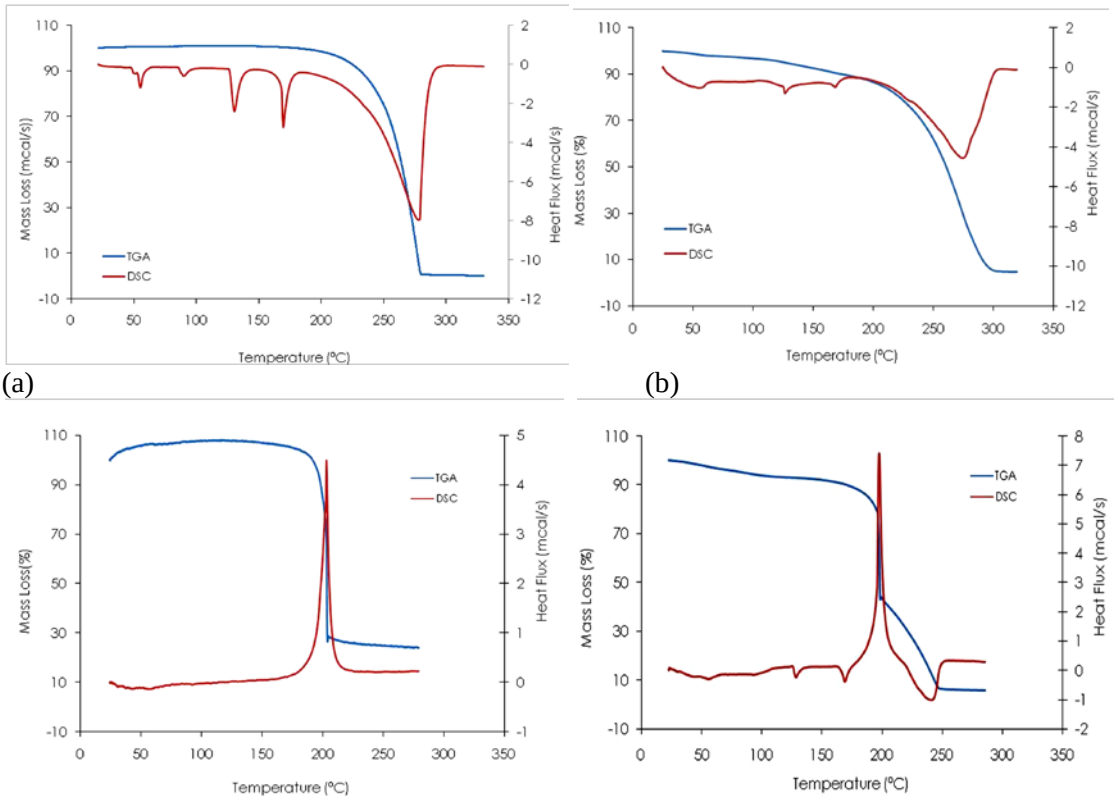

Figure 3. DTA and TGA curves for the: a) AN, b) emulsion explosive, c) single base powder and d) mixture of single base powder with emulsion explosive. All the experiments were performed at heating rate of 10 ºC/min.

4. Conclusion

The demilitarization path in which the demilitarized energetic materials are incorporated within civilian explosives has energetic and environmental advantages over the traditional incineration routes. For the particular case of the single based powder tested, its mixture with a commercial grade emulsion explosive does not show any chemical incompatibilities.

The presence of the single based powder changes the thermal decomposition behaviour of the emulsion explosive. Both compositions, with single and with double based powders, present a higher detonation velocity than the standard emulsion explosive. The addition of the double based powders to the emulsion explosives slightly increases its sensitivity.

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