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COMPATIBILITY TESTING OF ENERGETIC MATERIALS AT TNO-PML AND MIAT

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Abstract

Compatibility is an important property for energetic materials and their additives such as a casing material or a binder. If these substances are incompatible an extra risk is introduced in handling and storage of ammunition and explosives. As part of a co-operation program between the Dutch TNO-PML and the Polish MIAT several compatibility tests are performed and compared with each other. All tests are performed according to a NATO Standard in which several tests are described which can be used to determine the compatibility of an energetic material and an additive. These tests were performed on a huge set of energetic materials e.g. propellants (single and double base), explosives (RDX, PETN, HMX and TNT) and several additives like Teflon, polypropylene, self-burning case, inhibitors etc. The results of pressure vacuum stability tests, dynamic thermogravimetry measurements and differential scanning calorimetry tests with several combinations of energetic materials and additives used during the co-operation program are presented and discussed.

Keywords: compatibility, DSC, explosives, propellants, PVST, TG

Introduction

The purpose of a compatibility test is to provide evidence that a material may be used in an item of ammunition without detriment to the safety or reliability of an explosive with which it is in contact or proximity.

There are two classical examples showing non-compatibility of two elements of parts of ammunition: explosive and 'inert' material. For example, the reaction of picric acid with the steel coat of shells or lead parts of ammunition gives iron picrate or lead picrate. Those compounds are very sensitive to mechanical stimuli as impact or friction. The formation and presence of these chemical compounds were the reason of many accidents. Artillery shells containing iron picrate exploded during the transportation and loading into the guns. Because of the very poor ballistic parameters of these shells they also show failures during firing such as an early explosion [1].

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The second example is the migration of nitroglycerine from gun or mortar propellant to the adjacent environment (inhibitor or self-burning containers). Nitroglycerine migration causes decrease of energetic characteristics and as a consequence a decrease of ballistic properties of propellants [2, 3].

TNO-PML and MIAT had a co-operation program during the last three years about the stability and safety of munitions and explosives [4]. A part of this program was to build up experience with compatibility techniques and methods as described in STANAG 4147 [5].

TNO-PML performed vacuum stability tests (VST) and thermogravimetry (TG) measurements and MIAT performed differential scanning calorimetry (DSC), TG and VST measurements. All experiments were performed on several explosives and propellants (single base and double base) with seven different additives.

After finishing the measurements the results from the different compatibility tests were compared and merits of the test methods are described. This comparison already lead to one presentation of a small part of the results presented in this paper [6]. In some other literature these techniques have been described [7, 8].

Experimental

All measurements are performed according to STANAG 4147. Although STANAG describes several methods to determine compatibility (vacuum stability test (VST), heat flow calorimetry (HFC), TG, DSC and chemical analysis (CA)), three methods have been used in the program. Those are VST, TG and DSC. The details about the methods are described in the chapter ‘Techniques’.

The most preferred test method is the VST, because it is a well-known test, the criteria are widely accepted and it is a relatively short test. The amount of sample used in this test is much more representative than the amount used in e.g. TG or DSC. Of course VST has also some drawbacks with nitrate ester based propellants (e.g. a negative extra gas evolution). Therefore it is always necessary to perform extra tests when needed.

Techniques

Vacuum stability test

The volume of gas evolved, when a mixture of equal parts of the energetic material and additive is heated at a constant temperature of 100°C for 40 h (80°C and 240 h for double base propellants) in an initial vacuum, is compared with the volumes evolved from the energetic material and the additive when heated separately under otherwise identical conditions. Compatibility is judged by means of the volume of additional gases produced because of the contact between the two components of the mixture. The evolved gas volume can be determined by means of a mercury capillary (MVST) or with a pressure transducer (PVST). At TNO-PML the transducer method is used.

The gas production is calculated according the following formula:

$$V=\left(V_{\mathrm{c}}+V_{\mathrm{t}}-\sum\frac{m_{\mathrm{i}}}{d_{\mathrm{i}}}\right)\left(\frac{P_2\cdot 273}{273+t_2}-\frac{P_1\cdot 273}{273+t_1}\right)\frac{1}{1.013} \quad (1)$$

in which

V	volume of gas liberated from the sample at STP/mL
V_c	volume of the transducer and adapter/mL
V_t	volume of the heating tube/mL
P_1	calculated pressure at the beginning of the test/bar
P_2	calculated pressure at the end of the test/bar
t_1	room temperature at the beginning of the test/°C
t_2	room temperature at the end of the test/°C
m_i	mass of each substance tested/g
d_i	density of each substance tested/g mL^{-1}

Compatibility is calculated with the following formula

$$V_{\mathrm{R}}=M-(E+S) \quad (2)$$

in which

V_R	volume of gas produced as a consequence of reaction between the components of the test mixture at STP/mL
M	volume of gas from 2.5 g of energetic material mixed with 2.5 g of additive at STP/mL
E	volume of gas from 2.5 g of energetic material at STP/mL
S	volume of gas from 2.5 g of additive at STP/mL

V_R may not exceed 5 mL at STP; otherwise the mixture is incompatible. If V_R is between 3 and 5 mL at STP, another method is recommended to perform an extra compatibility measurement. A scheme of the apparatus used at TNO–PML and MIAT is given in Fig. 1.

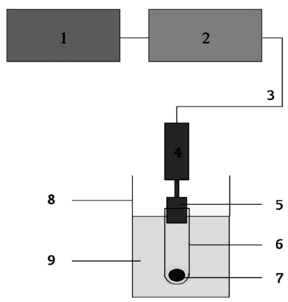

Fig. 1 Pressure vacuum stability test, schematic; 1 – computer, 2 – data acquisition unit, 3 – data cable, 4 – pressure transducer, 5 – extension part, 6 – glass tube, 7 – sample, 8 – oil bath and 9 – oil

Thermogravimetry

The difference between the observed mass loss and the total calculated mass loss of the energetic material and the additive in the mixture at the derivative TG peak temperature of the mixture is noted. If the observed mass loss of the mixture is more than 4% greater than that of the sum of the individual energetic material/additive (total calculated), then this is an indication of incompatibility. If the observed mass loss is between 4 and 20% another method is recommended to perform an extra compatibility measurement. If the observed mass loss is >20% the mixture is incompatible.

The test conditions are as follows

Apparatus	Seiko TG/DTA 320 (TNO–PML) and Shimadzu TG 50 (MIAT)
Heating rate	2°C min^{-1}
Atmosphere	Nitrogen, 50 mL min^{-1} (TNO–PML) and air, no flow (MIAT)
Sample cups	Aluminium open pans
Sample mass	~10 mg

Differential scanning calorimetry

The samples are heated with a heating rate of 2°C min^{-1}. Shifts in peak temperature of a single exotherm corresponding to the decomposition of the energetic material are examined. A shift in this peak temperature indicates an interaction between the energetic material and the additive. If the shift of the peak is towards a lower temperature, this indicates that the presence of the additive has accelerated the decomposition of the propellant. If the shift in peak temperature is more than 20°C the mixture is incompatible. If the shift in peak temperature is between 4 and 20°C another method is recommended to perform an additional compatibility measurement.

The test conditions are as follows

Apparatus	Shimadzu DSC 50
Heating rate	2°C min^{-1}
Atmosphere	Air, no flow
Sample cups	Aluminium open pans
Sample mass	~2 mg

Sample description

Several propellants and explosives are used in the test programme. Both parties delivered some substances. A description of all the samples and their pre-treatment is given in Table 1.

Table 1 Samples used in the test program

Sample description	Pre-treatment
	Delivered by MIAT
KB 7305, single base propellant	Ground
KB 7306, double base propellant	Cut into pieces and ground
RDX	None
TNT	Sliced and cut into pieces
Tarflen (=Polish teflon)	None
Polypropylene	Cut with scissors into pieces
Self-burning case	Cut into pieces and ground
Inhibitor for double base propellants	Cut with a knife into pieces
Inhibitor single base propellants	Cut with a knife into pieces
Mixture – RDX/Tarflen 96/4 *m*/*m*%	None
Mixture – double base propellant with inhibitor	DB propellant is cut off with a knife into pieces
Mixture – single base propellant with inhibitor	SB propellant is cut off with a knife into pieces
	Delivered by TNO–PML
KB 7071, single base propellant	None
KB 6917, double base propellant	Ground
HMX	None
PETN	None
Teflon membrane	Cut with scissors into pieces
Nylon 6/6	None
Cotton bag for propellants	Cut with scissors into pieces
Aluminium tape	Cut with scissors into pieces

Results

Vacuum stability test results

The extra gas production (Vr) calculated from the PVST measurements according to formula 1 for all the mixtures measured are given in Tables 2 and 3. The measurements, which are performed at MIAT, are included in Table 2. These measurements have been performed in the same way as at TNO–PML and with the same kind of equipment. This PVST equipment was installed at MIAT by TNO–PML as a part of the co-operation program.

Table 2 Results mixtures with propellants

Sample	*Vr*/mL						
	KB 7305	KB 7305, ground	KB 7071	KB 6917	KB 7306	DB propellant	SB propellant
Tarflen	–0.01	0.49	–0.01/0.15*	–1.60	–0.26	–	–
Polypropylene	0.26	0.06	0.19/0.70*	–1.39	–0.09	–	–
Self-burning case	0.17	–0.03	–0.13	–3.48	0.41	–	–
Teflon	–0.13	0.63	0.04	–1.67	0.22	–	–
Nylon 6/6	–0.14	–0.10	–0.11	0.59	1.68	–	–
Cotton bag	0.10	0.30	0.12	–1.12	0.96	–	–
Aluminium tape	4.04	–0.05	1.45	–3.24	0.20	–	–
Inhibitor SB	–	–	0.20*	–	–	–	–0.25
Inhibitor DB	–	–	0.32*	–	–	–1.60	–

*measurement performed at MIAT

Table 3 Results mixtures with explosives

Sample	*Vr*/mL			
	RDX	TNT	HMX	PETN
Tarflen (1:1)	–0.13	–0.24	0.02	0.28
RDX:Tarflen (96:4)	–0.58	–	–	–
Polypropylene	–0.10	–0.20	0.29	0.23
Self-burning case	–0.04	1.32	0.10	0.41
Teflon	–0.30	0.37	0.00	0.29
Nylon 6/6	–0.10	0.38	0.26	0.01
Cotton bag	–0.16	0.11	0.02	–0.02
Aluminium tape	0.94	–	0.60	1.16

In Fig. 2 a typical PVST result is shown. The figure shows raw pressure data *vs.* time. With the pressure at the beginning and the end of the experiment, the gas production can be calculated according formula 1. With formula 2 the extra gas volume (*Vr*) produced by the mixture is calculated.

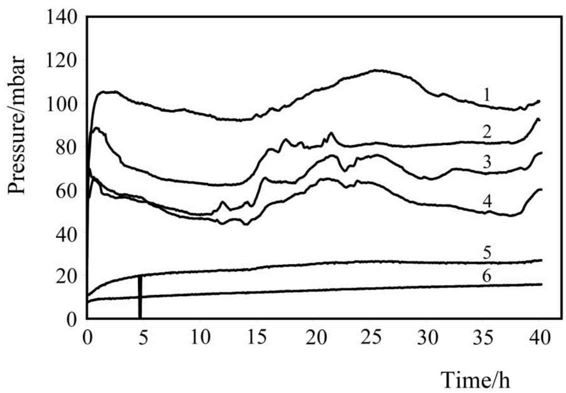

Fig. 2 A typical PVST result. 1 – KB 7305/Alu tape, 2 – KB 7305/Nylon 6/6, 3 – KB 7305, 4 – Nylon 6/6, 5 – Blank and 6 – TNT

Thermogravimetry results

The results from thermogravimetry measurements performed at MIAT and TNO–PML are presented in Table 4.

A positive mass loss difference (MLD) means that the mixture has a lower mass loss than the calculated mass loss from the two components of the mixture together. This means that the additive has no influence on the stability of the mixture (the mixture is compatible). A negative MLD is an indication for incompatibility. The exact criteria are given in chapter 'Techniques'.

Table 4 TG results

	MLD/%					
	KB 7305	KB 7071	KB 7306	KB 6917	RDX	TNT
Tarflen	0	–2	–3	2	0	1
Teflon	2	–1 (33*)	–4	1	1	5
Polypropylene	–4	3	–6	4	–34/–22	–3
Cotton bag	2	2	3	3	4	–4
Aluminium tape	3	–4	1	2	–21	–11
Nylon 6/6	3	–3	1	2	–9	5
Inhibitor SB	2	1	3	1	–	–
Inhibitor DB	2	–5	1	1	–	–

*measurement performed at TNO–PML

Differential scanning calorimetry results

All DSC measurements have been performed at MIAT. The results of these measurements are presented in Table 5. A positive temperature shift (*Td*) means that the mixture gives a higher decomposition temperature than the energetic compound itself. This means that the mixture is compatible. A negative temperature shift is an indication for incompatible. Again the exact criteria are given in the chapter 'Techniques'.

Table 5 DSC results

	Td/°C					
	KB 7305	KB 7071	KB 7306	KB 6917	RDX	TNT
Tarflen	3	1	–1	2	1	2
Teflon	1	2	–3	1	1	2
Polypropylene	2	–5	–5	3	–6	3
Cotton bag	1	0	–3	1	0	–3
Aluminium tape	4	–1	2	0	–9	–1
Nylon 6/6	2	–4	–2	1	–22	0
Inhibitor SB	0	–1	–1	3	–	–
Inhibitor DB	1	1	–2	1	–	–

Comparison of different methods

In Tables 6 and 7 a comparison is made with the three different methods performed in the two institutes.

The letters in the tables are codes, which stand for Y=yes, compatible; N=no, incompatible; G=grey area, another method is recommended.

Table 6 Overall results, mixtures with propellants

Method	KB 7305			KB 7071					KB 7306			KB 6917			SB propellant	DB propellant
	1	3	4	1	2	3	4	5	1	3	4	1	3	4	1	1
Tarflen	Y	Y	Y	Y	–	Y	Y	Y	Y	Y	Y	Y	Y	Y	–	–
Polypropylene	Y	Y	G	Y	–	G	Y	Y	Y	G	G	Y	Y	Y	–	–
Self-burning case	Y	–	–	Y	–	–	–	–	Y	–	–	Y	–	–	–	–
Teflon	Y	Y	Y	Y	Y	Y	Y	–	Y	Y	G	Y	Y	Y	–	–
Nylon 6/6	Y	Y	Y	Y	–	G	Y	–	Y	Y	Y	Y	Y	Y	–	–
Cotton bag	Y	Y	Y	Y	–	Y	Y	–	Y	Y	Y	Y	Y	Y	–	–
Aluminium tape	G	Y	Y	Y	–	Y	G	–	Y	Y	Y	Y	Y	Y	–	–
Inhibitor SB	–	Y	Y	–	–	Y	Y	Y	–	Y	Y	–	Y	Y	Y	–
Inhibitor DB	–	Y	Y	–	–	Y	G	Y	–	Y	Y	–	Y	Y	–	Y

1 – PVST TNO–PML, 2 – TG TNO–PML, 3 – DSC MIAT, 4 – TG MIAT, 5 – PVST MIAT

Table 7 Overall results, mixtures with explosives

Method	RDX			TNT			HMX	PETN
	1	3	4	1	3	4	1	1
Tarflen	Y	Y	Y	Y	Y	Y	Y	Y
RDX:Tarflen (96:4)	Y	–	–	–	–	–	–	–
Polypropylene	Y	G	N	Y	Y	Y	Y	Y
Self-burning case	Y	–	–	Y	–	–	Y	Y
Teflon	Y	Y	Y	Y	Y	Y	Y	Y
Nylon 6/6	Y	N	G	Y	Y	Y	Y	Y
Cotton bag	Y	Y	Y	Y	Y	G	Y	Y
Aluminium tape	Y	G	N	–	Y	G	Y	Y

1 – PVST TNO–PML, 3 – DSC MIAT, 4 – TG MIAT

Discussion

PVST measurements

- The compatibility results for high energetic materials with aluminium tape are not as good as the others because of the shortness of sample material.
- All measured mixtures are compatible according to STANAG 4147 (*Vr* smaller than 5 mL, even smaller than 3 mL).
- Double base propellants show a higher gas production with Nylon 6/6 than with other additives.

TG measurements

- As can be seen in Table 4 the mixtures of RDX with Polypropylene and Aluminium tape are incompatible. For some mixtures (with a mass loss difference between 4 and 20%) another method is recommended to verify the TG result which is in the grey area.

DSC measurements

- As can be seen in Table 5, only the mixture of RDX with Nylon 6/6 is incompatible. For some mixtures (with a temperature shift between 4 and 20°C) another method is recommended to verify the DSC result which falls in the grey area.

Comparison of the three methods

- As can be seen from the Tables 6 and 7 there is not one mixture, which is in the grey area in all used methods.
- Mixtures with polypropylene and Nylon 6/6 show relatively more G's and N's than other mixtures. Also in the PVST was shown that mixtures with Nylon 6/6 show a

negligible higher gas production than other mixtures but still have a *Vr* smaller than 3 mL.
- Mixtures with aluminium tape show relatively more G's and N's than other mixtures but this can be explained by the fact that there was not enough sample to perform correct measurements.
- PVST appears to be the most reliable method to use for compatibility measurement because in TNO and in MIAT measurements all mixtures were compatible and the other results (DSC and TG) sometimes conflicted with each other.

Conclusions

The following conclusions may be drawn from this co-operation program, after completion of all the tests:
- PVST is the most reliable method to use for compatibility tests
- DSC and TG sometimes show large differences with PVST results
- mixtures with Polypropylene and Nylon 6/6 are relatively more incompatible than other mixtures but are still compatible in the sense of STANAG 4147
- measurements performed with aluminium tape are not reliable because there was not enough sample to make accurate measurements.

List of abbreviations

CA	Chemical analysis
DB	Double base
DSC	Differential scanning calorimetry
HFC	Heat flux calorimetry
HMX	Octogen
MIAT	Military Institute of Armament Technology
MLD	Mass loss difference
MVST	Mercury vacuum stability test
NATO	North Atlantic treaty organisation
PETN	Penta erythrol tetra nitrate
PML	Prins Maurits laboratory
PVST	Pressure vacuum stability test
RDX	Hexogen
SB	Single base
STANAG	Standardization agreement
STP	Standard temperature and pressure
TG	Thermogravimetry
TNO	Toegepast natuurwetenschappelijk onderzoek (applied scientific research)
TNT	Tri nitro toluene
VST	Vacuum stability test

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