

Short communication

Investigation of the stability of a mixture of single-based propellants and resins or polymers

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Abstract

The stabilisation of single-based propellants (SBP) with equal quantities of bisphenol A-based epoxy resin (ER), bromine-containing epoxy resin (BER), chlorinated polyvinylchloride (PCV) and chlorinated rubber (CR) were investigated by viscosimetry and calorimetry. All compounds were thermodynamically compatible with SBP. The degree of stabilisation of SBP was measured after accelerated ageing and was evaluated by the loss of weight and by means of differential scanning calorimetry (DSC). All compounds produced a significant decrease in the loss of weight, typically by more than a factor of 15 compared with unstabilised SBP. The stability of the compounds decreased in the order: CR > BER > PCV > ER. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Single-based propellants (SBP) and stabilisers form thermodynamically stable mixtures on a molecular level. They are compatible. One of the methods for determination of the compatibility is the measurement of viscosity of the solutions of investigated compounds. The efficiency of the stabilisers is related usually to their capacity to react with the products of degradation of nitrocellulose and to keep their initial concentration in the propellant for a long time. The degradation of propellants and stabilisers is accelerated by heating [1,2]. The application of differential scanning calorimetry (DSC) for investigation of propellants has been the aim of many articles [3]. The evaluation of the ageing with IR spectroscopy was

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made in [4–7]. In the last work, the authors compared the efficiency of several methods such as DSC, differential thermal analysis/thermogravimetry and pressure/vacuum stability test, with compatibility measured by microcalorimetry for propellants and polymers: polymethyl methacrylate, polyvinylchloride (PVC) and polyamides. For the first two polymers the results are the same. Only polyamides give variable results for the different test methods.

The aim of this investigation is to estimate the compatibility of SBP with resins and polymers and to evaluate the stabilising activity of these compounds after accelerated ageing.

2. Experimental

The investigations were made with seven-perforated SBP (Arsenal, Bulgaria), which had been stored for 12 years in a military storehouse without air condition and regulation of temperature. The compatibility of SBP and the compounds was investigated by means of viscosimetry and calorimetry of their diluted solutions in cyclohexanone. The compounds were: epoxy resin (ER) Diepox 600 (Lakprom, Bulgaria), bromine-containing epoxy resin (BER) Rütapox (Dow Chemical, USA), Perchlorovinyl (PCV; Russia) and chlorinated rubber (CR) Pergut (Höchst, Germany). The viscosity of the solutions was measured at 20 ± 0.1 °C with Ostwald viscosimeter and $\eta_{sp/C}$ were obtained according to [8]. The maximal differences $\Delta\eta_{sp/C}$ between the curves of additive viscosities and viscosity of the mixtures were measured. The calorimetry was carried out with an accuracy of ± 0.001 °C and the values ΔT were measured after mixing of the solutions of SBP with the investigated compound. Ageing of the films, obtained from mixtures SBP–resins or polymers was made in Xenotest (Germany) with ultraviolet (375 W) and infrared (250 W) illumination lamps according to the method described in [9]. The ageing at different temperatures, from -60 to $+70$ °C according to [10], was carried out in Ilka Foitron (Germany). DSC was made by means of Perkin-Elmer (USA) using the metal standards In, Sn, Pb, Zn from 20 to 500 °C with a rate of heating of 2.5 °C/min in an argon atmosphere under a pressure of 0.1 MPa; all samples were 4–6 mg weight.

3. Results and discussion

The stabilisers and nitrocellulose had to be compatible to form thermodynamically stable solutions on a molecular level. The investigated compounds ER and BER contain an epoxy group, acceptor of acids. The epoxy group content is 18% in ER and 6.7% in BER. If the stability is a function only from the quantity of the acid acceptor groups, ER has to be 2.6 times better stabiliser. CR has a content of double bonds of 28.12%, but the activity of epoxy group is greater in the addition reaction. On the other hand, the flexibility of the structure of CR is very high—the size of the mechanical segment is seven carbon atoms and this is the reason to form globules. On the basis of the molecular weights of SBP and CR and the equation $(h^{1/2})^2 = BM$, where $(h^{1/2})^2$ is the distance between the ends of the macromolecule, B a coefficient, M the molecular weight, the values for the nitrocellulose in the investigated SBP and CR were calculated. The results are 27.6 and 5 μm . In this way, the activity of double bonds decreased because the diffusion of acid in the globules was

Table 1
Effect of the composition of the mixtures on the values of $\Delta\eta_{sp/C}$ (cm³/g)^a

No.	Composition of the compounds (%)	SBP + BER ($\Delta\eta_1$)	MPM + BER ($\Delta\eta_2$)	NC + BER ($\Delta\eta_3$)
1	80:20	1.000	0.810	0.150
2	60:40	2.205	1.125	0.180
3	40:60	1.050	1.105	0.180
4	20:80	1.255	0.730	0.170

^a SBP contain 1.5% diphenylamine and 1.6% camphor; model propellant mixture (MPM) contains only nitrocellulose with nitrogen content equal to the nitrogen content of SBP; NC has 12.5% nitrogen.

limited by the rate of the reaction. PCV does not have a group capable to react with acids, therefore, after ageing, the mixtures with SBP must show a degradation equal or greater than pure nitrocellulose because HCl is possible to be formed from PCV. The results from the compatibility investigations are summarised in Tables 1 and 2. With the values $\eta_{sp/C}$ (ordinate) and composition of the mixtures (abscissa) the dependencies were obtained, and $\Delta\eta_{sp/C}$ was measured as the difference between theoretical additive values—the curve, obtained with $\eta_{sp/C}$ of solutions of SBP, and of the investigated compound.

The differences in the values of $\Delta\eta_{sp/C}$ can be explained by H-bond formation between NO₂ or ON groups of NC and protons from BER, and between OH group and O atom of BER and protons from NC. All values of $\Delta\eta_{sp/C}$ are different from zero—the compounds are thermodynamically compatible. The values of $\Delta\eta_{sp/C}$ and ΔT confirmed the compatibility of the compounds.

The results from the measurements with DSC of SBP and the mixtures with BER are in Figs. 1 and 2 and in Table 3.

The differences between the ΔH of SBP and the mixture SBP–BER are very large. On the other hand, in the two figures, ΔH increases with increasing time of illumination may be because of formation of radicals and oxides. The investigation of SBP, which had been stored for 52 years, by means of DSC shows a dependence of ΔH from the rate of heating. For the SBP, stored for 12 years, there is no dependence and the values of ΔH are similar (Table 4).

Table 2
Effect of the composition of the mixtures on the values $\Delta\eta_{sp/C}$ and ΔT^a

No.	Composition	$\Delta\eta_{sp/C}$ (cm ³ /g)	ΔT (°C)
1	ER + SBP	−1.7	1.48
	ER + NC	0.1	0.2
2	BER + SBP	−1.6	1.4
	BER + NC	0.18	0.2
3	CR + SBP	1.6	1.2
	CR + NC	0.3	0.4
4	PCV + SBP	1.5	1.09
	PCV + NC	0.6	0.36

^a All compositions have one and the same quantity of components: 50% SBP or NC and 50% of investigated compounds.

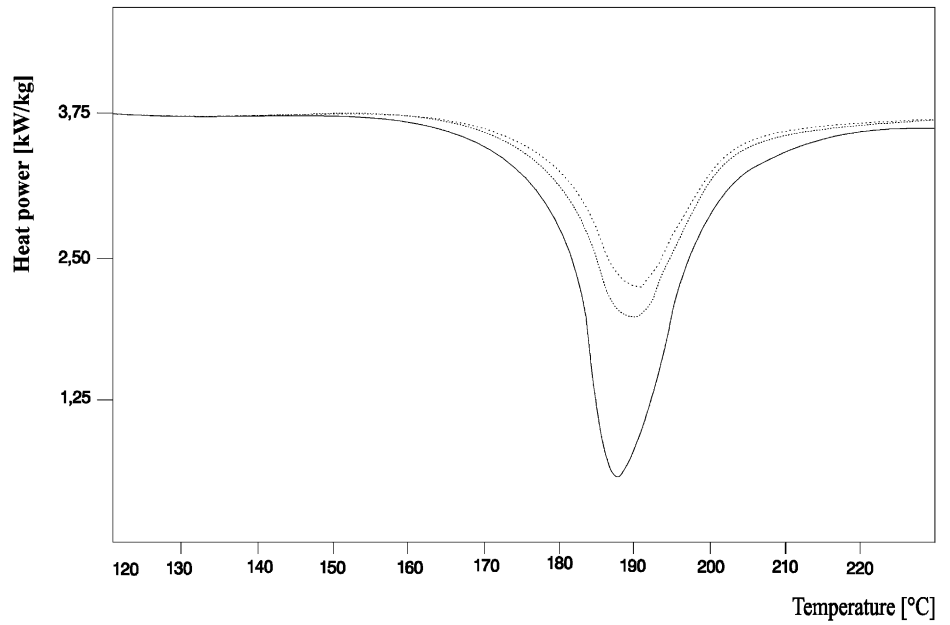


Fig. 1. DSC curves of the mixtures SBP-BER: before ageing; after 120 h illumination; after 240 h illumination.

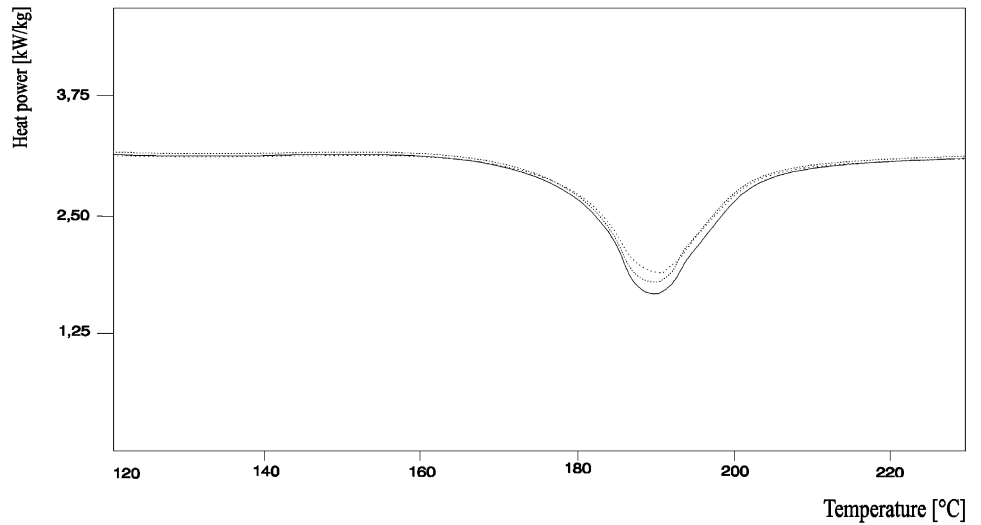


Fig. 2. DSC curves of SBP: before ageing; after 120 h illumination; after 240 h illumination.

Table 3
Effect of time of illumination on the results of DSC

No. and sample	Ageing (h)	ΔH (kJ/kg)	ΔW (%)	T_p (°C)
SBP				
1	0	770	57.7	118.4
2	120	905	64.6	187.4
3	240	1406	64.5	187.2
SBP + BER				
1	0	805	28.1	190.9
2	120	770	30.0	190.1
3	240	778	31.8	191.1

Table 4
Effect of the rate of heating on the ΔH of SBP

No.	Rate of heating (°C/min)	ΔH (kJ/kg)	
		52 years	12 years
1	2.5	1950–2000	1530–1580
2	1.25	1830–1870	1580–1690
3	0.625	1680–1720	1560–1610

From Table 4, the increase of ΔH with time of ageing is evident. The values of ΔH (kcal/mol) for nitrogen oxides formation are: N_2O 1.99; NO 21.6; NO_2 8.091; N_2O_4 2.309; N_2O_3 20.0; N_2O_5 3.6. The nitrogen content of SBP decreased after ageing and the formation of different oxides may change ΔH .

The decrease of the weight of the samples was also measured after thermal ageing (Table 5).

The activity of the investigated compounds in the stabilisation of SBP decreased in the order $CR > BER > PCV > ER$.

The explanation of the results obtained will be made after investigation of the mechanisms of the reactions between SBP and compounds.

Table 5
Effect of the time of ageing on the loss of weight ΔW of samples

No.	Ageing (h)	ΔW (%) of samples				
		SBP + ER	SBP + BER	SBP + PCV	SBP + CR	SBP
1	360	0.56	0.38	0.36	0.34	4.98
2	504	0.24	0.18	0.20	0.14	4.59
3	672	0.42	0.30	0.33	0.33	5.04
Total		1.22	0.86	0.89	0.81	14.61

4. Conclusions

The stabilisation of SBP with compounds containing epoxy group or double bonds was investigated. All compounds were thermodynamically compatible with SBP and used in equal amounts. The stabilising activity of the compounds was obtained by accelerated ageing of the films made from mixtures SBP–resin or polymer. This activity did not depend on acid acceptor group concentration. Weight loss was typically reduced by more than a factor of 15 compared with unstabilised SBP. Stabilisation decreased in the order: CR > BER > PCV > ER; the effectiveness of the first three being broadly similar.

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