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Research paper

Effects of Azide-Hydroxyl-Terminated Polybutadiene on the Properties of Solid Heterogeneous Rocket Propellants

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Abstract: Solid heterogeneous rocket propellants (SHRPs) are increasingly used, mainly in the armaments industry. SHRPs are usually based on an inert binder – hydroxy-terminated polybutadiene (HTPB). The use of an inert polymer reduces the performance of the propellants, therefore this paper presents the preparation of propellants with different contents of the previously synthesized azide-HTPB and the results of research on their properties, such as density, calorific value, mechanical and thermal parameters and burning rate. An improvement in the tested parameters was noted in comparison to the properties of propellants without azide-HTPB. An increase in the calorific value of the propellants with the addition of azide-HTPB was noted, with a simultaneous reduction in the amount of oxidant in the SHRP composition. Azide-HTPB as a rocket propellant component has a significant impact on the mechanical properties of the propellant and also increases the propellant's burning rate and the maximum pressure in the motor chamber.

Keywords: HTPB, azide-HTPB, energetic binder, burning rate

1 Introduction

A rocket propellant is defined as a chemical compound or mixture of chemicals that releases significant amounts of heat and high-temperature gases during their combustion process. The kinetic energy generated by the gaseous products acts as a propulsion source for rocket motors [1]. Liquid and solid propellants are used in the military and space fields. However, solid propellants, including solid heterogeneous rocket propellants (SHRPs), have advantages over liquid propellants due to features such as long storage life, simplicity and reliability of operation [2]. Designing an SHRP composition with favorable ballistic, energetic and physicochemical characteristics requires the appropriate selection of its components and their content in the propellant. SHRPs are composed of a powdered fuel and a crystalline oxidant bound together in a binder matrix, together with others components such as a plasticizer, a curing agent and ingredients to improve the properties of the propellant and its technological processes. On account of their structure, SHRPs are also called composite propellants [3-5].

The most common polymer used as the binder is hydroxyl-terminated polybutadiene (HTPB). Its low viscosity allows the use of more solid components and the production costs of propellants containing this polymer are not high due to the low price and ready availability of HTPB. Additionally, the process of hardening the propellants and forming a polyurethane matrix is possible at relatively low temperature. Propellants with polyurethanes based on HTPB are characterized by long storage possibilities due to the stability of their properties, resistance to moisture, frost and insensitivity to mechanical stimuli because of their good dispersion [1, 6]. HTPB, despite its unique physicochemical properties, has a significant disadvantage – it is an inert compound [7]. A non-energetic binder requires a high level of oxidizer to be incorporated in the propellant, thus creating highly filled compositions and obstructing further stages in the propellant manufacture. In addition, binders that do not contain energetic groups have a negative effect on the propellant's specific impulse. For this reason, the development of energetic polymers has been investigated, which would allow the above-mentioned disadvantages of commonly used binders to be avoided and would improve other propellant properties, *e.g.* density and burning rate [8, 9]. HTPB is a chemically reactive compound, so numerous modifications have been described in the literature to confer energetic properties and to maintain physicochemical properties similar to the unmodified form. HTPB derivatives may contain nitro groups [10-13], dinitrate ester groups [14, 15], azide groups [16, 17] or azide and dinitrate ester groups simultaneously [18]. Moreover, HTPB was functionalized by attaching nitrogen rich molecules at the terminal carbon

atoms of the polymer [19-24]. Among the HTPB derivatives prepared, those containing azide groups are promising due to the high positive heat of formation, high density, high burning rate and good thermal stability of the high nitrogen content polymer [8, 25].

The main objective of the present article was in modifying HTPB by attaching azide groups along the polymer backbone (azide-HTPB, Figure 1), as in the synthesis reported by Pant *et al.* [17], testing the compatibility of azide-HTPB with the basic SHRP components, preparing a propellant containing the previously obtained azide-HTPB and determining its properties.

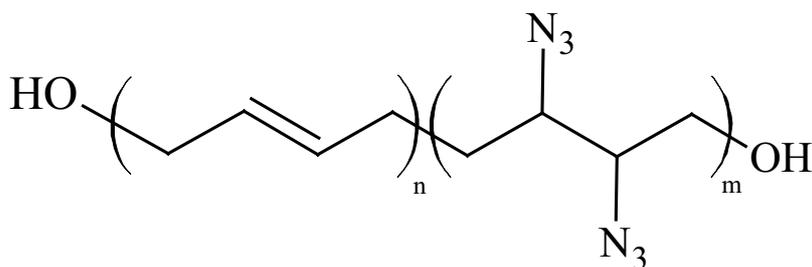


Figure 1. Chemical structure of azide-HTPB

2 Materials

The following materials were used. Oxidizer ammonium chlorate(VII) (AP, Aldebaran Sistemas S.L.), plasticizer dioctyl adipate (DOA, Boryszew ERG, Poland), dimeryl di-isocyanate (DDI, Beijing YANAXA Technology Development Co., Ltd.), HTPB (R45HTLO, Cray Valley), aziridine HX-752 (Tanyun Junrong Chemical Research Institute) and antioxidant AO 2246 (Sigma-Aldrich). Carbon tetrachloride (analytical grade, Chempur), bromine (analytical grade, Chempur), N,N-dimethylformamide (DMF, analytical grade, Chempur) and sodium azide (analytical grade, Chempur) were used as purchased.

3 Test Methods

The azide-HTPB obtained was characterized using Fourier transform infrared spectroscopy. The spectra were measured in the wavenumber range 4000-450 cm^{-1} in the transmittance mode of an FT-IR spectrometer, Spectrum Two, Perkin Elmer.

Elemental analysis of the final product was performed with a CHNS analyzer (Elementar, model Vario EL III) in order to determine the percentage content of the chemical elements, including nitrogen atoms introduced in the form of the azide groups.

Compatibility tests were carried out in accordance with Standardization Agreement STANAG 4147 (edition 3), test 3 – Dynamic Thermogravimetry. The thermogravimetric analysis (TG) was conducted using the TGA5500 (TA Instruments), under nitrogen gas (25 mL/min), from room temperature to 550 °C, at heating rate 2 °C/min, using aluminium pans. For safety reasons, the sample masses of individual components were reduced in relation to the masses indicated in STANAG 4147. The prepared sample mass of individual compounds was approximately 0.5 mg.

The densities of the prepared propellants were measured using a helium pycnometer, Micromeritics AccuPyc II 1340.

The calorific value (isochoric heat of combustion) was measured using an adiabatic calorimeter IKA WERKE C2000. The mass of the tested samples was about 0.5 g.

The percentage mass loss of the prepared propellants was measured using a thermal analyzer SDT650 (TA Instruments), under nitrogen gas (25 mL/min) at heating rate 10 °C/min, using alumina pans. The sample mass was approximately 1.5 mg and the temperature range was from room temperature to 600 °C.

A statistical uniaxial tensile test was carried out on an Instron 3366 two-column testing machine. Constant velocity tensile measurement (50 mm/min) was performed at room temperature.

Burning rate tests were made using a small scale laboratory rocket motor. The motor consisted of a nozzle part with a replaceable nozzle, a cylindrical combustion chamber, a propellant charge, an igniter and a chamber closure. A pressure sensor, an amplifier and a computer were connected to the system. The software recorded the burning time and pressure in the combustion chamber.

4 Results

4.1 Synthesis of azide-HTPB

As described in reference [17], azide-HTPB was prepared by a two-step synthesis. The first step was bromination of the polymer by reacting bromine with HTPB. In the second step, the brominated HTPB was treated with sodium azide to introduce the azide groups by substitution of the bromide atoms. Figure 2 shows the scheme for modification of HTPB by azide groups.

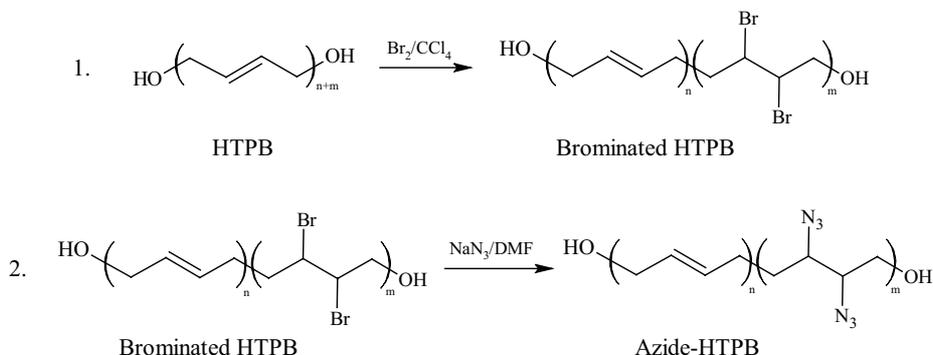


Figure 2. Synthesis of azide-HTPB

The HTPB (R45HTLO, Cray Valley) used for the synthesis was dried at 120 °C under continuous vacuum to remove moisture and was then stored in a closed vessel at 0 °C. Carbon tetrachloride (analytical grade, Chempur), bromine (analytical grade, Chempur), *N,N*-dimethylformamide (DMF, analytical grade, Chempur) and sodium azide (analytical grade, Chempur) were used as purchased.

The analysis of the FT-IR spectra of both the unmodified HTPB and azide-HTPB (Figure 3) showed the peaks characteristic for the structure of HTPB:

- stretching vibrations [cm^{-1}]: 2914 ($\nu_{\text{C-H,asym}}$), 2844 ($\nu_{\text{C-H,sym}}$) and 1639 ($\nu_{\text{C=C}}$),
- scissoring vibrations: 1436 cm^{-1} ($\delta_{\text{C-H}}$) and
- bending out-of-plane vibrations [cm^{-1}]: 964 ($\gamma_{\text{C=C(1,4-trans)}}$), 911 ($\gamma_{\text{C=C(1,2-vinyl)}}$) and 681 ($\gamma_{\text{C=C(1,4-cis)}}$),

indicating that the HTPB structure was preserved in the synthesized compound. The synthesized product exhibited an additional peak belonging to bonds of the azide groups (stretching vibrations $\nu_{\text{-N}_3, \text{asym}}$: 2100 cm^{-1}), indicating complete reaction and the formation of the expected HTPB derivative [26, 27].

Elemental analysis of the final product (duplicate measurement) were made for azide-HTPB and were used to calculate the average values (measurement difference less than 0.06%). The results of the elemental analysis are presented in Table 1. The content of nitrogen atoms in azide-HTPB was 1.77%.

Table 1. Elemental analysis of azide-HTPB

Sample	Chemical element [%]		
	C	H	N
Azide-HTPB	82.08	10.43	1.77

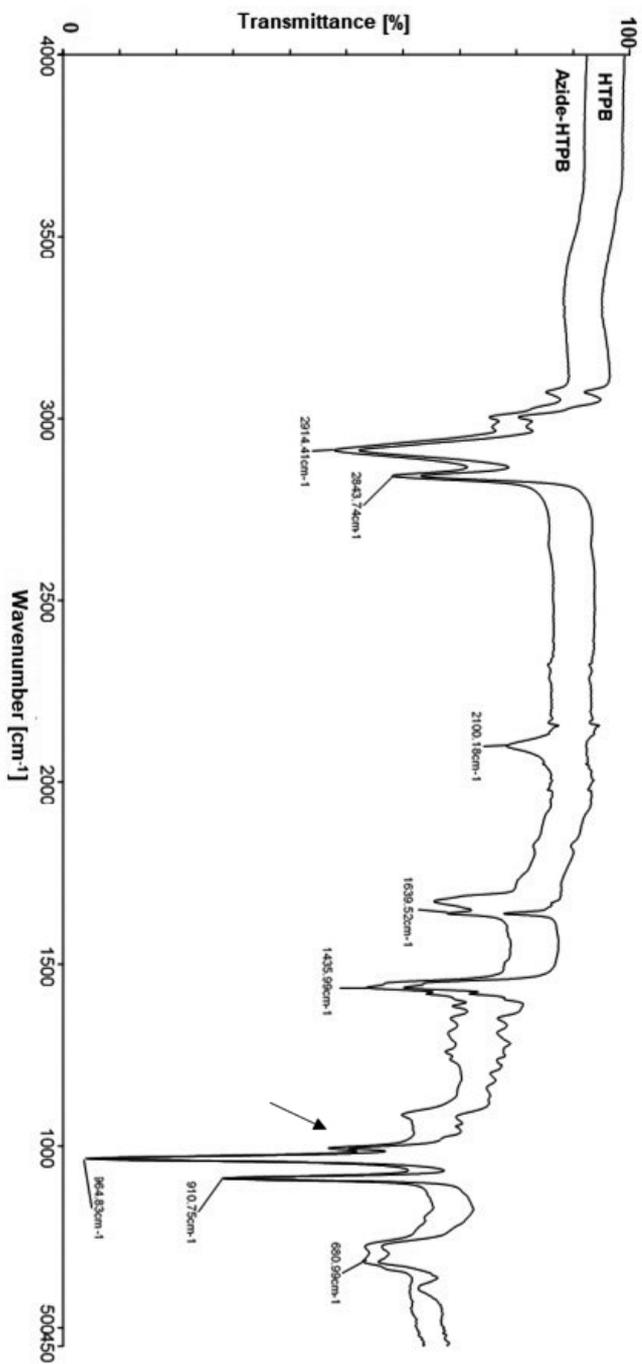


Figure 3. FT-IR spectra of HTPB and azide-HTPB

4.2 Compatibility of azide-HTPB

Chemical compatibility with other components in the formulations is an important property, which decides on the usability of a new compound as a propellant ingredient. Before making the propellants containing azide-HTPB, the compatibility of the modified polymer with other propellant components, such as AP and DOA was tested.

First, the measurements of the individual components (azide-HTPB, AP, DOA) were performed, then their mixtures in a 1:1 ratio by weight were measured using TG. By comparing the TG curves of the individual components and their mixtures, the compatibility or incompatibility can be detected. The compatibility/incompatibility was assessed by determining the difference between the observed weight loss of a mixture and the calculated sum of the weight losses of the components in the mixture (Equation 1). The experimental mass loss was taken at the temperature of the lowest derivative TGA peak of the sample.

$$W_R = W_M - W_{M,calc} = W_M - \frac{m_1 \cdot W_1 + m_2 \cdot W_2}{m_1 + m_2} \quad (1)$$

where W_R is the mass loss due to inter-reaction [%], W_M is the mass loss of the mixture [%], $W_{M,calc}$ is the calculated mass loss of the mixture, without inter-reaction [%], W_1 and W_2 are the mass losses of the first and the second compound, respectively, in the single measurement [%] and m_1 and m_2 are the masses of the first and the second compound, respectively, in the mixture [mg].

If the change (calculated by Equation 1) between experimental (W_M) and calculated mass loss ($W_{M,calc}$) is less than 4%, the tested compounds are deemed compatible. Changes in the range of 4-20% indicate a degree of incompatibility and the further tests are required. A mass difference greater than 20% indicate incompatibility of the ingredients [28].

The compatibility assessment was carried out by determining the mass losses of individual compounds and mixtures at 351 °C (azide-HTPB and AP) or 186 °C (azide-HTPB and DOA), at the maximum peak of the derivative TGA peak of the first stage of mixture decomposition. The TG curves obtained are shown in Figures 4 and 5, and the calculations are listed in Table 2. The negative W_R values imply compatibility of azide-HTPB with both AP and DOA. A W_R value of less than zero indicates the compatibility of the systems tested and confirms that they can be used safely in such compositions.

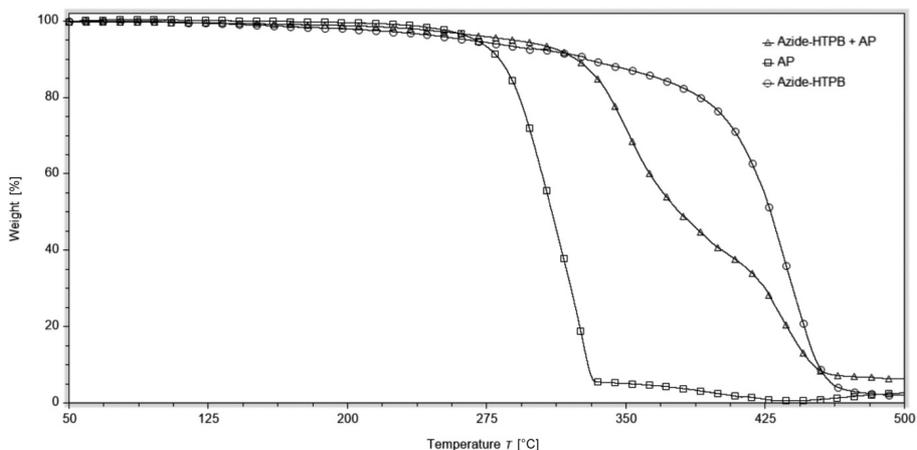


Figure 4. TG curves of azide-HTPB, AP and a mixture of azide-HTPB and AP

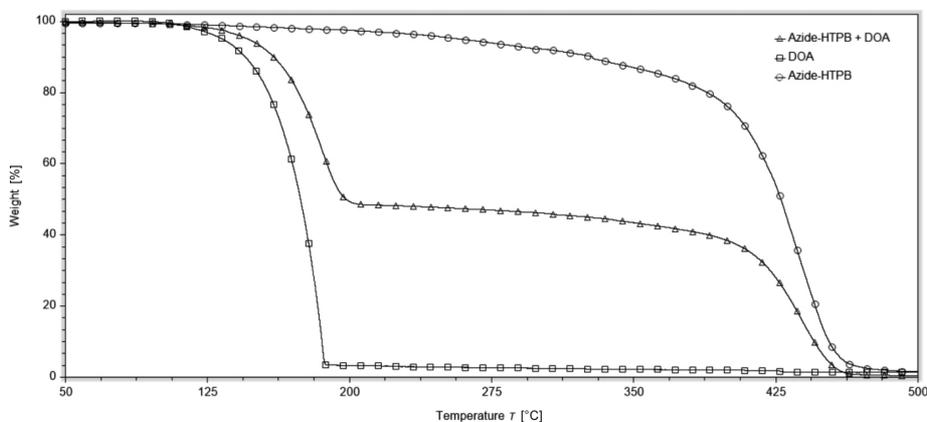


Figure 5. TG curves of azide-HTPB, DOA and a mixture of azide-HTPB and DOA

Table 2 The compatibility test results

Mass loss [%]	Compatibility	
	Azide-HTPB + AP	Azide-HTPB + DOA
W_M	28.85	37.80
$W_{1(\text{azide-HTPB})}$	12.11	1.84
$W_{2(\text{AP})}$	96.59	—
$W_{2(\text{DOA})}$	—	96.29
$W_{M,\text{calc}}$	54.89	49.71
W_R	-26.04	-11.91

4.3 Propellant preparation

In order to observe the effects of the synthesized HTPB derivative on the properties of solid heterogeneous rocket propellants, three test charges were produced, two of which contained azide-HTPB.

Two fractions of AP with crystal sizes of approximately 200 μm (AP200) and 20 μm (AP20) were used as the oxidant. The polymer matrix consisted of DDI and HTPB. In the case of the two propellants containing azide-HTPB, 5% or 10% of the base HTPB was replaced with azide-HTPB polymer. The technological additives used during the preparation of the charges were DOA, aziridine HX-752 and antioxidant AO 2246. Table 3 lists the percentages of individual propellant components.

The test rocket propellants were prepared in a laboratory planetary mixer, Netzch, model PML 1. The temperature was set to 65 °C using a thermostat and dosing of the ingredients was commenced. The formulations were mixed under reduced pressure. After mixing was complete, the mixer was aerated and the prepared propellants were transferred to the filling funnel, which is a part of the vacuum chamber. The propellants were casted into moulds under vacuum. The moulds with propellant were placed in a chamber at 65 °C to accelerate the curing process.

Table 3. The compositions of the prepared propellants

Component	Content [%] in sample		
	0% azide-HTPB	5% azide-HTPB	10% azide-HTPB
HTPB	8.40	7.98	7.56
azide-HTPB	–	0.42	0.84
DOA	2.40	2.40	2.40
AP200	65.13	65.13	65.13
AP20	21.71	21.71	21.71
DDI	1.75	1.75	1.75
AO 2246, HX-752	0.61	0.61	0.61

4.4 Density

The densities of the prepared propellants were measured using a helium pycnometer (Table 4). Increasing the amount of azide-HTPB in the propellant mixture resulted in an increase in the final propellants' densities.

Table 4. The densities of the prepared propellants

Sample	0% azide-HTPB	5% azide-HTPB	10% azide-HTPB
Density [g/cm ³]	1.6944 ±0.0004	1.7019 ±0.0036	1.7133 ±0.0026

4.5 Calorimetric study

The calorific value (isochoric heat of combustion) was measured using an adiabatic calorimeter. Table 5 lists the average of two measurements, which did not differ by more than 15 J/g. The propellants containing azide-HTPB were characterized by higher calorific values compared to the propellant without the HTPB derivative. In the case of the propellant in which 5% of the unmodified HTPB was replaced by azide-HTPB, a greater increase in calorific value (311 J/g) was observed than in the case of the propellant with replacement of 10% of unmodified HTPB (213 J/g).

Table 5. The calorific values of the prepared propellants

Sample	0% azide-HTPB	5% azide-HTPB	10% azide-HTPB
Calorific value [J/g]	5 826	6 137	6 039

4.6 Thermal studies

The 0% azide-HTPB propellant, which does not contain modified HTPB, was characterized by a two-stage decomposition on heating to 600 °C. The presence of azide-HTPB in the propellants contributed to a significant reduction in the percentage mass loss during the first stage of decomposition and at the same time resulted in the decomposition of the propellants at higher temperatures. The total mass losses of 0%, 5% and 10% azide-HTPB propellants were similar to each other. Figure 6 shows a comparison of the mass loss curves obtained with the thermal analyzer SDT for the three prepared propellants.

Table 6. The mass losses of the prepared propellants

0% azide-HTPB		5% azide-HTPB		10% azide-HTPB	
Mass loss [%]		Mass loss [%]		Mass loss [%]	
1st step	2nd step	1st step	2nd step	1st step	2nd step
10.74	85.67	3.07	93.75	2.35	93.79
Total mass loss [%]		Total mass loss [%]		Total mass loss [%]	
96.41		96.82		96.14	

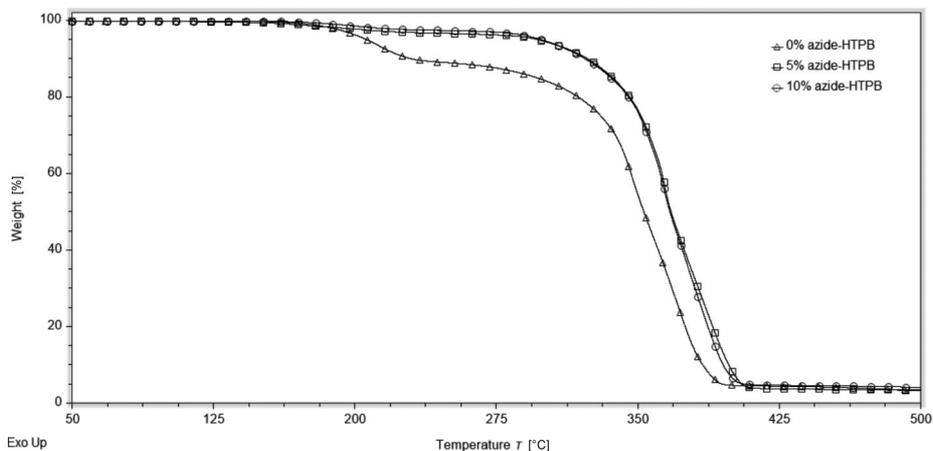


Figure 6. TG curves of the tested azide-HTPB propellants

4.7 Mechanical properties

The propellant samples were previously cut to specific sizes (Figure 7). A sample was placed in the holder of the testing machine. The forces acting on the sample, length changes, maximum load and deformation were recorded (Table 7).

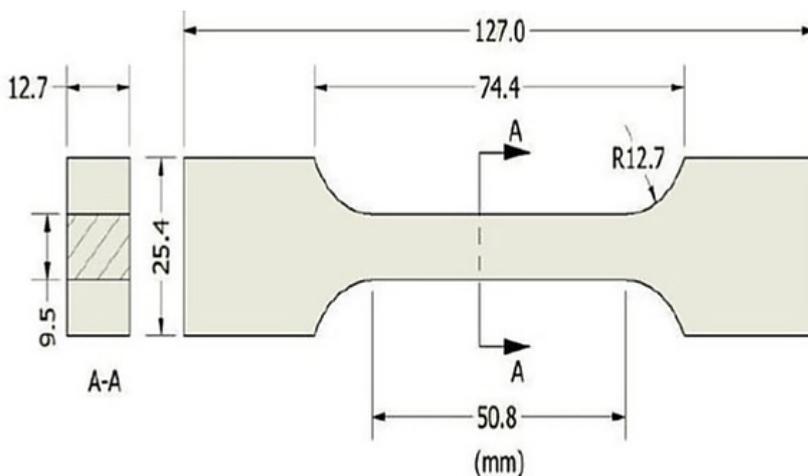


Figure 7. Shape and dimensions of a sample for the mechanical tests

Table 7. The mechanical properties of the prepared propellants

Mechanical property	Sample		
	0% azide-HTPB	5% azide-HTPB	10% azide-HTPB
Maximum strength F_m [N]	96.15	99.16	99.40
Elongation after fracture [%]	41.14	20.04	28.10
Young's modulus [GPa]	0.01	0.01	0.01

Use of 5% azidated HTPB resulted in a reduction of about 50% in elongation during stretching. A similar effect was observed with the use of 10% energetic binder. The use of azidated HTPB did not have such a large effect on the maximum strength. The addition of azide-HTPB caused a slight increase in the force needed to break the propellant sample. Young's modulus did not change.

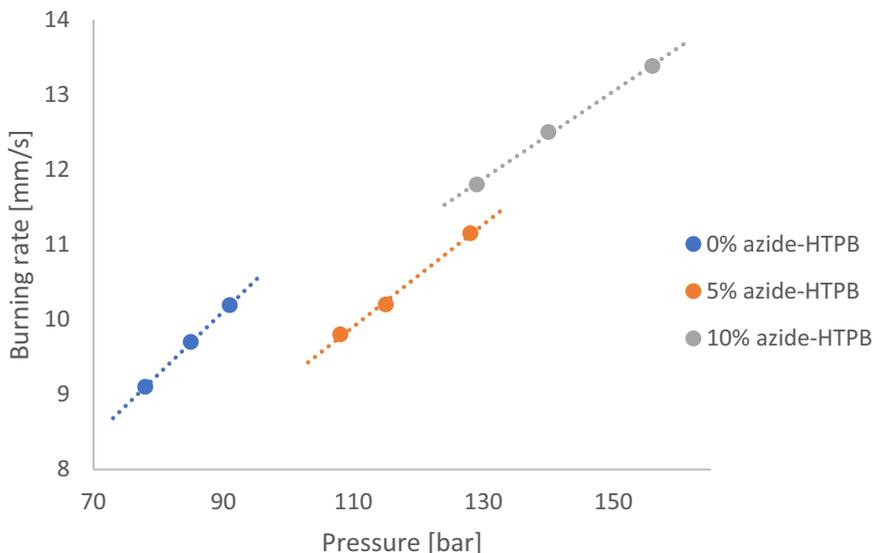
4.8 Burning rate

A cylindrical, non-inhibited charge of each of the tested propellants (Figure 8), with dimensions of 17.5×29 mm (diameter × length) and an internal diameter of 7 mm, was placed in the combustion chamber. An igniter was constructed consisting of an initiating mass of an electric igniter unit, a black powder pellet with dimensions of 6×2 mm and a mass of 0.2 g. The igniter was placed behind the propellant. The tests were performed with 2.0, 2.5 and 3.0 mm diameter nozzles. The maximum pressure in the chamber during propellant combustion and the propellant burning rate were determined.

**Figure 8.** The shape of a sample for testing the propellant burning rate

Table 8. Burning rate of prepared propellants

Sample	Nozzle [mm]					
	2.0		2.5		3.0	
	Burning rate [mm/s]	P_{\max} [bar]	Burning rate [mm/s]	P_{\max} [bar]	Burning rate [mm/s]	P_{\max} [bar]
0% azide-HTPB	10.19	91	9.7	85	9.1	78
5% azide-HTPB	11.15	128	10.2	115	9.8	108
10% azide-HTPB	13.38	156	12.5	140	11.8	129

**Figure 9.** Effect of azide-HTPB additive on the burning rate of the propellants

The addition of the energetic binder had a significant impact on the burning rate of the propellant. A 10% addition of azide-HTPB significantly increased the burning rate. The addition of 5% azide-HTPB resulted in a slight increase in the burning rate. Replacing the base binder with an energetic binder caused a significant increase in the maximum pressure in the motor chamber during propellant combustion. When replacing 10% HTPB with azide-HTPB, the pressure was increased from 91 to 156 bar with the smallest nozzle. The addition of the energetic polymer caused an increase in pressure in the combustion chamber and therefore an increase in the burning rate value.

5 Conclusions

- ◆ Azide-HTPB was synthesized and used in the preparation of propellants, in which 5% or 10% of unmodified HTPB was replaced. Comparing the properties of the solid heterogeneous rocket propellants obtained with propellant without modified HTPB, it is concluded that the use of azide-HTPB contributed to improvements in the final performance of the SHRP. Therefore, the azide-HTPB can be classified as a novel energetic additive for solid propellant formulations.
- ◆ An increase in the calorific value of the propellants with the addition of azide-HTPB was noted, with a simultaneous reduction in the amount of oxidant in the SHRP composition.
- ◆ Additionally, increasing the density of the propellant contributes to an improvement in their performance. The azide-HTPB has been demonstrated to be an excellent energetic additive, that not only eliminates partially the inertia of unmodified HTPB, but also improves the durability of the propellant, improving the safety and conditions of their use and storage.
- ◆ The effect of azide-HTPB resulted in a higher mass loss of propellant at higher temperatures than the propellant without modified-HTPB, which is important in terms of safety during the use of rocket motors.
- ◆ The use of azide-HTPB as a rocket fuel component has a significant impact on the mechanical properties of the propellant. It lowers the tensile strength and slightly increases the force needed to break the sample.
- ◆ The replacement of a part of the inert binder by the energetic binder increases the propellant burning rate and the maximum pressure in the motor chamber for a given nozzle diameter.
- ◆ The addition of azide-HTPB to existing propellant systems would be an interesting alternative to replacing inert HTPB by energy binders such as GAP, polyAMMO or polyNIMMO.

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