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Praca doświadczalna / Research paper

Temperature sensitivity of solid heterogeneous rocket propellant AP/HTPB/AI Wrażliwość temperaturowa stałego heterogenicznego

Wrażliwość temperaturowa stałego heterogenicznego paliwa rakietowego AP/HTPB/AI

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Abstract: The results of research on solid heterogeneous rocket propellant (SHRP) containing: ammonium chlorate(VII) (AP) as an oxidant, a binder based on liquid synthetic rubber, i.e. hydroxylterminated polybutadiene (HTPB), aluminium (Al) and technological additives in a laboratory rocket motor (LRM) are presented to determine the thermal sensitivity of the propellant.

Streszczenie: Przedstawiono wyniki z badań stalego heterogenicznego paliwa rakietowego (SHPR) zawierającego jako główne składniki: chloran(VII) amonu (AP) jako utleniacz, lepiszcze na bazie cieklego syntetycznego kauczuku (HTPB), glin (Al) oraz dodatki technologiczne w laboratoryjnym silniku rakietowym (LSR) pozwalające na wyznaczenie wrażliwości termicznej paliwa.

Keywords: solid heterogeneous rocket propellant, HTPB, laboratory rocket motor, temperature sensitivity **Słowa kluczowe:** Stale heterogeniczne paliwa rakietowe, HTPB, laboratoryjny silnik rakietowy, wrażliwość termiczna

1. Introduction

Combustion of solid heterogeneous rocket propellants (SHRPs) is characterised by the fact that their surface changes or remains constant during the process of burning. The linear burning rate is the distance travelled by the flame front in a unit of time measured perpendicularly to the combustion surface. It is assumed that this front is regular and, in most cases, progresses in a direction parallel to itself, which has been experimentally confirmed (within the accuracy of measurements of the burnt profile) by stopping the combustion of propellant and examining the surface. The linear combustion rate (r) as a function of pressure (p) is expressed, e.g. in [1], by the relationship given by Saint Robert and Vieille:

$$r = a \cdot p^n \tag{1}$$

which in the logarithmic form is:

$$\ln r = \ln a + n \cdot \ln p \tag{2}$$

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where n is the so-called exponent dependent on the composition of SHRP, and a is a constant dependent on the initial chemical composition of the propellant and its initial temperature. The a coefficient in Equation 1 is, among others, dependent on the initial propellant temperature. This relationship has been determined empirically and has the following form:

$$a = a_0 \exp[\sigma_p(T_1 - T_0)] \tag{3}$$

where: T_0 – reference temperature, T_1 – propellant temperature, a_0 – propellant burning rate constant at T_0 , a – propellant burning rate constant at T_1 , σ_p – temperature sensitivity of the burning rate.

The temperature sensitivity of the burning rate, σ_p , is determined by changing the burning rate for two temperatures, temperature T_0 and T_1 in accordance with:

$$\sigma_{\rm n} = (r_1 - r_0)/(T_1 - T_0)/r_{\rm av} \tag{4}$$

$$r_{\rm av} = (r_1 + r_0)/2$$
 (5)

where r_1 – burning rate for propellant with initial temperature of T_1 , r_0 – burning rate for propellant with initial temperature of T_0 , r_{av} – average burning rate.

The relationship r = f(p, T) is determined on the basis of the obtained results of the combustion of the model load, among others, in the laboratory rocket motor (LRM) [2]. Then we examine the so-called sensitivity of pressure in the rocket engine to changes in the initial temperature of the rocket propellant. The change in the combustion rate resulting from the change in the initial temperature of the rocket propellant changes the equilibrium pressure (p_k) in the rocket motor. Thus, the temperature sensitivity of the pressure in the combustion chamber (π_k) must be entered, which is defined analogously to σ_0 :

$$\pi_{k} = (p_{1} - p_{0})/(T_{1} - T_{0})/p_{av} \tag{6}$$

$$p_{\rm av} = (p_1 + p_0)/2$$
 (7)

where p_1 and p_0 indicate pressures in the combustion chamber at T_1 and T_0 , respectively, and p_{av} is the average pressure. The above relationship is valid for Kn = const. Kn is defined as the ratio of the propellant combustion area (S_b) and the critical cross-sectional area of the nozzle (A_1) :

$$Kn = S_b/A_t$$
 (8)

There is a relationship between the π_k and σ_p coefficients, which has the following form [1]:

$$\pi_{\mathbf{k}} = \sigma_{\mathbf{p}}/(1-n) \tag{9}$$

$$\sigma_{\rm p} = (1 - n)\,\pi_{\rm k} \tag{10}$$

The type and amount of the utilised combustion rate modifiers, *i.e.* metallic inorganic and organic chemical compounds, have an impact on the SHRP combustion rate and its pressure dependence. As the metallic chemical compounds, primarily iron compounds are used: oxides, nanoxides, ferrocene and its derivatives [3-8].

2. Experimental part

2.1. Receiving loads for testing

dough To receive loads from solid heterogeneous rocket propellant with a composition in mass % (Table 1), the propellant was made from the following raw materials:

- α,ω-dihydroxy-polybutadiene, HTPB (hydroxyl-terminated polybutadiene), with an OH group content of 0.96 meq/g (obtained as part of the project [9]),
- dioctyl adipate, DOA, pure (prod. Boryszew Erg S.A.),
- catocene, pure (prod. Island Pyrochemical Industries, IPI),
- aluminium dust, Al, clean, 32 μm (prod. Benda-Lutz Skawina Sp. z o.o.),
- ammonium chlorate(VII), AP, pure, 200 μm and 50 μm fractions (prod. IPI),
- dimeryl diisocyanate, DDI, pure, containing 14.05% NCO (prod. IPI).

Table 1. Propellant composition

Component	НТРВ	DOA	Catocene®	Al	DDI	AP*	Technological additives
Composition [%]	9.79	2.11	0.20	16	1.65	70	0.25

^{* –} two fractions (200 μ m and 50 μ m) in a 70/30 mass ratio

A NETZSCH laboratory planetary mixer was used to mix the propellant dough. The propellant mass formation process was carried out at a temperature of 333 K in accordance with the propellant mass formation procedure used by the Ł-IPO [10]. After mixing, the propellant dough was poured under reduced pressure and at a higher temperature (338 K) into rectangular molds. After curing (7 days at 338 K), the SHRP was machined. Three SHRP lots were prepared, the dimensions and weight of which are presented in Table 2.

Table 2. Loads data

No.	Thickness	Width	Length	Mass
110.		[g]		
1.	25.03	50.22	99.07	215
2.	24.98	50.73	99.20	218
3.	24.83	50.04	99.75	216

2.2. Ballistics research

Testsing of the lots presented in Table 2 was carried out in a LRE [11, 12] at the ballistic test stand at ZPS "Gamrat" in Jasło. The tests were carried out at three initial propellant temperatures: 233, 291 and 323 K. The test equipment consisted of: the LRM, a strain gauge pressure sensor by HBM, a digital amplifier MGC Plus and a computer set allowing the recording of the p = f(t) characteristics, which are presented in Figure 1.

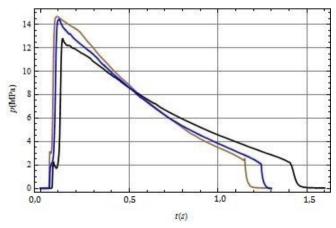


Figure 1. p = f(t) characteristics for the tested propellant with the initial temperature of: 233 K (black line), 323 K (brown line) and 291 K (blue line)

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As the initial propellant temperature increases, shortening of the propellant load combustion time and an increase in the maximum pressure in the chamber are observed, which undoubtedly translates into an increase in the propellant combustion rate.

2.3. Determination of the linear burning rate

According to the adopted algorithm described in [13], on the basis of the registered characteristics p = f(t), using the Wolfram Mathematica® 10 software, the r = f(p) relations were *determined for* individual initial temperatures of the tested propellant. The characteristics of r = f(p) are shown in Figure 2.

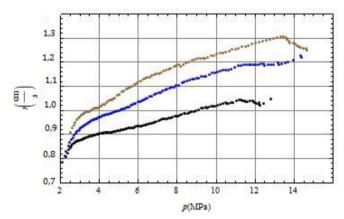


Figure 2. r = f(p) characteristics for the tested propellant with the initial temperature of: 233 K (black line), 323 K (brown line) and 291 K (blue line)

Using the regression module of the Mathematica® 10 software, the dependence of the linear burning rate on pressure was determined for the tested propellant with different initial temperatures. These relationships are as follows:

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a) for a temperature of 233 K:
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-\ln r = -0.284942 + 0.128318 \ln p, R^2 = 0.974442,

-\ln a = -0.284942, n = 0.128318;
```

b) for a temperature of 323 K:

```
-\ln r = -0.241736 + 0.192679 \ln p, R^2 = 0.999432, -\ln a = -0.241736, n = 0.192679;
```

c) for a temperature of 291 K:

```
-\ln r = -0.306370 + 0.193522 \ln p, \quad R^2 = 0.982903, \\ -\ln a = -0.306370, \quad n = 0.193522.
```

From the characteristics presented in Figure 2, it can be clearly seen that exponents n as well as a are variable and depend on the initial propellant temperature.

2.4. Calculation of the temperature sensitivity coefficient π_k

The temperature sensitivity coefficient can be calculated from Equation 6, knowing the pressure dependence on the value of Kn for a given propellant burned in the LRM at a specific initial temperature. Figure 3 presents the dependence of the pressure in the LRM combustion chamber on Kn and the initial propellant temperature.

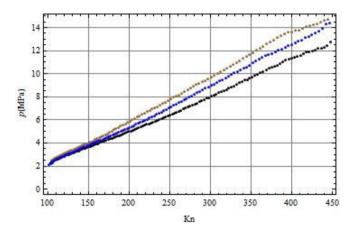


Figure 3. Dependence of pressure on *Kn* for the tested propellant with the initial temperature of: 233 K (black line), 323 K (brown line) and 291 K (blue line)

From Equation 6, after substituting pressure values for propellant temperatures of 323 and 291 K as well as 291 and 233 K, the temperature sensitivity coefficient π_k was calculated for the selected Kn values. The dependence of the coefficients on Kn is shown in Figure 4. For the first case in the range of changes in the value of Kn from 290 to 350, the coefficient has a constant value, $\pi_k \approx 0.002$ K⁻¹, while for the second case in the range of changes in Kn from 290 to 370 it has a constant value, $\pi_k \approx 0.0025$ K⁻¹, which shows that the rocket motor pressure sensitivity to changes in the initial rocket propellant temperature is greater for the propellant with an initial temperature of 323 K than for the one with an initial temperature of 233 K.

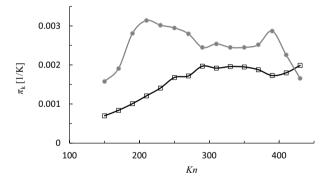


Figure 4. The dependence of the π_k factor on Kn calculated for temperatures:

- grey line (\bullet): T₁ = 323 K, T₀ = 291 K,
- black line (□): $T_1 = 291 \text{ K}$, $T_0 = 233 \text{ K}$

3. Summary

The conducted tests on the combustion of cuboid-shaped loads in LRE allow the determination of the linear burning rate depending on the pressure in a wide range of pressure changes, to be made. Moreover, during combustion of loads with different initial temperatures, the temperature sensitivity factor π_k can be determined. Studies have also shown that the n exponent in the combustion law depends not only on the chemical composition of the propellant, but also on its initial temperature. In the case of the tested propellant with a specific composition, it was observed that within a certain range of changes in Kn, the π_k coefficient takes a constant value – it is independent of changes in Kn.

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References

- [1] Kubota N. 2007. Propellants and explosives: thermochemical aspects of combustion. Weinheim: Wiley.
- [2] Florczak B., Dzik A., Białek M. 2016. Determination of burning rate in a laboratory rocket motor with different configurations. (in Polish., ed. transl.) In: *Solid heterogeneous rocket propellants*. (in Polish., ed. transl.) (Florczak B., ed.), Ch. 6, pp. 109-121; ISBN 978-83-914922-4-6
- [3] Gore G.M., Tipare K.R., Bhatewara R.G., Prasad U.S., Gupta M., Mane S.R. 1999. Evaluation of ferrocene derivatives as burn rate modifiers in AP/HTPB-based composite propellants. *Def. Sci. J.* 49 (2): 151-185.
- [4] Patil Prajakta R., Krishnamurthy V.N., Joshi Satyawati S. 2006. Differential scanning calorimetric study of HTPB based composite propellants in presence of nano ferric oxide. *Propellants Explos. Pyrotech.* 31 (6): 442-446.
- [5] Ghosh K., Behera S., Kumar A., Padale B.G., Deshpande D.G., Kumar A., Gupta M. 2014. Studies on Aluminized, High Burning Rate, Butacene® Based, Composite Propellants. Cent. Eur. J. Energ. Mater. 11 (3): 323-333.
- [6] Bogusz R., Florczak B., Skupiński W., Chmielarek M. 2017. Badania stałego heterogenicznego paliwa rakietowego zawierającego Butacen®. Materiały Wysokoenergetyczne / High Energy Materials 9: 178-186.
- [7] Ide K.M. 2002. Composite Propellants with Bi-Plateau Burning Behaviour. Report DSTO-GD-0344.
- [8] Saravanakumar D., Sengottuvelan N., Narayanan V., Kandaswamy M., Varghese T.L. 2011. Burning-rate enhancement of a high-energy rocket composite solid propellant based on ferrocene-grafted hydroxylterminated polybutadiene binder. *J. Appl. Polymer Sci.* 119: 2517-2525.
- [9] Badania nad przeniesieniem skali otrzymywania α,ω-dihydroksypolibutadienu (HTPB) z reaktora 1 dm³ do reaktora 10 dm³ oraz badania aplikacyjne otrzymanego HTPB. (in Polish) Research Project PBS 180743.
- [10] Bogusz R., Magnuszewska P., Florczak B., Maranda A., Drożdżewska K. 2016. Studies of the Influence of Nano Iron(III) Oxide on Selected Properties of Solid Heterogeneous Propellants Based on HTPB. Cent. Eur. J. Energ. Mater. 13 (4): 1051-1063.
- [11] Florczak B., Kwilosz S., Cholewiak A., Białek M., Miszczak M. 2015. Laboratory rocket motor. (in Polish., ed. transl.) Patent PL 406258 A1.
- [12] Florczak B., Bogusz R., Skupiński W., Chmielarek M. 2015. Study of the effect of nitrated hydroxy-terminated polybutadiene (NHTPB) content on the properties of heterogeneous rocket propellant. Cent. Eur. J. Energ. Mater. 12 (4): 841-854.
- [13] Florczak B., Białek M., Cholewiak A. 2014. Determination of the Internal Ballistic Properties of Solid Heterogeneous Rocket Propellants. Cent. Eur. J. Energ. Mater. 11 (4): 589-601.
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