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Microcalorimetric study applied to the comparison of compatibility tests (VST and IST) of polymers and propellants ☆

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Abstract

A few years ago, a discussion was started to update the test method for determining the chemical compatibility of ammunition components with explosives and propellants. According to this test and also a military test method, a reactivity test to establish the amount of compatibility of single- or double-base propellants with other materials by the vacuum stability test (VST) has been standardised. For several decades, the VST was the most commonly used test to determine the compatibility of propellants with other materials. However, the VST has some well-recognised drawbacks. For example, only processes that result in gas evolution can be measured. Processes such as migration and absorption, which are important for safety and performance considerations for propellants, are not taken into account in the test criteria.

Therefore it was decided at the Prins Maurits Laboratory TNO to start a research project to obtain more information about aspects related to compatibility. As deterioration of materials is accompanied by the release or absorption of heat, the microcalorimeter test (IST) was a logical choice. Several combinations of polymers (to obtain a quick fingerprint) and propellants were tested in the VST and in the microcalorimeter, simultaneously, under isothermal conditions. Six propellants (single-base, double-base and DEGN propellants) and polymers were combined.

The compatibility tests in the VST for the single-base propellants were performed over 40 h at a temperature of 100°C, while 40 h at 90°C was used for double-base propellants. In the microcalorimeter, the propellants were measured for a period of 168 h at a temperature of 85°C. The results of these tests present a few problems concerning the interpretation of the test results. It turns out that the absence of extra gas evolution in the VST gives no guarantee of compatibility as the heat generated in the microcalorimeter test can be very high for the same combination of

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materials. It is therefore recommended that an extra test in addition to the VST be performed to determine compatibility.

Keywords: IST; Microcalorimetry; Polymer; Propellant; VST

1. Introduction

The compatibility of energetic materials with other components used in ammunition is extremely important in connection with the high demands made on their safety and functioning. The ideal case of compatibility would be that the materials do not react with each other even after long storage periods at various conditions. For practical reasons, materials are judged compatible if during and after a specified storage period the functioning and safety of the components are still acceptable.

Perhaps the most reliable way to investigate compatibility is to use a variety of techniques to investigate chemical and physical reactions and to perform ageing experiments as close to storage conditions as possible. In most cases this is very time-consuming. In practice, one expects reliable results from a compatibility investigation in a short time. To do this, some tests based on accelerated ageing at higher temperatures are available, measuring gas evolution (vacuum stability test), heat effects (heat flow calorimeter, differential scanning calorimeter), weight loss (thermogravimetry) or stabiliser loss. Real cases of (chemical) incompatibility can be measured by these methods without problem. But it is difficult to predict an incompatibility which will become evident only after a long period at storage conditions.

Of these methods the vacuum stability test is perhaps the most frequently used. This compatibility test is described in MIL-STD's [1,2] and also in STANAG 4147 [3]. These descriptions include compatibility criteria which are valid unless other criteria apply.

However, the vacuum stability test has some drawbacks: condensation, adsorption/reaction of gaseous products with test materials (polymers), and not all chemical reactions produce gases. It has long been felt that the results obtained from the vacuum stability test give satisfactory compatibility indications for high explosives but not for nitrate-ester-based propellants. In some countries, determination of the compatibility of propellants with the vacuum stability test alone is not accepted.

These points of concern were recognised long ago [4] and a logical choice was to investigate compatibility with methods that detect heat generation instead of gas evolution. All spontaneous chemical and physical processes are associated with heat effects. Later, more effort was put into investigations into the compatibility of propellants based on heat flow measurements with a heat flow calorimeter [5, 6].

Therefore, and because no suitable data were available on TNO-PML, an investigation into the compatibility of propellants with polymers was started using the heat flow calorimeter as well as the vacuum stability test to obtain data that may give insight into the relation between the results obtained from the two tests and to formulate compatibility criteria that are useful for practical application.

2. Experimental

2.1. *Vacuum stability test*

The vacuum stability test (or reactivity test), shown in Fig. 1, was performed according to STANAG 4147, Procedure 1: The Vacuum Stability (Reactivity) Test, using mercury manometers. This method corresponds largely to MIL-STD-286B [1]. The main difference is that according to STANAG 4147 the particle size of the ground propellants and polymers should be 0.2–2 mm (unless the material is finely powdered), while in MIL-STD-286B the particle size should be approximately 12 mesh (1.68 mm).

Mixtures of 2.50 ± 0.01 g propellant and 2.5 ± 0.01 g polymer, as well as the separate components (each also 2.50 ± 0.01 g), were tested in duplicate during 40 h at 100°C (single-base propellants) or 40 h at 90°C (other propellants).

When the gas produced by the mixture is 5.0 ml in excess of the sum of the gas evolved by the separate components, the mixture is considered to be incompatible. Excess gas evolution due to reactivity in a mixture of between 3.0 and 5.0 ml is judged as moderately reactive; these materials should not be used in ammunition without further investigation. For special applications other criteria can be valid.

2.2. *Microcalorimetry*

The heat flow calorimeter or microcalorimeter is a sensitive heat generation measuring instrument. The technique has been used at TNO-PML since the late sixties [7]; the amount of energetic material to be investigated is usually 5–10 g.

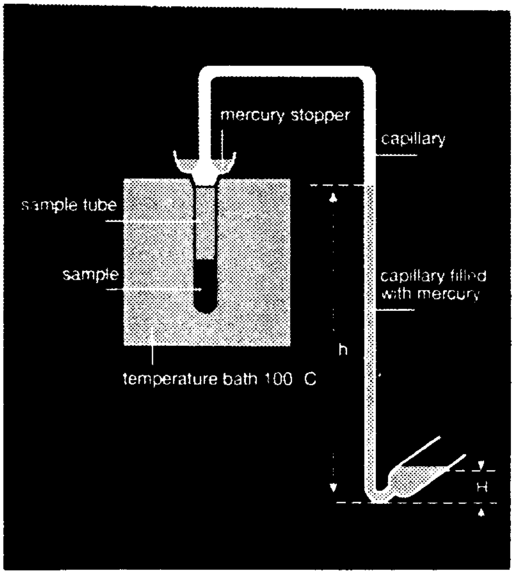

Fig. 1. Schematic design of the manometric vacuum stability test.

In the heat flow calorimeter, the heat generated by reacting or decomposing substances at a constant temperature is measured as a function of time. Performance of these measurements at a series of temperatures can lead to a quantitative understanding of the relation between temperature and the heat generation of the substance under investigation. The heat flow calorimeter is applicable to solids, liquids, pastes and dispersions.

The heat flow calorimeter (Fig. 2) consists of a large heat sink (an aluminium block) which is kept at a constant temperature. In the block are two holes with a very sensitive heat flow meter, e.g. a Peltier element, at the bottom of each hole. Identical holders are placed on both heat flow meters. One holder contains the sample, the other an inert substance.

The heat generated by the sample results in a voltage signal from the heat flow meter which is proportional to the heat flow. Random fluctuations in the heat flow are avoided by monitoring the voltage differences between both heat flow meters. The stainless steel sample holder has a volume of 70 cm^3.

The heat release rate during isothermal storage simulates thermal ageing for a certain time at storage temperature. Measurements can be performed in the temperature range 250–390 K, under confined or under atmospheric conditions. In the former case, the sample vessel is closed gas-tight (for example by means of an inert membrane and a Teflon membrane to prevent volatile products from escaping). Heat generations can be measured between the lower limit of 5 $mW\,kg^{-1}$ and the upper limit of 5 $W\,kg^{-1}$ with an accuracy of at least 30% in the lower range to 5% in the higher ranges.

The apparatus, including the reference sample vessel, has to be brought to the test temperature prior to inserting the sample vessel into the apparatus. Before a measure-

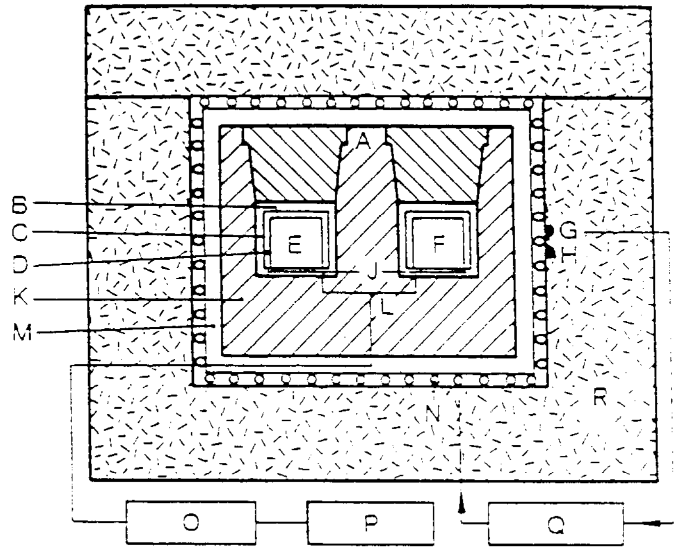

Fig. 2. Schematic design of the isothermal storage test (IST).

ment can be performed, the blank signal and the sensitivity of the heat flow meter have to be determined. Both can be temperature-dependent. After insertion of the sample vessel, temperature equilibration must be attained before the actual measurement can start, usually after 4 h.

The temperature fluctuations are very low, about 0.02°C at a temperature of 85°C for a period of at least two weeks.

For the experiments with the propellants, a storage period of 168 h at 85°C was used. The rather high temperature was chosen to perform the measurements in a reasonable time. Mixtures of 5.00 ± 0.01 g propellant and 5.00 ± 0.01 g polymer, as well as the separate components (each also 5.00 ± 0.01 g), were tested.

2.3. *Propellants and polymers*

For this test programme, six propellants and a number of polymers were investigated. In Table 1, the composition of two single-base, two double-base, and one triple-base propellants and a DEGN propellant used in the experiments are presented. Before testing, the propellants were ground to particle sizes less than 2 mm. There was no further sample preparation.

Table 2 lists the polymers used in the experiments. These polymers were in storage for at least 10 years. The polymers did not have a known relation with practical situations in ammunition. The polymers CA, PMMA, PVA and PVC were finely powdered. The other polymers were ground before testing. The fractions with a particle size of 0.2–2 mm were used for the test. There was no further sample preparation.

Table 1
Composition of the propellants (as specified by the manufacturer)

	KB 5417	KB 5692	KB 5916	KB 6975	KB 6981	KB 6982
Nitrocellulose	21.15	83.35	60.20	98.50	59.43	59.50
Nitroglycerine	19.60		15.10		31.69	
Nitroguanidine	55.20					
DEGN						24.80
Dinitrotoluene		9.20	13.60			
Ethylcentralite	3.70	0.20	1.90		0.94	
Diphenylamine		1.10		1.26		
Acardite II						0.74
Dibutyl phthalate		4.60	6.80			
Potassium salt		0.80	1.30	0.01	7.40	0.04
Vaseline			0.40			
Graphite			0.20		0.59	0.05
Others	0.10					
Water	0.20	0.65	0.40	1.20	0.42	0.41
Solvents	0.05	0.10	0.10			
Production year	1964	1968	1974	1989	1990	1990

Table 2
Polymers used for the investigation

Polymer	Description	Manufacturer
CA	Cellulose acetate	BDH
Delrin	Polyacetal	DuPont Delrin
Nylon	Polyamid	Nylon-12
PMMA	Polymethyl methacrylate	DuPont Lucite 2041
PS	Polystyrene	Dow Styron 664
PVA	Polyvinylalcohol	Baker
PVC	Polyvinylchloride	ACF

3. Results

The results for the compatibility test using the vacuum stability test are shown in Table 3. According to the vacuum stability test, most combinations of propellants and polymers show a negligible reactivity or no reactivity at all (negative extra gas). Exceptions are the following combinations: Nylon-12 shows a moderate or excessive reactivity with the double- and triple-base propellants; Polyvinylchloride shows a slight reactivity with the double- and triple-base propellants (with PH6981 and PH5417, a moderate reactivity).

Most polymers turned yellow during the test. These polymers were not analysed after the test. Also there was no investigation into any change in mechanical or physical properties. These measurements can reveal a serious reason for incompatibility (especially the migration of nitroglycerine in some of the polymers).

The heat generation for some polymers, as measured separately, is shown in Fig. 3. All polymers revealed a small peak in the heat generation of 10–50 mW kg^{-1} during the

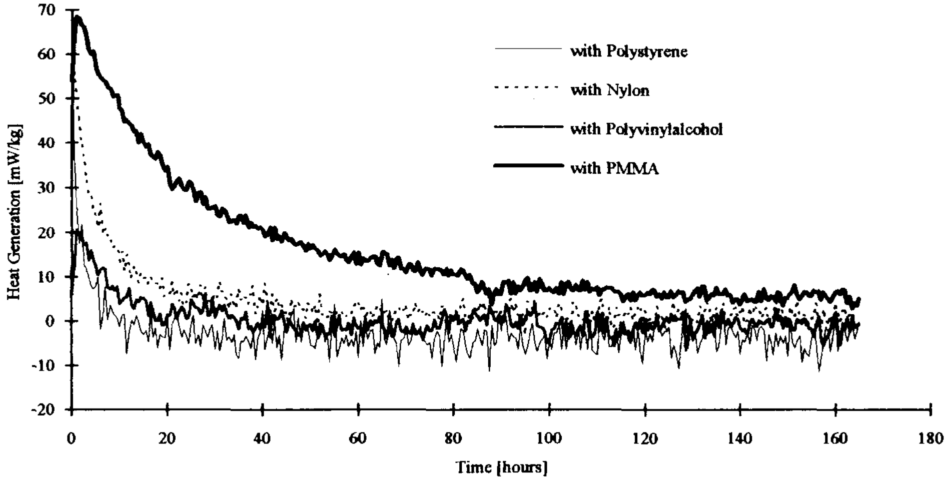

Fig. 3. Heat generation for some polymers.

Table 3
Results of the compatibility tests

Propellant	Mixed with polymer	Vacuum stability test		Heat flow calorimetry 168 h at 85 °C			
		Extra gas/ (ml at NPT)	Reactivity	Enthalpy/(kJ kg^{-1})^{a} mixture	**Extra** enthalpy		Compatibility
					Absolute	Relative^{b}	
KB5417	–	40 h at 90 °C		33.1 Prop.			
triple base	Cellulose acetate	−0.88	–	43.3	10.0	30%	Compatible
	Delrin	1.45	–	51.6	18.0	54%	Compatible
	Nylon-12	10.14	**Excessive**	244.2	208.0	575%	**Incompatible**
	PMMA	−0.92	–	71.9	30.3	73%	Compatible
	Polystyrene		–	34.4	0.9	3%	Compatible
	Polyvinylalcohol	0.39	–	77.3	44.0	132%	**Incompatible?**
	Polyvinylchloride	3.34	Moderate	53.7	21.3	66%	Compatible
PH5692	–	40 h at 100 °C		27.9 Prop.			
single base	Cellulose acetate	−0.57	–	24.7	−3.4	−12%	Compatible
	Delrin	−0.64	–	40.9	12.5	44%	Compatible
	Nylon-12	−0.53	–	33.7	2.7	9%	Compatible
	PMMA	−1.12	–	28.2	−8.2	−23%	Compatible
	Polystyrene			24.3	−4.0	−14%	Compatible
	Polyvinylalcohol	−0.67	–	37.8	9.7	35%	Compatible
	Polyvinylchloride	−0.75	–	26.5	−0.7	−3%	Compatible
PH5916	–	40 h at 90 °C		22.4 Prop.			
double base	Cellulose acetate	−1.51	–	103.8	81.2	359%	**Incompatible**
	Delrin	−0.05	–	40.4	17.5	76%	Compatible
	Nylon-12	4.84	Moderate	124.2	98.7	387%	**Incompatible**
	PMMA	−2.57	–	45.7	14.8	48%	Compatible
	Polystyrene		–	31.5	8.7	38%	Compatible
	Polyvinylalcohol	−1.10	–	58.0	35.4	157%	**Incompatible?**
	Polyvinylchloride	2.41	Slight	36.7	15.0	69%	Compatible

Table 3 (*Continued*)

Propellant	Mixed with polymer	*Vacuum stability test*		*Heat flow calorimetry 168 h at 85°C*			
		Extra gas/ (ml at NPT)	Reactivity	Enthalpy/(kJ kg^{-1})[a] mixture	**Extra** enthalpy		Compatibility
					Absolute	Relative[b]	
KB6975	-	40 h at 100°C		22.0 Prop.			
single base	Cellulose acetate	−0.22	-	28.1	5.9	27%	Compatible
	Delrin	0.11	-	37.6	15.1	67%	Compatible
	Nylon-12	0.10	-	20.7	−4.4	−18%	Compatible
	PMMA	0.12	-	29.8	−0.7	−2%	Compatible
	Polystyrene			20.9	−1.5	−7%	Compatible
	Polyvinylalcohol	0.08	-	27.3	5.1	23%	Compatible
	Polyvinylchloride	−0.14	-	46.5	25.2	118%	**Incompatible?**
KB6981	-	40 h at 90°C		21.8 Prop.			
double base	Cellulose acetate	−0.39	-	34.0	12.0	55%	Compatible
	Delrin	1.48	-	37.5	15.2	68%	Compatible
	Nylon-12	9.82	**Excessive**	212.4	187.5	753%	**Incompatible**
	PMMA	−0.55	-	48.7	18.4	61%	Compatible
	Polystyrene	0.09	-	24.7	2.5	11%	Compatible
	Polyvinylalcohol	0.31	-	74.8	52.8	240%	**Incompatible**
	Polyvinylchloride	3.48	Moderate	34.2	13.1	62%	Compatible
KB6982	-	40 h at 90°C		18.7 Prop.			
double base	Cellulose acetate	−0.29	-	27.5	8.5	45%	Compatible
	Delrin	1.15	-	27.7	8.5	44%	Compatible
	Nylon-12	4.49	Moderate	96.0	74.2	340%	**Incompatible**
	PMMA	−0.58	-	69.9	42.7	157%	**Incompatible**
	Polystyrene			44.4	25.3	132%	**Incompatible?**
	Polyvinylalcohol	−0.06	-	57.6	38.7	205%	**Incompatible**
	Polyvinylchloride	2.28	Slight	35.9	17.7	97%	Compatible

[a] kJ kg^{-1} propellant.

[b] The relative percentages are calculated as follows (example KB5417 + Delrin): 18/(51.6 − 18) × 100% = 54% rounded to integers. The origin for this is the presentation of the VST results according to STANAG 4147.

first hours after insertion of the sample vessel into the heat flow calorimeter. At later times the heat production is essentially zero up to 168 h (7 days) within the accuracy of the experiment. The total heat generation over the measuring period of 168 h was very small except for PMMA (8.5 kJ kg^{-1}).

The heat flow of the propellants (not shown) was never larger than 100 mW kg^{-1}. The total heat flow over the measuring period for the ground propellants was 18–33 kJ kg^{-1}.

The results obtained with the heat flow calorimeter for the mixtures are shown in Table 3. They indicate in some cases a different behaviour when compared to the results obtained from the vacuum stability test.

An example is the mixture of the double-base propellant KB6982 with PMMA which is compatible according to the vacuum stability test but shows a very large heat generation in the heat flow calorimeter compared to the heat generated by the separate components, as shown in Fig. 4. The heat generation is particularly high on the first day.

Other examples are PVC and CA mixed with the double-base propellant KB5916 (see Figs. 5 and 6). In the heat flow calorimeter, PVC reveals an extra peak in the heat generation not present in the curves of components. The extra heat generated by the mixture of CA with KB5916 decreases with time.

A final example is the triple-base propellant KB5417 with PVA. According to the vacuum stability test, this shows a negligible reactivity. Microcalorimetry shows an increased heat generation during the whole test time (see Fig. 7).

Frequently, pronounced differences between the heat generation of the mixture and the sum of the heat generations of the separate components can be observed during the first 20 h after insertion of the sample vessel into the heat flow calorimeter. At later times, the differences become less pronounced and often approximate the calculated sum of the heat generated by the components.

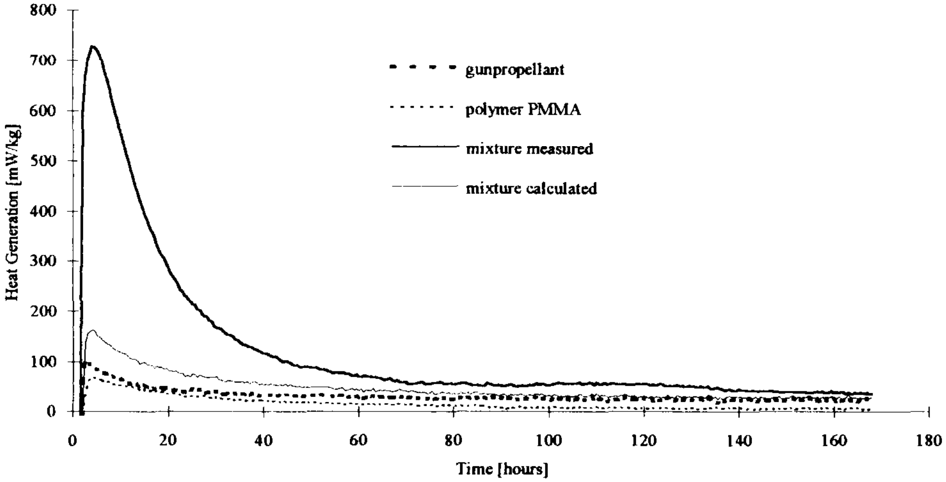

Fig. 4. Heat generation of the components and mixture of PMMA and propellant KB6982.

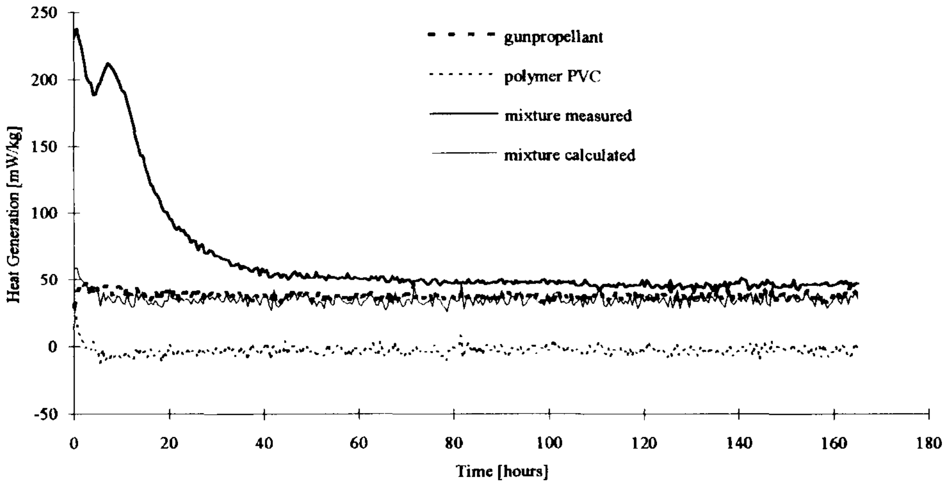

Fig. 5. Heat generation of the components and mixture of PVC and propellant KB5916.

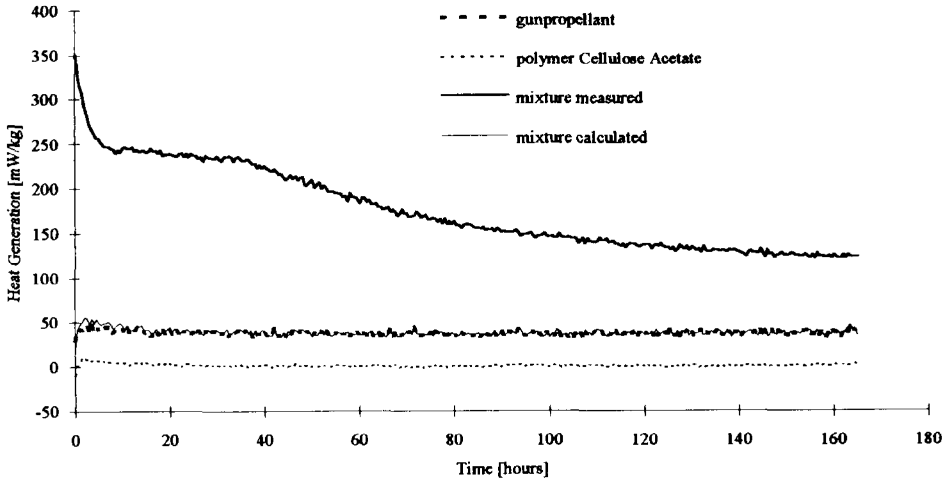

Fig. 6. Heat generation of the components and mixture of PVA and propellant KB5916.

In summary, the following types of curves for the mixtures relative to the sum of the component curves were observed: enhanced heat generation for the mixture, but the shape is similar to the curve of the sum of the components; enhanced heat generation for the mixture with a different shape but no extra peaks; enhanced heat generation and extra peaks.

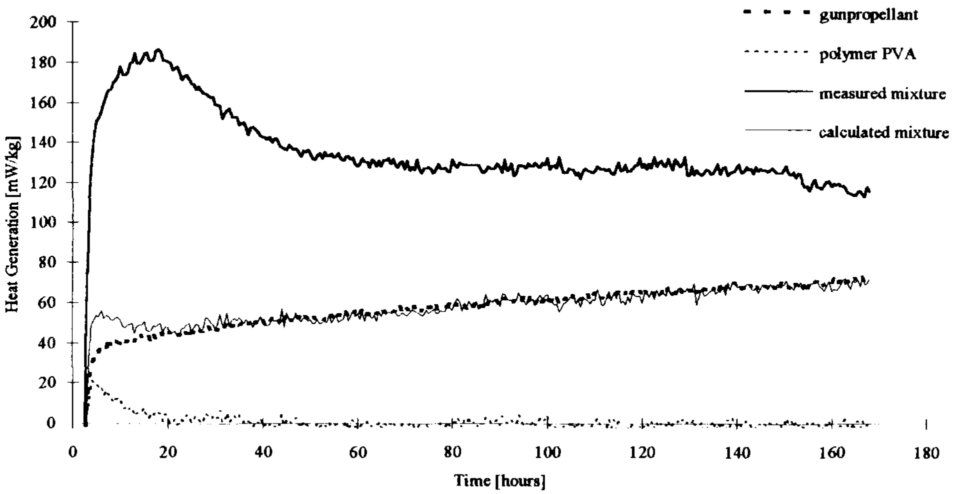

Fig. 7. Heat generation of the components and mixture of PVA and propellant KB5417.

4. Discussion

It is clear that the results of the heat flow calorimeter test and the vacuum stability test do not fully correspond. It is evident that the heat flow calorimeter gives valuable information on the reactivity as reflected by the extra heat generation of the mixture.

The choice for incompatibility criteria is always somewhat arbitrary. In this case, a limited number of heat flow calorimeter measurements are available measured under the same test conditions (168 h at 85°C) without support from long-term ageing experiments. Possible criteria can be based on the absolute or relative difference of the heat generation of the mixture compared to the sum of the heats generated by the components.

Let us focus on the wide variety of heat generation curves of the mixtures and of the separate components. The formulation of generally applicable criteria is faced with the following problems:

1. When criteria are *relative*, the extra heat generation is sometimes taken relative to a rather stable propellant with a low heat generation. A small increase in the heat generation, small in the absolute sense, due to contact with another component might be relatively large and is therefore considered to indicate incompatibility. The same increase in the heat generation of a less stable propellant would indicate compatibility. As the heat generations of the propellants tested in this investigation do not differ very much, this effect cannot be verified. Tests with other

explosive compounds are necessary. Also the influence of other test conditions (lower test temperature) has to be investigated.

2. When criteria are *absolute*, the same extra heat generation for stable and less stable explosive compounds would lead to the same compatible/incompatible assignment. Test conditions should be chosen which correspond with a long storage period. TNO-PML measurements of compatibility of propellants using the heat flow calorimeter were expressed as the safe diameter for the propellant.
3. Sometimes an extra heat generation peak is observed for the mixture (in most cases during the first days). How problematic is an extra peak in view of the long-term application in ammunition? The relative effect of this peak on the total heat generation will decrease with a longer test time; the absolute extra heat generation will not show this problem.
4. The test time and temperature can (and in some cases will) be of influence to the compatible/incompatible assignment.
5. The observation of the heat generation is an indirect parameter for compatibility testing. Actually, after a compatibility test the physical (including mechanical) and chemical parameters relevant for performance and safety of the mixture in its final use must give decisive criteria for compatibility.

Keeping in mind the limited amount of data, the following suggestions for compatible criteria are suggested.

Relative criteria

1. An increase in the heat generation by mixing of 200% (see Table 3 footnotes) is incompatible.
2. An increase in the heat generation by mixing of 100–200% requires further investigation.
3. An increase in the heat generation below 100% is compatible.

Absolute criteria

1. An increase in the heat generation by mixing of 40 kJ kg^{-1} is incompatible.
2. An increase in the heat generation by mixing of 30–40 kJ kg^{-1} requires further investigation.
3. An increase in the heat generation below 30 kJ kg^{-1} is compatible.

The values for these criteria can, of course, be disputed, but they can be used as a starting point for further investigations.

5. Final remarks

Chemical compatibility is a complex parameter. In general, it has to be assessed for all materials that are in direct or indirect contact in ammunition to obtain a product that can be used safely and satisfactorily during its lifetime. If no reactivity at all is allowed, the variety of products available will then be very limited and in fact we restrict ourselves too much by discarding combinations of materials that are still very useful. We then arrive at a diffuse region. To what extent should components be allowed to interact?

The answer lies in the safety and performance requirements guaranteed during a certain period: chemical interaction is allowed if safety and performance does not suffer from interaction during this period. To guarantee these safety and performance requirements, such design parameters must be considered and, indeed, this type of compatibility testing has been reported in the literature. It is this type of testing that gives the strongest support to compatibility.

Nevertheless, it is of practical use to have tests available that can be performed relatively quickly and give indications of compatibility. The vacuum stability test is such a test and microcalorimetry is another. Results of compatibility investigation should always be interpreted carefully.

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