

PROPERTIES OF SOLID ROCKET PROPELLANTS DIFFERING IN UTILIZED BINDER

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Introduction

The main components of solid propellants is the oxidising agent and binder, the latter of which also fulfils the role of fuel. These components are typically supplemented by auxiliary components, such as metallic fuels, combustion modifiers, plasticisers, and other additives [1].

Many solid rocket fuels described in literature utilise hydroxyl-terminated polybutadiene (HTPB) as a binder [1], due to the fact that HTPB exhibits favourable properties, such as good adhesive properties, high heat of combustion and high stability [2,3]. On the other hand, the use of HTPB requires it to be cross-linked. This process is usually carried out using highly toxic isocyanates and further decreases the already strongly negative oxygen balance of HTPB [4]. This contributes to the fact that HTPB-based solid propellants must contain a large amount of oxidising agent, which translates to the need to achieve high loading of the HTPB matrix with solid particles [2,3]. Unfortunately, the use of large amounts of the oxidising agent limits the use of auxiliary components quite significantly. This further translates into lower performance of this group of solid propellants.

Consequently, an emergent trend in the development of solid rocket propellants is to utilise polymers containing explosophore groups as binders. Such explosophore groups include nitrate (ONO₂), nitro (NO₂) and azido (N₃) groups [5].

The aim of the work was to study the effect of the choice of binder used (hydroxyl-terminated polybutadiene as a non-energetic binder and glycidyl azide polymer as an energetic binder) on the properties of rocket propellants. In addition, the prepared rocket propellants samples differed in the utilised oxidising agent - it was, respectively, ammonium perchlorate belonging to the "traditional" oxidants and phase-stabilised ammonium nitrate - its "green" alternative.

Materials and methods

The materials used in this project are shown in Table 1.

Table 1 Materials used in this project.

Ingredients	% wt.			
	SRP-1	SRP-2	SRP-3	SRP-4
GAP	25	-	25	-
HTPB	-	25	-	25
AP ^a	52	52	-	-
PSAN ^b	-	-	52	52
Mg	18	18	18	18
NQ ^c	2	2	2	2
MDI ^d	3	3	3	3

where:

- a – ammonium perchlorate
- b – phase-stabilised ammonium nitrate [6]
- c – nitroguanidine
- d – methylene diphenyl diisocyanate

Glycidyl azide polymer (GAP) and nitroguanidine (NQ) have been synthesised according to the literature. GAP was synthesized according to the literature [7]. The first step was the polymerisation of epichlorohydrin using ethylene glycol, boron trifluoride-diethyl ether adduct (BF₃-Et₂O) as the catalyst and dichloromethane as the solvent. The next step was the substitution of chloride groups with azide groups in a reaction with sodium azide.

Nitroguanidine was prepared according to [8]. Nitroguanidine was obtained by reacting concentrated sulfuric acid with guanidine nitrate.

As part of the research task, the effect of the substances used on the ignition temperature of the tested rocket propellants was measured. The sensitivity to mechanical stimuli of the prepared formulations, as well as linear combustion velocity was determined. Using differential scanning calorimetry (DSC), the heat of combustion of rocket propellants was investigated and the thermal decomposition characteristics of the binders used were determined. The activation energy values were also determined from the DSC measurements, which were calculated using the Kissinger method.

Results and Discussion

a) Friction and impact sensitivity

Regardless of the oxidising agent used, propellant formulations with GAP as a binder showed greater friction sensitivity than those containing HTPB (Table 2). It can be related to more rigid polymer chain.

Table 2 Friction and impact insensitivity of the produced solid rocket propellant samples.

Sample	Friction sensitivity [N]	Impact sensitivity [J]
SRP-1 [GAP+AP]	84	5
SRP-2 [HTPB+AP]	120	2
SRP-3 [GAP+PSAN]	112	7.5
SRP-1 [HTPB+PSAN]	160	50
SRP-1 [GAP+AP]	84	5

Higher sensitivity to impact of HTPB-based samples can be related to higher hardness of GAP-based samples – released mechanical energy is consumed for fracturing the cured polymer matrix.

b) Determination of ignition/explosion temperature

Results from determination of ignition/explosive temperature are listed in Table 3.

Table 3 Results of determination the ignition/explosive temperature.

Sample	SRP-1 [GAP/AP]	SRP-2 [HTPB/AP]	SRP-3 [GAP/PSAN]	SRP-4 [HTPB/PSAN]
Ignition/explosive temperature [°C]	320	336	229	259

Despite the oxidizer used, GAP-based samples have lower ignition temperature. It can be related to higher sensitivity to flame of this samples.

c) Determination of linear velocity of combustion

Table 4 Determination of linear velocity of burning

Sample	SRP-1 [GAP/AP]	SRP-2 [HTPB/AP]	SRP-3 [GAP/PSAN]	SRP-4 [HTPB/PSAN]
Linear combustion velocity [mm/s]	6.3	4.0	3.5	2.2

Interestingly, higher linear velocity of combustion value is observed for formulations containing GAP – regardless the oxidizer used (Table 4). Higher linear velocity of samples containing GAP as a binder can be linked to presence of additional high-energy azide groups in the polymer.

d) Study of the kinetics of energetic transformations

DSC studies were performed using different heating rates: K/min, 5 K/min, 7 K/min, 10 K/min, 12 K/min, and 15 K/min to determine the activation energy. In the case of SRP-4 (HTPB/PSAN), the results obtained could not be considered reliable. Despite taking additional measurements, the thermograms did not show repeatability. Consequently, the activation energy was not determined for this formulation.

The results of the E_a investigation are presented in Table 5.

Table 5 Results of determination of activation energy.

Sample	E_A [kJ/mol]
SRP-1 [GAP/AP]	148.5
SRP-2 [HTPB/AP]	189.7
SRP-3 [GAP/PSAN]	129.2

The sample, containing GAP and PSAN has the lowest activation energy, while the sample containing HTPB and AP had the highest activation energy. From the point of view of rocket propellants, it is more favourable to obtain lower activation energies, as this indicates that high-energy decomposition reactions occur more easily.

Summary

The aim of this project was to identify the effect of the binder used on the properties of solid rocket fuels. As expected, the tests performed showed a strong influence of the utilised binder, on the parameters that characterize SRP formulations. It is worth noting that the use of an energetic binder (GAP) together with a "green" oxidant leads to the lowest activation energy. When considering the requirements for solid rocket fuels, it turns out that it is more advantageous to use an energetic binder. The presence of additional azide groups (explosive groups) in the polymer backbone contributes to improved properties.

Referenses

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