Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 1123-1131

COMPATIBILITY TESTING OF ENERGETIC MATERIALS, WHICH TECHNIQUE?

W. P. C. de Klerk, M. A. Schrader and A. C. van der Steen*

TNO Prins Maurits Laboratory, Researchgroup Properties Energetic Materials, P.O. Box 45 2280 AA Rijswijk, The Netherlands

Abstract

Compatibility is an important safety aspect related to the production and storage of energetic materials. To test different combinations of materials a simple test method with clear criteria is advisable. At the last ESTAC the use of microcalorimetry and the vacuum stability test for the compatibility testing of propellants were presented. This paper presents DSC, DTA/TG and (pressure) vacuum stability test results for the same combination. For three polymers (PMMA, PVC and CA) the results for all tests are the same. Only Nylon-6/6 gives a variable result for the different test methods.

Keywords: compatibility, decomposition, energetic materials, peak temperature, polymers, TG

Introduction

To determine the compatibility of energetic materials the use of the right technique is an important factor. The techniques that are available at the moment are:

- DSC Differential Scanning Calorimetry
- TG/DTA Thermogravimetry / Differential Thermal Analysis
- IST Isothermal Storage Test
- PIST Pressure Isothermal Storage Test
- MVST Manometric Vacuum Stability Test
- PVST Pressure Vacuum Stability Test

Advantages of the thermal analytical techniques (DSC and TG) for compatibility testing are the use of small amounts of test materials and the short time needed for the measurements. The small sample amount could also be a disadvantage in the case of inhomogeneities.

Using IST and PIST offers the possibility for a larger sample mass and the opportunity to measure under different atmospheres and/or pre-pressures. A disadvantage is the relatively long test-period of 168 h at least.

* Author for correspondence: e-mail: klerk@pml.tno.nl

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The MVST-technique has been in use for a long time and has proven to be a cheap and reliable test. It has a number of disadvantages associated with the use of the mercury manometer. Due to the toxicity of mercury the experiments are time consuming because a large amount of handling is need with filling, emptying, and cleaning the mercury manometer. The PVST uses pressure transducers, instead of the toxic mercury in the MVST to measure the increase of pressure, which shortens the experimental time considerably. Another big advantage of the PVST, as compared to the MVST, is the continuous registration of the gas production as a function of time. This makes the observation of adsorption and desorption processes possible.

Problems related to the difference in temperature between the heating tube and the manometer are still not solved for both test methods.

To assess the usefulness of those techniques, a research program was performed using all six techniques. These techniques, except the PIST, are described in STANAG 4147, a guideline to determine the compatibility of mixtures with energetic compounds.

The compatibility of a double base propellant (nitrocellulose and nitroglycerine are the main components) with different polymers was studied. In a former paper [1] the IST results were presented. The double base propellant showed to be incompatible in combination with Nylon-6/6. This paper presents the results of the DSC/TG/DTA and MVST/PVST. A comparison for all these techniques is made.

Sample description

The investigated propellant KB 6981 (produced in 1990) has the composition as given in Table 1.

Table 1 Composition of propellant KB 6981, in mass percentages

Nitrocellulose	59.4	Moisture	0.42
Nitroglycerine	31.7	Potassium salts	7.40
Ethylcentralite	0.94	Water	0.42
Graphite	0.59		

The compatibility of the propellant was investigated with the polymers given in Table 2.

Table 2 The investigated polymers

Polymer	Chemical name	Manufacturer
Nylon-6/6	polyamid 6/6	Janssen Chimica
PMMA	polymethyl methacrylate	Du Pont Lucite 2041
PVC	polyvinylchloride	ACF
CA	cellulose acetate	BDH

Test equipment

Thermoanalytical methods

DSC and TG/DTA are techniques that are generally used and well known. The apparatus are a TG/DTA 350 and a DSC220-C, both manufactured by Seiko Inc.

The measurements were carried out by using open aluminum cups, a heating rate of 10°C min^{-1}, and a nitrogen atmosphere. In STANAG 4147 a heating rate of 2°C min^{-1} was specified.

The criteria for (in)compatibility as presented in STANAG 4147 are as follows:

• TG/DTA	mass loss difference <4%	compatible
	mass loss difference 4<x<20%	degree of incompatibility
	mass loss difference >20%	incompatible
• DSC peak temperature shift <4°C		compatible
	temperature shift 4<x<20°C	degree of incompatibility
	temperature shift >20°C	incompatible

Isothermal storage test

The Isothermal Storage Test (IST) or Heat Flow Calorimeter (HFC) is a sensitive heat generation measuring instrument. The technique is in use at TNO-PML since the late sixties [2]; the amount of energetic material to be investigated is usually 5 to 10 g. The technique is described in [1 and 6].

To obtain more insight into the correlation of the gas evolution in the VST and the heat production in the IST, an IST apparatus is equipped with a pressure transducer. With this extended IST, called Pressure IST (PIST), the gas and the heat evolution can be recorded simultaneously and as a function of time [6].

To determine the compatibility, first the heat of reaction of the three samples has to be calculated, followed by a factor D, which is defined as;

$$D = (2M)/(E + S)$$

With M=heat of reaction of mixture (propellant and additive), E=heat of reaction of energetic material, S=heat of reaction of additive.

The criteria used are as follows:

D<2	mixture is compatible
2<D<3	a degree of incompatibility
D>3	incompatible

Manometric vacuum stability test

The manometric vacuum stability test (MVST) is performed according to STANAG 4147, Test 1, Procedure A: 'The Vacuum Stability (Reactivity) Test, manometer method' [3]. This method corresponds largely to MIL-STD-286B [4]. In this test a mixture of 2.50±0.01 of an explosive and 2.50±0.01 g of the testmaterial are kept at a constant temperature of 90.0+/–0.2°C for 40 h (for double base propel-

lants) in an initial vacuum. The volume of gas evolved (calculated at STP=standard temperature and pressure) is compared to the volumes evolved from 2.5 g of the explosive and 2.5 g of the test material when kept separately under identical conditions. Compatibility is judged from the volume of additional gas produced. This was achieved this by bringing the two components in contact with each other.

The criteria used are as follows:

extra volume of gas<5 ml mixture is compatible
extra volume of gas>5 ml mixture is incompatible

Pressure vacuum stability test

The PVST is performed according to STANAG 4147, Test 1, Procedure B: 'The Vacuum Stability (Reactivity) Test, transducer method' [3]. The preparation of the test is the same as described above. Also the criteria are the same.

The equipment used for this method is as follows;

- data-acquisition system
- pressure transducers
- water bath with sensor
- sample tubes

The Datascan 7000 apparatus (Measurement Systems) used (Fig. 1), consists of different modules. The central module (7010) is connected by an RS-232 port to a computer and measures and controls. It receives commands from the software Lab tech Notebook (version 7.1.1) which contains a special driver for the Datascan 7000 system. With the central module three modules (7021) were connected in series which could measure analogue signals. Each module had 8 channels for connecting transducers and PT-100 thermometers. At the modules 7021, a power supply was connected, which had a maximum frequency of 1.6 Hz and gave 1.8 V.

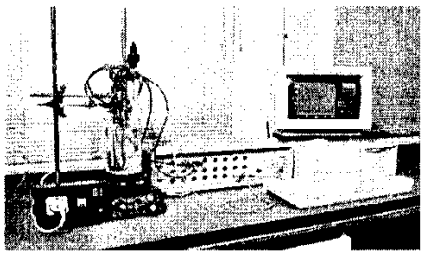

Fig. 1 Schematic design of the Pressure Vacuum Stability Test

The temperature of the bath and the room are measured by means of two platinum resistance thermometers PT-100 which can be used in the range of −20 to 175°C. The transducers are of type BHL-4250 (Trans Instruments) and can be used from 0 to 1 bar. They are resistant against corrosive materials and can be used in the temperature range from 0 to 150°C.

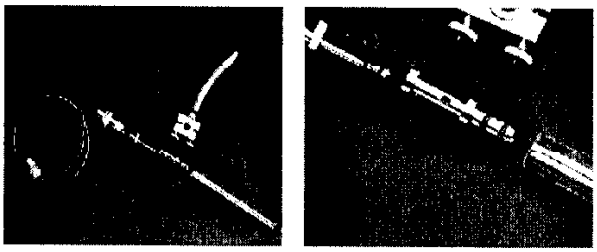

Fig. 2 Schematic design of the test-tube (with close-up) with transducer

The tubes and transducers, used for the test are different from the models described in the STANAG [3]. At the screw thread of the transducer a special made lengthening-piece is connected. The lengthening-piece has three O-rings: one at the top and two on the side (Fig. 2). The O-rings are lightly smeared with silicon grease to prevent leakage [5]. Only the lengthening-piece fits into a glass tube, the transducer itself is too wide. The glass tube has a little hole for the gas extraction. The tube is placed in a special holder, that the hole is situated between two O-rings for connecting a vacuum pump.

Results

All the test methods are performed on the propellant KB 6981, the polymers and with mixtures of them.

In Fig. 3 the results of the PVST and MVST are given. The presented curves are from the propellant KB 6981 b), the polymer Nylon-6/6 c), a mixture a) and the difference d) between the mixture and the sum of the single components. The dots in the figure are the results from the MVST at 16, 23 and 40 h, for the same samples. The data-points of the MVST are in the same range of gas volume as the PVST-values. So it may be concluded, that the two VST-methods are in good agreement with each other for the determination of the compatibility for propellants with polymers.

The mixture is compatible because the extra volume is less than 5 ml.

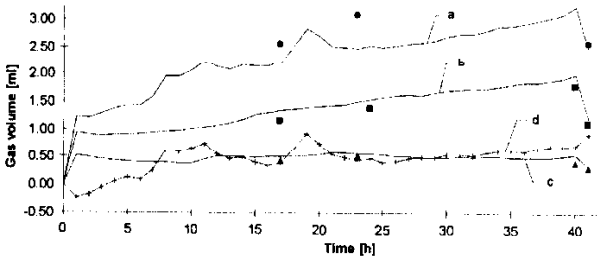

Fig. 3 Plot of the MVST and PVST-measurement of KB 6981 with Nylon 6/6 for 40 h at 90°C, explanation of the indices is given in the text

In the IST and PIST experiments described in [6] the mixture was kept at 85°C for 168 h. To compare the results of the PIST with the vacuum stability test a PVST is carried out for a period of 168 h also but at 90°C. The results are given in Table 3.

Table 3 Results of the pressure vacuum stability test with KB 6981, all at 90°C

	ml gas for 2.5 g explosive after	
	40 h	168 h
Propellant KB 6981	1.20 1.26	4.33–4.39
Nylon 6/6	0.32–0.31	0.41–0.42
KB 6981 with Nylon 6/6	2.43–2.45	12.15–12.77

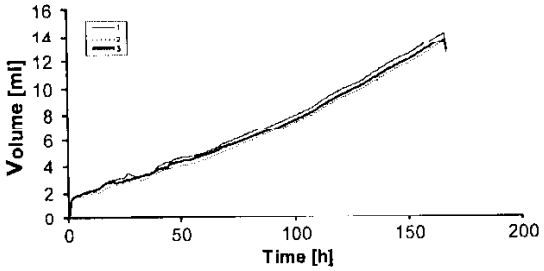

Fig. 4 PVST results of KB 6981 with Nylon 6/6 for a period of 168 h, 3 measurements at 90°C

In Fig. 4, the result of this long-term test has been plotted. A continuously increase of gas evolution is observed. The test was performed in triplicate and the reproducibility is very good. The increase of gas evolution indicates a continuous decomposition of the substance. This effect is also observed with the (P)IST measurement [6], where a continuous increase of the heat generation and pressure is observed. The pressure increase of 0.25 bar observed in the PIST, compares to a volume of 11.8 ml. This value is in line with the PVST-value of 12.5 ml.

In the last part of this research program the thermal analytical techniques were used.

The results of the different combinations of KB 6981 with polymers are presented in Table 4 and Fig. 5 for the DSC part. In Table 4, T_e represents the temperature of the

Table 4 Compatibility investigations by DSC

Composition	T_p/°C	T_e/°C
Pure KB 6981	195	189
With Nylon 6/6	193	190
With Cell. Acetate	194	190
With PVC	194	190
With PMMA	201	190

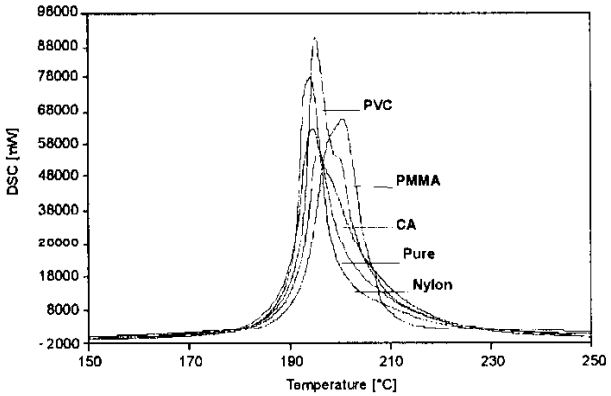

Fig. 5 DSC-plot of propellant KB 6981 with additives

extrapolated onset and T_p represents the maximum temperature of the peak. Based on the results of Table 4 it could be concluded that all the combinations investigated are compatible. The influence of the amount of polymer is negligible because the main reaction is caused by the decomposition of the propellant.

The difference between the observed mass loss and the total calculated mass loss of the energetic material and test material at a given temperature results in an indication for the compatibility (Table 5). First the calculated mass loss of the single compounds has to be determined, corrected for the mass fraction in the mixture. The sum of the single compounds has to be compared with the observed mass loss of the mixture. The difference between this values is an indication for the compatibility. An example; at an arbitrarily chosen temperature of 182°C (close to the derivative TG-peak) is as follows: the observed mass loss for KB 6981 pure is 21.3, for the additive (PVC) 0.1%. The expected mass loss for a mixture of 66.8 KB 6981 and 33.2% PVC is 14.3%. The TG-test results in a mass decrease of 12.5%. This result shows that, according to the criteria of the STANAG 4147, the mixture is compatible.

Based on the results of Table 5, it could be concluded that the combination of KB 6981 with PVC, CA and PMMA are compatible according to STANAG 4147 [3].

Table 5 Results of compatibility-research by TG at a temperature of 182°C

Composition	Mass decrease of TG-test {pure}/%	Mass decrease of TG-test {mixture}/%	Calculated mass loss/%
Pure KB 6981	21.3		
With nylon 6/6	2.0	21.1	14.9
With cell. acetate	4.2	15.4	14.7
With PVC	0.1	12.5	14.3
With PMMA	2.2	10.3	13.9

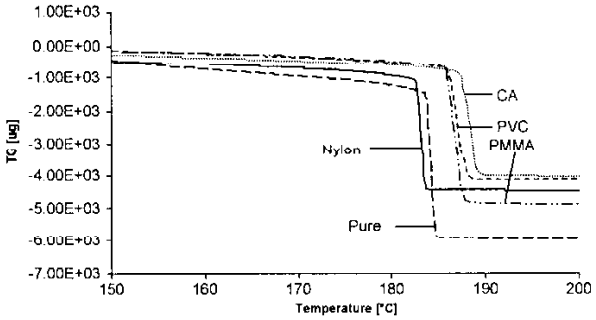

Fig. 6 TG-curve of propellant with additives

The mixture with Nylon 6/6 lies in the gray area, so kinetic research is advisable. It should be noted that kinetic studies are extremely time-consuming.

Comparison

An overview of all results is presented in Table 6.

Table 6 All the results of KB 6981 in combination with polymers

KB 6981	MVST	IST	PVST	DSC	TG
CA	COMP	COMP	COMP	COMP	COMP
PMMA	COMP	COMP	COMP	COMP	COMP
PVC	COMP	COMP	COMP	COMP	COMP
Nylon-6/6	COMP	INCOMP	COMP	COMP	INCOMP/COMP

The only discrepancy between the investigated test methods is the mixture of KB 6981 with Nylon-6/6 as measured in TG/DTA and IST. The result for the TG/DTA lies in the 'gray' area, so other test methods are advisable. Also it is advise to perform a kinetic study by TG/DTA. For the IST result the test can be determined as incompatible.

Conclusions

According to this paper the following conclusions can be made:

- depending on the material, at least two compatibility methods have to be performed.
- at least one vacuum stability test method has to be performed, because of the clear criteria in STANAG 4147.

- the results of the PVST are in good agreement with the results obtained by MVST.
- the combination KB 6981 with Nylon-6/6 could be indicate as incompatible.
- if it is possible, a test method with a larger sample mass is preferable.

* * *

We thank the Ministry of Defense for funding this research project.

References

1 W. P. C. de Klerk, N. v. d. Meer and R. Eerligh, Thermochim. Acta, 269/270 (1995) 231.
2 J. L. C. van Geel, Self-ignition Hazard of Nitrate Ester Propellants, Ph. D. Thesis, Delft Technical University, 1969.
3 NATO Standardization Agreement STANAG 4147, Chemical Compatibility of Ammunition Components with Explosives and Propellants (Non-nuclear Applications) draft edition 2, January 1996.
4 Mil-Std 286-B, (Propellants, solid), Method T403.1.3 (Vacuum Stability Test (90 and 100°C)) and Method T408.1 (Reactivity Test (90 and 100°C)), 30 December 1975.
5 R. Duffield and N. MacLeod, Application of the vacuum stability test/gas chromatography to the study of colloidal propellant stability, Joint International Symposium on Compatibility of plastics and other materials with explosives, propellants, Virginia Beach (USA), 1989, 356.
6 W. P. C. de Klerk and B. J. v. d. Meer, Compatibility investigations using a (pressure) heat flow calorimeter, TNO-PML report 1995-A-20, August 1995.