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Studies on compatibility of energetic materials by thermal methods

Abstract: *The chemical compatibility of explosives, pyrotechnics and propellants with those materials is studied to evaluate potential hazards when in contact with other materials during production, storage and handling. Compatibility can be studied by several thermal methods as DSC (differential scanning calorimetry), TG (Thermogravimetry), VST (Vacuum stability test) and others. The test methods and well defined criteria are the most important elements when a compatibility study is being accomplished. In this paper, the compatibility of two very important high explosives used in ammunition, RDX (Cyclo-1,3,5-trimethylene-2,4,6-trinitramine) and HMX (Cyclotetramethylene tetranitramine) was studied with the materials: fluoroelastomer (Viton) and powdered aluminum (Al), using DSC and VST methods. The criteria to judge the compatibility between materials is based on a standardization agreement (STANAG 4147, 2001), and the final conclusion is that explosives and this materials are compatible, but in DSC it was observed that the peak of decomposition temperature of the admixture of RDX with Al decreased in 3° C and another peak appeared after the decomposition peak.*

Keywords: *Compatibility, Energetic materials, Differential scanning calorimetry, Vacuum stability test.*

INTRODUCTION

Energetic materials such as propellants, pyrotechnics and explosives have been studied for several years. The purpose of these studies is the development of new products and new utilities to these materials for military and non-military application.

Important information about behavior of energetic materials is acquired by thermal methods. This information is essential to a safe production, storage, handling and disposal. Thermal methods can be used to predict life time, to choose an adequate storage condition or to determine compatibility between materials.

As energetic materials are usually components of a system such as an armament or a rocket, and they are rarely used pure, the incompatibility reaction between the energetic material and the other components may accelerate the aging and alter the thermal stability of the energetic material itself, impairing the safety and functionality of the entire system. This could generate unexpected explosions due to decomposition reactions. Therefore, stability and compatibility of an explosive, as well as pyrotechnics and propellants, should be investigated carefully before they are manufactured and used with safety in technical applications (Vogelsanger, 2004).

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Klerk, Meer and Eerlingh (1995) defined the ideal of compatibility as the situation in which the materials do not react with each other even after long storage periods, in varied conditions. For practical reasons, materials are considered compatible if during and after a specific storage period the functionality and the safety of the components are still acceptable. An accomplished analysis in that way would consume a great period of time. For that reason, in practice, it is expected that reliable results for a compatibility investigation be obtained in a short period of time. The solution is the use of some tests based on accelerated aging at higher temperatures such as the measurement of gas liberated after heating under vacuum using the VST technique (vaccum stability test), the study of continuous effects of heating using the DSC technique (differential scanning calorimetry), the study of the mass loss with heating using the TGA technique (thermogravimetric analysis) and others. Among the mentioned methods, the vacuum stability is perhaps the most frequently used. It is considered a basic method used for high explosives, propellants and gunpowder, being complemented by a repeated examination after accelerated storage, and DSC is routinely used to detect cases of gross incompatibility (May, 1978). Vacuum stability test can be accomplished with different pieces of equipment, where the pressure generated by the gasses is measured using mercury manometer or other pressure meters (Chovancová and Zeman, 2007).

According to Silva (2003), the thermal analysis methods are the mostly used for the characterization and study of the decomposition and compatibility of explosives. Recently, Sorensen, Konott and Bell (2008) affirmed that it is necessary to pay attention to safe shelf life of energetic materials, and using thermal methods to compatibility studies of materials over extended periods has been readily accepted.

The main advantages of the thermal analysis techniques aiming at compatibility tests in energetic materials are the use of small amounts of material and quicker measurements (Klerk, Schrader and Steen, 1999). In spite of the advantage presented in the use of thermal analysis, STANAG 4147 suggests the use of more than one test method for evidence compatibility, as found in the studies on the explosive TNAD (trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin), in which besides the technique of DSC, other methods as DTA / TG or VST were employed for confirmation when obtaining incompatible results of that explosive with inert or energy materials (Yan *et al.*, 2008).

When using DSC as a technique to determine the compatibility, the results obtained for the pure product in the parameters of decomposition temperature and the format of the peak are compared to the results obtained for the mixtures. If the peak regarding mixture moves for temperatures lower than the peak regarding the energetic material or the material in test, it is an indication incompatibility. The incompatibility degree is measured by the difference of temperature among the peaks. In the vacuum stability test, the volume of liberated gas, when the mixture of parts is similar to an explosive and the materials in test are heated at 100°C for 40 hours, is compared to the volume of gas liberated by the energetic material and the material in test when heated separately, in identical conditions. The compatibility is evaluated through the volume of additional gas produced due to the contact between the two components of the mixture (STANAG 4147, 2001).

The energetic materials RDX and HMX are two important explosives used in armaments and as energy components of propellants composites. They are usually incorporate to curable plastic materials, forming the plastic explosives. The powdered aluminum is frequently incorporate to the explosives to increase their efficiency with considerable earnings in explosion heat and obtainment of higher temperatures for the formed gases (Meyer, Köhler and Homburg, 2002).

The military use of explosives demands a high destruction power, but it has to be safe and easy to handle as well as stock-piled for long periods of time, even in adverse climatic conditions. These explosives should be hard to detonate, except in conditions of programmed detonation. Another important characteristic is that military explosives have to be loaded into armaments as shells, bombs, missiles and others without difficulties (Mathieu and Stucki, 2004).

To check if RDX and HMX accomplish the requirements, studies of compatibility between these explosives with other materials are necessary. This paper describes the compatibility studies of RDX and HMX relating to a fluoroelastomer (Viton) and to powdered aluminum (Al) using DSC and Vacuum stability tests in order to verify alterations in the thermal stability and the temperature of decomposition of the explosive, as well as alteration in the volume of gas liberated due to presence of inert material or aluminum.

The results obtained for the pure product and for the mixtures (RDX+ Viton, RDX + Al, HMX + Viton, HMX + Al) are herein reported. The methods employed were compared in relation to the reliability of the results.

MATERIALS AND METHODS

Material

RDX (80-120 #) was commercially obtained from IMBEL Company, and HMX (CL 1) was commercially obtained from SNPE Materiaux Energetics. Viton is the trade name of the series of fluoroelastomers manufactured by DuPont Dow Elastomeros Ltda. The aluminum PO 123 (Al) was obtained from Alcoa Company. All the materials were used as supply and were dried previously in a greenhouse at 60°C, in order to eliminate humidity.

Methods

For DSC test, the equipment used was the thermal analyzer DSC PerkinElmer-7 Series Thermal Analysis System, previously calibrated in the reason of heating of 2°C/min, with Indium. Individual sample masses of 1 mg were used, weighed directly in closed crucibles made from aluminium with a pinhole in the cap. For the mixture, 1 mg of the explosive and 1 mg of the material to be tested were directly weighed in the crucibles, so that the two materials were in contact. The heating reason was of 2°C/min, with strip of room temperature at 320°C for the samples with HMX and 270°C for the samples with RDX. The tests were carried out under inert atmosphere, with nitrogen in the flow of 50 mL/min. The results represent an average of three results.

The vacuum stability test is presented in the literature under the acronym VST and it can be accomplished with

several kinds of meters. For this study the vacuum stability test was accomplished according to the method used at the Chemical Laboratory of *Divisão de Sistemas de Defesa* (ASD) of *Instituto de Aeronáutica e Espaço* (IAE). In that test, denominated Chemical Vacuum Stability, the equipment employed consisted of thermostatic block of aluminum with cylindrical lodgings capable of maintaining the temperature in the limits of 100ºC + 0.5º, vacuum bomb with capacity up to 5 mmHg, glass group composed of capillary heating tube where there are the mercury columns and measurement support, with scale in millimeters. We weighed 2.5 g of each sample for the tests with the individual product. For the admixture, 2.5 g of the explosive and 2.5 g of the material whose compatibility is being evaluated were weighed. The equipment was prepared to previously reduce to zero the mercury column, and the samples were warmed under vacuum at 100ºC for 40 hours. The results show the amount of gas liberated, representing an average of three results.

The calculation of the gas volume released by the mixture and by the explosive material when heated individually was done using the formula presented in STANAG 4147, shown by Equation 1.

$$V_R = M - (E + S) \quad (1)$$

Where:

V_R = volume of gas produced as result of the reaction between the components of the test mixture.
M = volume of gas liberated from 2.5 g of explosive mixed with 2.5 g of the test material (mL, at STP).
E = volume of gas liberated from 2.5 g of explosive (mL, at STP).
S = volume of gas liberated from 2.5 g of test material (mL, at STP).

RESULTS AND DISCUSSION

The compatibility study consists of observing alterations when an explosive and inert material such as Viton or a material that increases the supply of energy such as aluminum are put together in thermal conditions that can alter chemical stability. If no alterations are observed, it indicates that the materials are compatible in the conditions of the test that tries to simulate the aging of the explosive aiming at guaranteeing the safety in its handling, storage and use.

In the study of compatibility of RDX with Viton, the DSC curves for pure RDX, pure Viton and RDX mixed with Viton are presented in Fig. 1. In the pure RDX DSC curve appears a sharp endothermic peak temperature of 205ºC and, immediately after, a wide exothermic peak temperature of 225ºC is observed. The first peak (endothermic) corresponds to the melting process and the second peak (exothermic) corresponds to the decomposition process (Pinheiro, 2003).

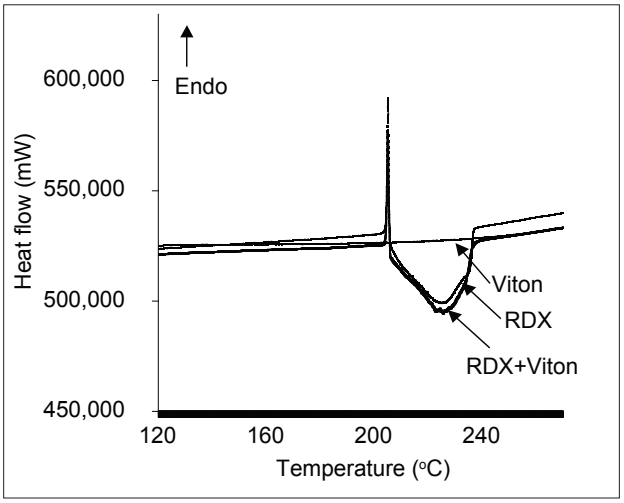

Figure 1: DSC curves of RDX, Viton and mixed RDX + Viton at a 2ºC min^{-1} heating rate.

The Viton DSC curve does not show any peak in the decomposition area of RDX. For the mixture between RDX with Viton, the DSC curve did not show alteration in the corresponding melting temperature and the corresponding decomposition temperature, indicating compatibility between the materials. The compatibility indication is confirmed because there is no alteration in the peak format or new peaks, and the decomposition peak begins at the same temperature with and without Viton.

For the compatibility study of the mixture of RDX with Al, the DSC curves are presented for pure RDX, pure Al and RDX with mixed Al. The endothermic peak temperature regarding the melting process is of 205ºC, the exothermic peak temperature regarding the decomposition process of RDX is of 225ºC and the exothermic peak temperature regarding the decomposition temperature of the mixture of RDX with Al is of 222ºC, as it can be observed in the Fig. 2. The aluminum does not present any peak in the decomposition area of RDX.

According to criteria established by STANAG 4147, temperature variation of 4ºC or more would be indicative of incompatibility; therefore, RDX and the aluminum would be considered compatible. However, it is observed that beyond the small displacement in the decomposition temperature, a new peak appears, in the temperature of 233ºC, which is a significant alteration, demanding further investigation before using that mixture. As that peak appears after the decomposition temperature, it can be an indicative of secondary reactions happening between products of the decomposition of RDX and Al (Antic

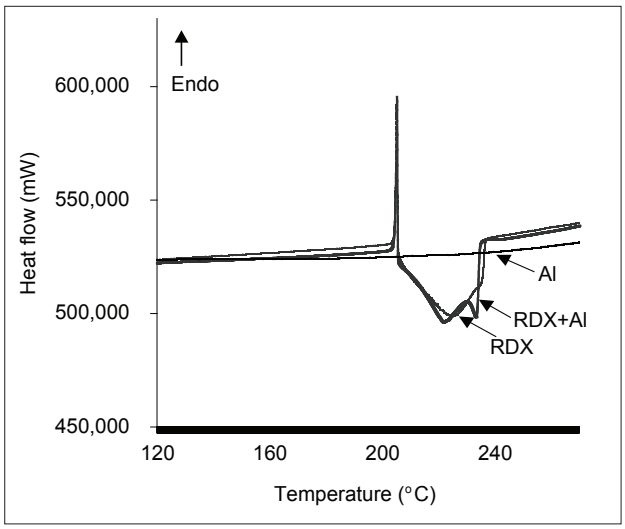

Figure 2: DSC curves of RDX, Al and mixed RDX + Al at a 2°C min^{-1} heating rate.

and Dzingalasevic, 2006;Keicher, Happ and Kretschmer, 1999). To obtain more data on Al possible interference in RDX, the compatibility study may be carried out using other methods such as TG before affirming that RDX and the aluminum are totally compatible.

In the studies with HMX, the DSC curves present small endothermic peaks in the strip from 170 to 190°C, which correspond to the crystalline transition of the β-HMX for the form crystalline δ-HMX (Pinheiro, 2003). The exothermic peak temperature of 274°C indicates the decomposition of HMX with the presence of a small peak before the main peak. The presence of Viton do not show any interference in the peaks of crystalline transition, as it can be observed in the Fig. 3, in which the curves DSC of HMX with Viton, pure HMX and pure Viton are presented.

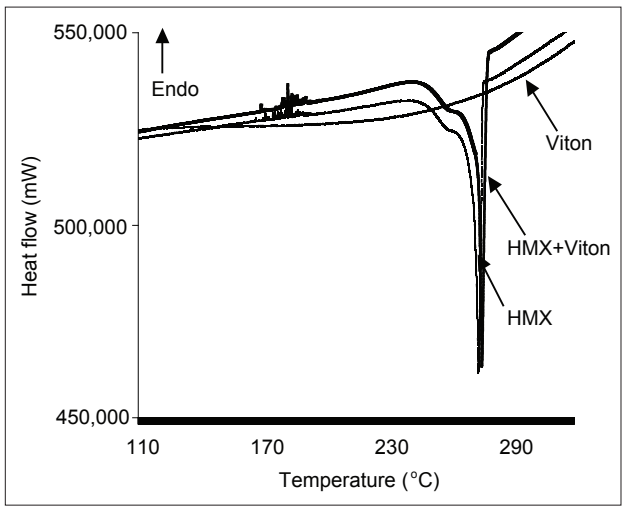

Figure 3: DSC curves of HMX, Viton and mixed HMX + Viton at a 2°C min^{-1} heating rate.

In the same way, the mixture with aluminum do not present variation in the results, and it can be observed in the DSC curves of HMX with Al, pure HMX and pure Al, as illustrated by Fig. 4.

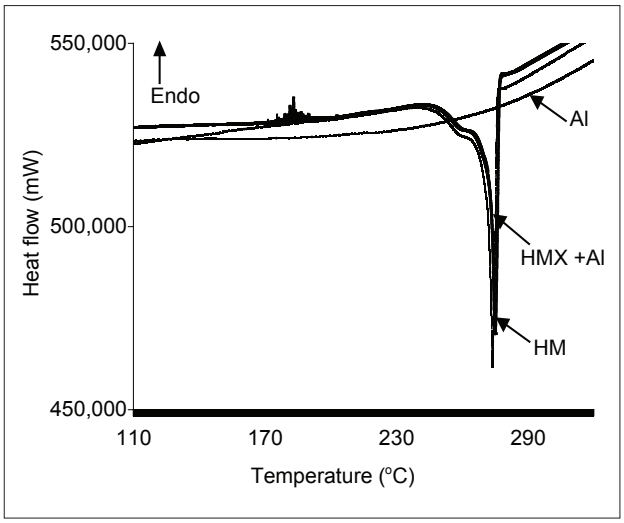

Figure 4: DSC curves of HMX, Al and mixed HMX + Al at a 2°C min^{-1} heating rate.

The presence of Viton or aluminum did not bring significant alterations for decomposition temperature, being in 275°C, in the mixture with the aluminum and in 276°C in the mixture with Viton. In the mixture with Viton, a small displacement of the peak appears, albeit no change in the format was observed. The existent peak of HMX decomposition before the exothermic peak also did not present alteration when the pure product and the mixtures were compared. Therefore, HMX presents indication of compatibility with Viton as well as with aluminum.

Table 1 displays the DSC values obtained for decomposition temperature of the pure explosives and of the mixture, as well as the observations about peaks alterations.

Table 1: Decomposition temperatures obtained by DSC and alterations observed on peaks of the explosives.

	T decomposition (°C)	**Format alterations on peaks**
RDX	225.3 ± 0.6	--
RDX + Viton	225.1 ± 1.0	None
RDX + Al	222.0 ± 1.0	New peak, after decomposition peak
HMX	274.0 ± 0.4	--
HMX + Viton	275.8 ± 0.3	None
HMX + Al	274.7 ± 0.4	None

Vacuum stability

The results of vacuum stability test provide the volume of liberated gas at 100ºC for 40 hours by HMX, RDX, Viton e Al and mixtures RDX + Al, RDX+Viton, HMX + Al and HMX + Al, as well as the difference between the pure products and the nixture.

Table 2 presents the volume of gas liberated, calculated through Eq. 1. The mixture of RDX with Al presents the largest increase in volume of gas liberated (0.75 mL), indicating that the aluminum alters the amount of liberated gas, but it cannot be considered to be indicative of incompatibility. The STANAG 4147 defines as a criterion for compatibility a maximum variation of 5 mL in the standard temperature and pressure conditions (STP) when materials are mixed and tested with the vacuum stability test; the difference is calculated between mixture and pure products. The values found for the mixtures are lower than 1 mL (STP), indicating compatibility of RDX with Viton, RDX with Al, HMX with Viton and HMX with Al.

Table 2: Volume of gas liberated obtained by the vacuum stability test.

	Volume of gas liberated (mL)	Value of volume of gas liberated by the mixture (mL)
RDX	0.07 ± 0.02	---
HMX	0.33 ± 0.00	--
Al	0.10 ± 0.01	---
Viton	0.05 ± 0.04	---
RDX + Al	0.92 ± 0.02	0.75 ± 0.02
RDX + Viton	0.60 ± 0.02	0.48 ± 0.04
HMX + Al	0.96 ± 0.03	0.53 ± 0.03
HMX + Viton	0.48 ± 0.01	0.10 ± 0.04

The greatest advantage of vacuum stability test in relation to DSC is the sample quantity. While in DSC amounts of samples are around 1 mg of each material to be studied, the vacuum stability test was accomplished with 2.5 g of each material, which increases the possibility of physical contact between them. However, the vacuum stability presents some disadvantages, mainly due to the use of mercury, a highly poisonous product, and to the consuming of a great amount of time in the handling and preparation of the test, completion of the column and cleaning of the mercury, all procedures that should be done very carefully.

A summary of the results obtained for the compatibility study are presented in Table 3.

Table 3: Summary of results obtained for the compatibility study using DSC and vacuum stability test.

	DSC		Vacuum stability test	
	Viton	Al	Viton	Al
RDX	C	C*	C	C
HMX	C	C	C	C

*A new peak appears after RDX decomposition peak.
C: Compatible.

CONCLUSION

To initiate a compatibility study, normally the DSC technique is used because it is faster and provides enough information to define the need of deeper studies; however, ideally, one should use two or more techniques for confirmation of compatibility among materials. As the results can vary using different equipment and different laboratories, the criteria, established in STANAG 4147, cannot be considered to be absolute. The careful analysis of the obtained results and the knowledge of the behavior of the materials provide more reliable criteria to evaluate the compatibility of systems.

The compatibility of the systems RDX with Viton, RDX with aluminum, HMX with Viton, HMX with aluminum was studied using the thermal methods: DSC and vacuum stability test. All systems were found to be compatible according to STANAG 4147. However, the mixture RDX and HMX Al may be considered relatively less compatible than the other mixtures, and this must be taken into account when ammunition is being developed and new applications are being studied.

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