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Compatibility examination of explosive and polymer materials by thermal methods

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Explosive materials must be compatible with polymer materials while they are in contact. For rapid examination of compatibility the thermal methods are applied. This article describes the methodology and criteria of application of differential scanning calorimetric and thermogravimetric analyses in compatibility examination of explosive materials, powder and double base propellant, with three types of polymer binders.

Key words: **powder, rocket propellant, polymer binder, compatibility, thermal methods.**

Introduction

THE compatibiliy of energetic materials with other ammunition components is extremely important in relation to high demands for their safety and functioning. The ideal case of compatibility would be when materials do not react with each other even after long storage periods under various conditions. For practical reasons, materials are classified as compatible if during and after a defined storing time 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, reliable results from a compatibility investigation are expected in a short time. To do this, some tests based on accelerated ageing at higher temperatures are available for measuring gas evalution (vacuum stability test), heat effects (microcalorimeter, differential scanning calorimeter (DSC)), weight loss (thermogravimetry (TG)), etc. Real cases of chemical incompatibility can be measured by these methods without problems. However, the problem arises when it is neccessary to predict an incompatibility case which will become evident only after a long period under storage conditions.

From the previously mentioned tests, the most often used one is the vacuum stability test. It is described in the MIL-STD [1] and in the STANAG 4147 [2].

The compatibility criteria according to the vacuum stability test are valid unless other criteria, i.e. other test methods, are applied.

However, the vacuum stability test has some drawbacks: condensation, adsorption of gaseous products with test materials (polymers), and the fact that not all chemical reactions produce gases. Results obtained from vacuum stability tests have long been known to give satisfactory compatibility indications for high explosives but not for nitrate-ester-based propellants.

Since the vacuum stability test imperfections were noticed long time ago [3], a new approach was to study compatibility by methods detecting heat generation instead of gas evolution.

All spontaneous chemical and physical processes are associated with heat effects. Heat flow measurements were used to investigate the compatibility of explosives with polymer materials by a microcalorimeter [4,5,6]. The microcalorimetric method is widely accepted in laboratories dealing with compatibility examinations of explosive and polymer materials [6].

Thermal analytical techniques, like DSC, TG and differential thermal analysis (DTA), use small sample masses and the results are available in a short period of time [7,8]. Nevertheless, small sample masses could be a disadvantage because of sample inhomogenity.

The best is to apply several available experimental techniques. On the basis of the results of several techniques, it is possible to make a reliable judgment about the compatibility of explosive and polymer materials [6].

Compatibility examinations by thermal methods, e.g. the DSC method, are based on monitoring the melting temperature [9], the glass transition temperatures [10] when two polymer materials are examined, and the activation energy of kinetic parameters [11].

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In STANAG standards [12] the compatibility criteria are based on various parameters. In the STANAG 4514 they are based on onset temperatures, enthalpy changes, specific heat under constant pressure, while in the STANAG 4147 only changes in onset temperatures are monitored. In both standards in thermogravimetric analyses mass changes are used for compatibility judgment.

The criteria for compatibility monitoring according to the DSC and TG methods, from the STANAG 4147 [12], are:

DSC	temperature shift $\Delta T < 4^oC$	compatible
	temperature shift $4^oC < \Delta T < 20^oC$	certain degree of incompatibility
	temperature shift $\Delta T > 20^oC$	incompatible
TG	mass loss difference $\Delta m < 4\%$	compatible
	mass loss difference $4\% < \Delta m < 20\%$	certain degree of incompatibility
	mass loss difference $\Delta m > 20\ \%$	incompatible

Experimental part

Three types of polymer binders were examined: polyurethane (PU), carboxy-terminated and hydroxy-terminated polybuthadiens (CTPB and HTPB). Their compositions are is given in Table 1. The examined explosive materials were the single-base powder NC-27 (composition: nitrocelullose, diphenyl amine and graphite) and the double-base propellant NGR-275 (composition: nitrocelullose, nitroglycerine, centralite I, dinitrotoluene, trinitrotoluene, vynophile S, lead oxide and vaseline).

Table 1. Qualitative composition of binder

Qualitative composition of binder		
PU-2 (Sample 1)	CTPB-4 (Sample 2)	HTPB-1 (Sample 3)
PPG		
U-10-01		
	CTL-1	
		R-45M
TDI		TDI
	MAPO	
FeAA		FeAA
DOA		DOA
	CLO	
FβNA		FβNA
		TET

PPG and U-10-01 – different prepolymer-polyether polyols

CTL-1 – prepolymer-carboxy-terminated polybuthadiens

R-45M – prepolymer-hydroxy-terminated polybuthadiens

TDI – curing agent-toluen-2,4-diisocianate

MAPO – curing agent-tris-1-(2-methyl)-azirydinyl-phosphinoxide

FeAA – curing catalizer-ferriacetylacetonate

DOA – plastisizer-dioctyladipate

CLO – plastisizer-mineral oil

FβNA – stabilizer, antioxidant-phenyl-β-naphtylamine

TET – agent for improving the adhesion between the binder and filler-triethylentetrammine.

The sample examinations were performed on Perkin-Elmer instruments: the differential scanning calorimeter DSC-4 and the thermogravimetric analyzer TGS-2.

The DSC examinations [13] were carried out under a nitrogen flow of 50ml/min. The samples were hermetically sealed in Al pans. The temperature range was from 50^oC to 300^oC. The heating rate (b) was always $10^oC/min$.

The TG examinations were performed in the same temperature range, under a nitrogen flow of 50ml/min. The heating rate was the same for both types of analysis.

All samples were examined as pure materials, and each explosive material with each single polymer material, on both instruments. The mixture of samples was prepared by cutting the explosive materials in thin layers and by placing the binder layers over them. The mass ratios of polymer and explosive materials were registered.

Results and discussion

The DSC curves are shown: in Fig.1-3 for polymer binder examinations, in Fig.4-5 for powder and propellant examinations.

The TG curves are shown: in Fig.6-8 for polymer binder examinations, in Fig.9-10 for powder and propellant examinations.

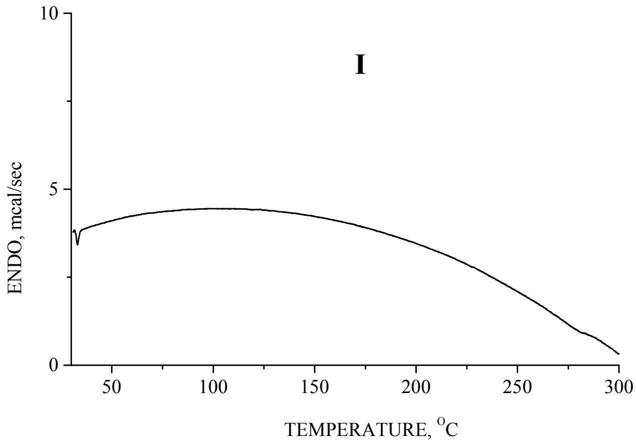

Figure 1. DSC curve of the PU-2 sample

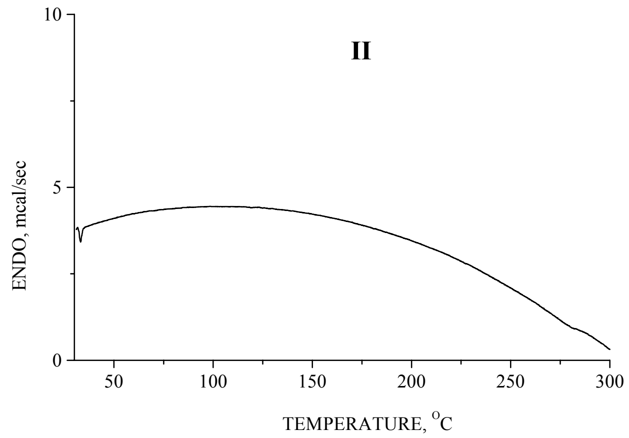

Figure 2. DSC curve of the CTPB-4 sample

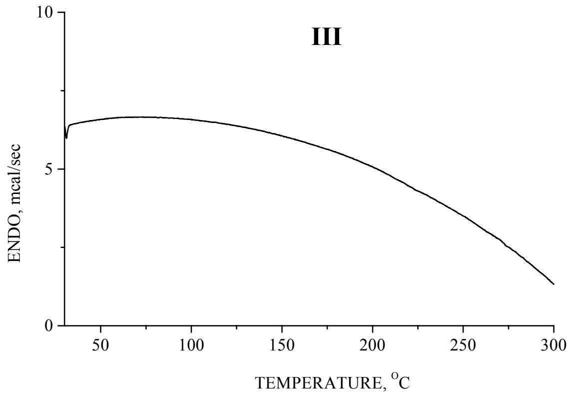

Figure 3. DSC curve of the HTPB-1 sample

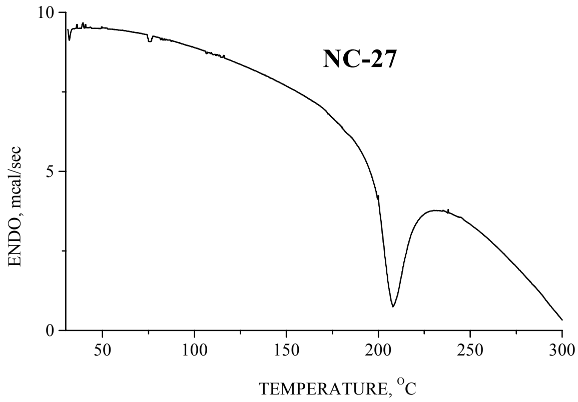

Figure 4. DSC curve of the NC-27 sample

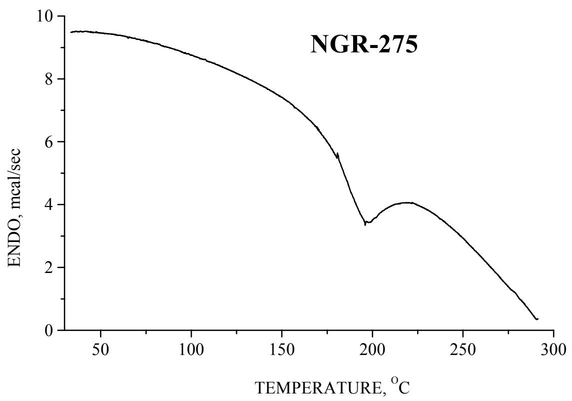

Figure 5. DSC curve of the NGR-275 sample

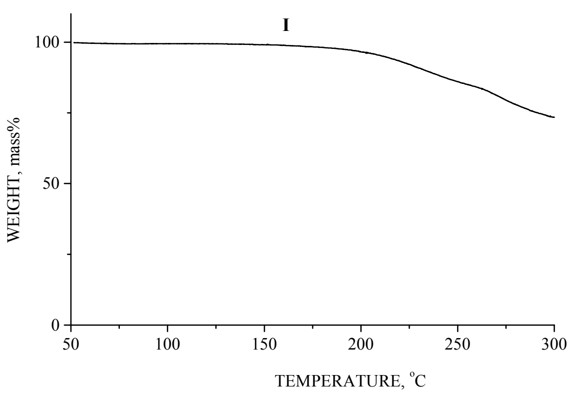

Figure 6. TG curve of the PU-2 sample

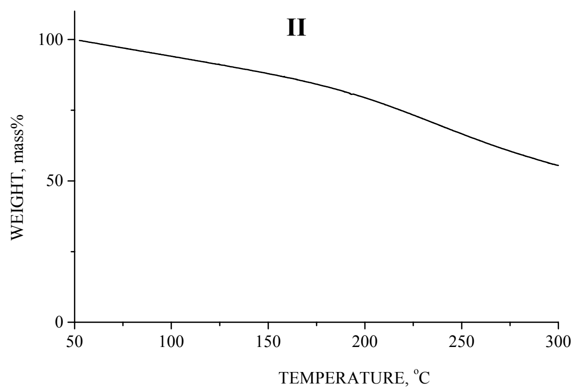

Figure 7. TG curve of the CTPB-4 sample

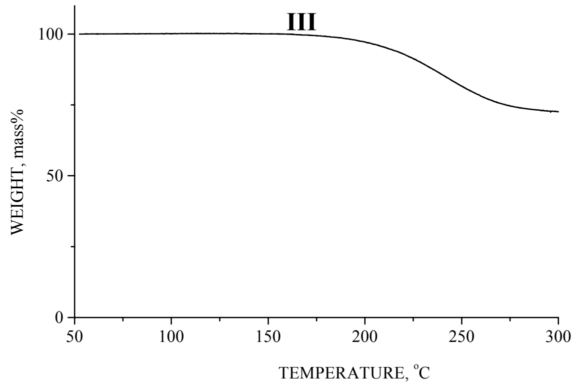

Figure 8. TG curve of the HTPB-1 sample

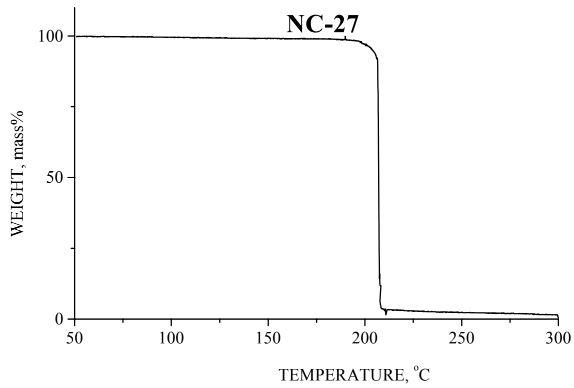

Figure 9. TG curve of the NC-27 sample

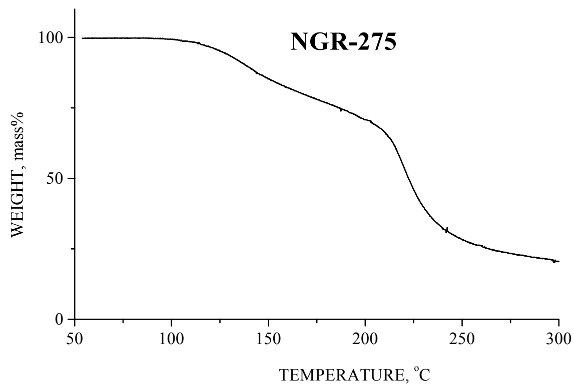

Figure 10. TG curve of the NGR-275 sample

The results of the DSC and TG examinations of the powder and propellant samples with different types of polymer binders are shown in Tables 2-5. Below each mixture of explosive and polymer binder its mass ratio is given in brackets.

Table 2. Results of the DSC compatibility tests with the powder NC-27

Sample	DSC, T_{onset}, °C			Compatibility judgment
	Pure	Mixture	ΔT	
NC-27	197,69			
PU-2+NC-27 (67,12%+32,88%) Sample 1/NC-27		197,03	0,66	Compatible
CTPB-4+NC-27 (44,9%+55,1%) Sample 2/NC-27		197,02	0,67	Compatible
HTPB-1+NC-27 (63,45%+36,55%) Sample 3/NC-27		197,04	0,65	Compatible

Table 3. Results of the TG compatibility tests with the powder NC-27

Sample	TG, Δm, mass% up to T_{onset} from DSC curve				Compatibility judgment
	Pure	Mixture	Theoretical	Δm	
NC-27	2,8				
PU-2+NC-27 (80,50%+19,50%) Sample 1/NC-27		1,4	3,6	2,2	Compatible
CTPB-4+NC-27 (48,11%+51,89%) Sample 2/NC-27		2,1	2,7	0,6	Compatible
HTPB-1+NC-27 (53,82%+46,18%) Sample 3/NC-27		1,4	2,8	1,4	Compatible

Table 4. Results of the DSC compatibility tests with the propellant NGR-275

Sample	DSC test, T_{onset}, °C			Compatibility judgment
	Pure	Mixture	ΔT	
NGR-275	183,3			
PU-2+NGR-275 (39,61%+60,39%) Sample 1/NGR-275		182,61	0,69	Compatible
CTPB-4+NGR-275 (59,63%+40,37%) Sample 2/NGR-275		188,36	5,06	Certain degree of incompatibility
HTPB-1+NGR-275 (54,11%+45,89%) Sample 3/NGR-275		181,44	1,86	Compatible

Table 5. Results of the TG compatibility tests with the propellant NGR-275

Sample	TG, Δm, mass% up to T_{onset} from DSC curve				Compatibility judgment
	Pure	Mixture	Theoretical	Δm	
NGR-275	25				
PU-2+NGR-275 (51,78%+48,22%) Sample 1/NGR-275		8,3	15,1	6,8	Certain degree of incompatibility
CTPB-4+NGR-275 (52,15%+47,85%) Sample 2/NGR-275		8,7	30,9	22,2	Incompatible
HTPB-1+NGR-275 (55,14%+44,86%) Sample 3/NGR-275		6,6	37,2	30,6	Incompatible

In the temperature range of the investigation of polymer on the DSC curves there is no peak. It means that the influence of the quantity of the used polymer material in the DSC examinations is negligible. Only the type of the polymer material is important. During the TG examination the mass loss at the explosive decomposition temperature (from the DSC examination) is registered. The theoretical value of the mixture mass loss is calculated as a sum of the explosive mass ratio multipled by its mass loss at the explosive decomposition temperature and the polymer binder mass ratio multipled by its mass loss at the explosive decomposition temperature. The theoretical value of the mass loss of the mixture of explosive and polymer materials during TG examinations is an ideal case of compatibility. The mixture behaves as if there were no interactions. Each deviation of the real mixture mass loss higher than 4 mass %, even in the case when a value of the mass loss is lower than the theoretical one (Table 5 with the TG examination results with the NGR-275), presents a sign of certain incompatibility and points out that the components interact in a degree which might be unfavourable for the system.

The TG compatibility criteria with their apsolute value of the mass loss should be differentiated from the microcalorimetric criteria in which each measured value of the mixture heat flow, lower than the theroretical one, is a proof of compatibility [5].

Conclusion

The DSC and TG methods have been successfully applied for compatibility examinations of explosive and polymer materials. The compatibility of three polymer materials (polyurethane, carboxy-terminated and hydroxy-terminated polybuthadiens), with the explosive materials (the single-base powder NC-27 and the double-base propellant NGR-275) was examined. On the basis of the on DSC and TG examinations, it is possible to conclude that the single-base powder NC-27 is compatible with all polymer materials. The double-base propellant NGR-275 is incompatible with the CTPB-4 and the HTPB-1, and its compatibility with the PU-2 should be additionaly examined with other methods. For a compatibility judgment it is neccessary to apply at least two methods. Being fast methods, the DSC and TG methods can be successfully used for a preliminary qualification of polymer usage with certain explosive material. Nevertheless, because of the safety reasons, the additional examinations should be performed, with greater sample masses, i.e. the microcalorimetric examination. The results of compatibility investigations should always be interpreted with care.

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Ispitivanje kompatibilnosti eksplozivnih i polimernih materijala termijskim metodama

Eksplozivne materije koje se nalaze u kontaktu sa polimernim materijalima moraju biti kompatibilne. Za brzo ispitivanje kompatibilnosti koriste se termijske metode. U radu su navedeni metodologija i kriterijumi primene diferencijalne skenirajuće kalorimetrijske i termogravimetrijske analize u ispitivanju kompatibilnosti eksplozivnih materijala, jednobaznog baruta i dvobaznog raketnog goriva, sa tri tipa polimernih veziva.

Ključne reči: **barut, raketno gorivo, polimerna veziva, kompatibilnost, termijske metode.**

Examen de la compatibilité des matériaux explosifs et polymères par les méthodes thermiques

Les matériaux explosifs en contact avec les matériaux polymères doivent être compatibles. Les méthodes thermiques sont utilisées pour l'examen rapide de la compatibilité. Cet exposé donne la méthodologie et les critères pour l'application de la calorimètrie thermique différentielle et la gravimétrie thermique dans l'examen de la compatibilité des matériaux explosifs-poudre et propergol à double base, avec trois types de liants polymères.

Mots-clés: **poudre, propergol, liant polymère, compatibilité, méthodes thermiques.**