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Investigation of Selected Ingredients of Composite Propellants Using DTA, SEM and Calorimetric Techniques

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Abstract: The results of instrumental analysis of some ingredients of composite propellants are presented. Scanning electron microscopy, water calorimetry, elemental analysis and differential thermal analysis were used for characterization of ammonium chlorate(VII), aluminum-magnesium alloy and polybutadienes. The results showed that the oxidizer is in the form of spheroidal particles with a diameter 100-200 μm. Morphological analysis of the aluminum-magnesium alloy showed that the powder contains several fractions differing in size and shape. The predominant fractions are polygons with edges joined at acute angles. The grain size of the main fraction does not exceed 100-150 μm. The commercial polymers tested have similar elemental compositions and heats of combustion in oxygen. The standard enthalpies of formation calculated for the tested polymers have positive values and are in good agreement with literature data for non-cured HTPB.

Keywords: analysis, energetic properties, composite propellants

1 Introduction

The reproducibility of the properties of the ingredients of composite propellants is very important for the proper working of rocket motors. Modern propellants

are characterized by dependability, high impulse, high energy efficiency and low sensitivity for accidental ignition [1, 2]. These properties are obtained by using components with the proper physical and chemical properties, structure and morphology [3]. The reproducibility of the characteristics of propellants requires the use of many advanced research methods in order to choose the ingredients with optimal properties [1]. The precise analysis of these component powders requires the use of scanning electron microscopy (SEM). Structural studies of the polymers used as binders (and typically fuel) requires spectroscopic methods such as nuclear magnetic resonance spectroscopy (NMR). The standard enthalpies of formation of these polymers are computed by thermodynamic calculations based on the results obtained by calorimetric methods [4, 5]. The characteristic temperatures of phase transitions and decomposition for propellants are calculated based on the results obtained by differential thermal analysis (DTA).

In this paper we present the results of the instrumental analysis of chosen ingredients used in solid rocket propellants. Composite propellants, prepared using the analysed ingredients, were tested with the DTA technique.

2 Scanning Electron Microscopy

Morphological analysis of commercial ammonium chlorate(VII) granules (AP1, made in Institute of Industrial Organic Chemistry (IPO), Warsaw) and aluminum-magnesium alloy (PAM4, supplied by Promet) was performed using a scanning electron microscope Gemini LEO 1530 operating at 3 kV, with a working distance cathode-sample of 5 mm. The SEM images are shown in Figures 1 and 2.

Analysis of the PAM4 sample showed that the powder contains several fractions, differing in size and shape. The predominant fractions were polygons with edges joined at acute angles, where one linear dimension is greater than the other. The grain size of the main fraction did not exceed 100-150 μm. The minor fraction was flakes in which the largest linear dimension did not exceed 5 μm. The thickness of the flakes did not exceed 250 nm. The flake-like structures were sufficiently different from the dominant fraction of polygons, that it may be suspected that sample PAM4 is an intentional mixture.

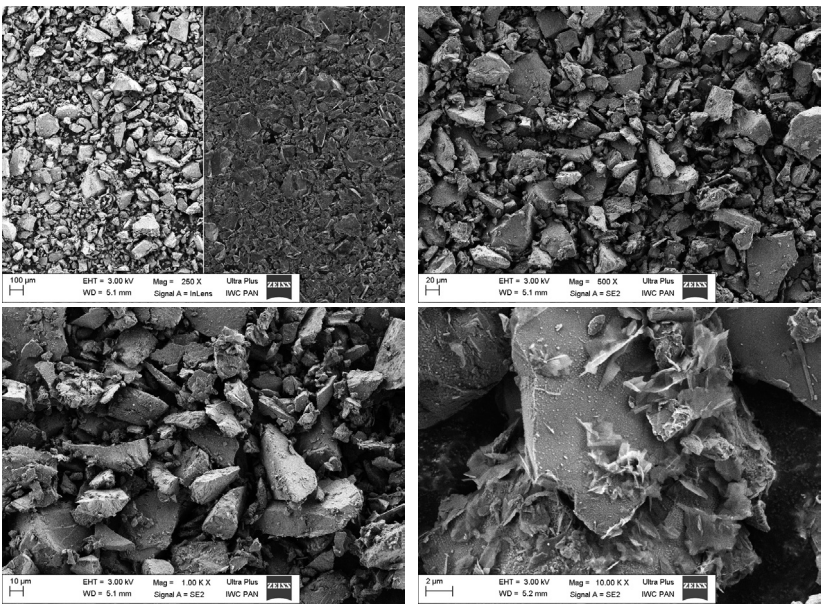

Figure 1. SEM images of aluminum-magnesium alloy (PAM4) at different magnifications.

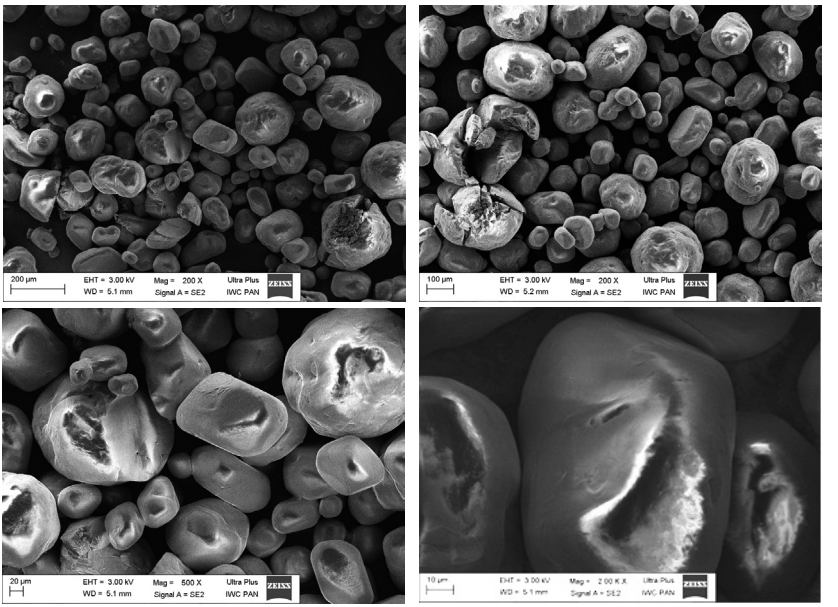

Figure 2. SEM images of ammonium chlorate(VII) granules (AP1) at different magnifications.

Analysis of the AP1 sample showed that it contained spheroidal particles with a diameter of 100-200 μm. The surface of the spheroids was smooth on the micrometer scale, but most of them exhibited visible craters with regular shapes. A cross-section of the granules did not reveal polycrystalline structure. The shape and internal structure of the granules at the microscopic level does not show the typical characteristics of an inorganic crystal, which suggests that the shape of the grains is not natural and has been produced intentionally.

3 Heat of Combustion

The heat evolved during the combustion of the tested commercial polymers (supplied by Cray Vallay, the acronyms originate from the manufacturer) in pure oxygen (30 bar) was recorded using a standard water calorimeter (KL-12, Precyzja, Bydgoszcz). The heat capacity of the calorimeter and bomb, determined under conditions identical to those used in the subsequent measurements, was 13150 J/K. The test results are shown in Table 1.

Table 1. Heat of combustion of the chosen polymers

Sample	Sample mass [g]	Heat of combustion [kJ/g]	Average heat of combustion [kJ/g]
R45M	0.824	43.436	44.277
	0.804	44.339	
	0.821	45.057	
R45 HTLO	0.813	44.724	44.657
	0.837	44.872	
	0.819	44.375	
LBH2000	0.850	44.925	45.038
	0.836	45.157	
	0.809	45.033	

The heats of combustion obtained for the polybutadienes tested are not significantly different. The lowest value was recorded for sample R45M and largest for sample LBH2000. The difference between these extreme values was approximately 0.76 kJ/g. The values of the heats of combustion (in oxygen) obtained are typical for chain hydrocarbons and polybutadienes [6]. The largest contribution to the heat of combustion of organic compounds is from hydrogen. The heat of combustion of the compounds increases with increasing hydrogen content in each sample.

4 Elemental Analysis

The measurements of the elemental compositions were performed using a Perkin-Elmer CHNS/O Model 2400, with the possibility of extended burning time. The oxygen contents were calculated as a complement to 100% after summing the other determined element contents. The chemical (empirical) formulas for hypothetical 100 g samples of each tested polymer were calculated on the basis of the results of the elemental compositions. With the empirical formulas and heats of combustion, the standard enthalpies of formation were calculated for all polymers. The calculations were made on the basis of a balanced thermodynamic cycle (for each polymer) where the standard enthalpy of formation was unknown. The equation formed on the basis of this cycle was as follows:

$$\Delta H_f = n \cdot \Delta H_c(C) + n \cdot \Delta H_c(H_2) - \Delta H_c(polymer)$$

where: ΔH_f – standard enthalpy of formation; ΔH_c – enthalpy of combustion.

The standard enthalpies of combustion for solid carbon and gaseous hydrogen were taken from the literature [7]. The measured and calculated results are shown in Table 2.

Table 2. Results of elemental analysis, empirical formulas and standard enthalpies of formation of the tested polymers

Sample	Elemental analysis, [%]				Empirical formula (for 100.00 g sample)	Standard enthalpy of formation [kJ/mol]
	C	H	N	O		
R45M	87.49	10.63	0.00	1.88	$C_{7.29}H_{10.52}O_{0.12}$	52.7
R45 HTLO	87.45	10.69	0.00	1.86	$C_{7.29}H_{10.58}O_{0.11}$	82.1
LBH2000	87.53	10.82	0.00	1.65	$C_{7.29}H_{10.71}O_{0.10}$	100.2

The tested polymers have very similar elemental compositions, the differences not exceeding 0.19% for hydrogen and 0.23% for oxygen (this element was not measured directly). The results of the elemental analyses and the calculated empirical formulas are in good agreement with the theoretical and experimental data for standard HTPB [8]. Because the empirical formulas of the polymers are similar, the differences in the values of the standard enthalpies of formation are probably due to structural differences.

5 Differential Thermal Analysis (DTA)

Differential thermal analyses were carried out with a LabSys-DTA-TG Setaram apparatus. Samples of the products of mass *ca*. 5 mg were heated in alumina crucibles from 25 to 400 °C at 5 K/min in a pure nitrogen atmosphere (flow rate *ca*. 50 cm^3/min). The DTA analyses were carried out for four samples of solid rocket propellants (made or supplied by IPO). Three of them are propellants from the rocket Proton series. Sample F was prepared in the Institute of IPO in Warsaw. The DTA curves of the samples tested are shown in Figure 3.

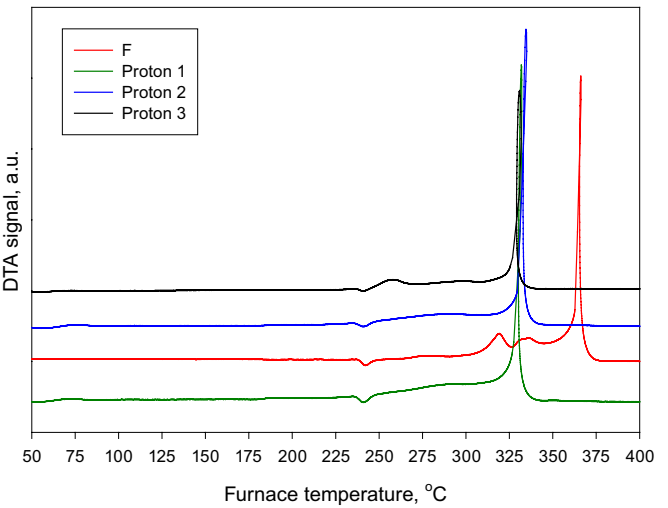

Figure 3. DTA curves for samples of the tested composite propellants.

The thermal stabilities of the Proton series samples were similar. The main decomposition peak of sample F was shifted to higher temperatures and appeared at a temperature about 50 °C higher in relation to the Proton series samples. A small endothermic peak with max. 242-244 °C appeared on the DTA curve of each sample and can be attributed to the transition from the orthorhombic to the cubic phase of NH_4ClO_4 [9]. After the phase transition of the oxidizer, a broad exothermic peak with small intensity appeared on each thermogram. For the Proton-series samples, a broad weak peak changed in a single step to a strong exothermic peak with a maximum in range 330.8-334.5 °C, which can be attributed to decomposition of the samples. Under the same conditions sample F showed a three-stage decomposition. The first two steps had similar character (broad peak, low intensity). The third stage of sample F decomposition had the highest rate at a peak maximum of 366 °C. If

the stability criterion is the main peak temperature, the highest thermal stability was recorded for sample F.

6 Conclusions

Scanning electron microscopy of commercial aluminum-magnesium alloy (PAM4) showed that the dominant fractions are polygons with edges joined at acute angles, where one linear dimension is greater than the other. The grain size of the main fraction did not exceed 100-150 μm. The minor fraction in the sample was flakes in which the largest linear dimension did not exceed 5 μm and the thickness of the flakes did not exceed 250 nm. Morphological analysis of ammonium perchlorate samples showed mainly spheroidal particles with a diameter 100-200 μm. The surface of the particles was relatively smooth on the micrometer scale. The cross-section of some granules did not reveal polycrystalline structure.

The heats of combustion obtained for the polybutadienes tested were not significantly different at about 44-45 kJ/g. With the results of the elemental analyses it was possible to calculate the standard enthalpy of formation of the studied polymers. Values of ΔH_f for the tested HTPBs varied from 50 to 100 kJ/mol. The DTA measurement of sample F exhibit the best thermal stability among other tested, but small endo- and exo-thermic peaks appeared before the main decomposition peak, in the same range as in all of the tested samples.

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