The influence of catocene on properties of heterogeneous solid rocket propellants with reduced quantity of HCl in combustion products

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Abstract

The aim of this work was to examine how catocene as a burn rate modifier, impacts on properties of heterogeneous rocket propellants, which contain scavenger compound and emit low amount of HCl during combustion. Usually burn rate modifier is added to propellant slurry in amount approximately 1% of propellant mass. During this work the amount of catocene was increased to 4.5%$_{mas}$ with the decreasing amount of binder. Seven samples of propellants were made, which had different quantity of catocene. Mechanical and ballistic properties, sensitivity to friction and impact and isochoric heat of combustion were determined.

Keywords: Solid rocket propellants, burn rate, catocene, combustion

1 Introduction

Depending on the purpose of the rocket motor and the designed characteristics of its operation, charges with adequate burning rate, burning surface and geometry of grain, are designed. One of the main ballistic parameter of heterogeneous solid rocket propellants (HSRP) is burning rate (r) and its dependence on pressure (p) [1, 2]. Mathematically this relationship can be expressed by Equation 1.

$$r = A \times p^n \tag{1}$$

where A – an empirical constant (depending on the composition of propellant and initial temperature of propellant), n – the pressure exponent.

The combustion of propellants largely depends on the decomposition of ammonium perchlorate, the most widely used oxidizer. Thermal decomposition of the oxidizer consists of many physical and chemical transformations running in two stages. In the first stage at temperature below 623 K, there are endothermal reactions between ammonia and perchloric acid, leading to form O_2, N_2O, Cl_2, NO. The second stage of the decomposition of the oxidizer runs at temperature above 623 K and consists of exothermal reactions with the release of volatile products such as H_2O, Cl_2, N_2O and NO [3].

One of the solution leading to modify burning rate is the addition of burn rate modifiers or the increment of their amount in the formulation. The most efficient catalysts of combustion of solid rocket propellants based on ammonium perchlorate as an oxidizer, are oxides of transitional metals for expample Fe_2O_3, numerous metal organic compounds, mainly ferrocene derivatives [4]. Particle sizes of burn rate catalysts has huge impact on burning rate of HSRP, the smaller particles the better mixing and the better distribution in propellant mass, which has a positive effect on catalytic action. The best effect in mixing with other ingredients of propellant have liquid burn rate catalysts [5]. Organic iron compounds are more catalytically active than inorganic burn rate modifiers, because their decomposition in combustion wave leads to a creation very small particles of iron oxide with great combustion surface, which causes great contact area with the oxidizer and accelerates the thermal decomposition of ammonium perchlorate [6].

2'-bis(ethylferrocenyl)propane (BEFP) (Fig. 1) called also catocene, is well-known ferrocene derivative, fulfilling the function of burn rate modifier causing the enhancement of burning rate in heterogeneous solid rocket propellants. It is viscous, dark red liquid, which is insoluble in water. Catocene is resistant to oxidation. It is obtained by condensation of appropriate alkylferrocenes with ketones in an acid/alcohol mixture (Fig. 2) [7].

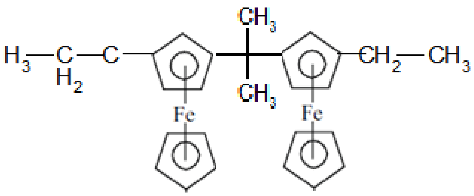

Figure 1. The structure of catocene [8].

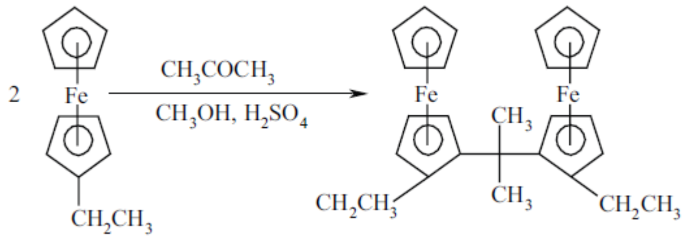

Figure 2. Formation process of catocene [7].

To follow the present trend in the development of solid rocket propellants namely the reduction of smoke, which is the emission of gaseous and solid products of combustion, there are more eco-friendly propellants obtained. These products cause the formation of white mark in the air behind working rocket motor. Because of tactical and strategic considerations this phenomena is highly undesirable. According to AGARD Standard Classification [9] smoke is determined by two main factors, which are ability of HSRP to emit primary smoke and secondary smoke. The document allows to term eco-friendliness of HSRP. Primary smoke are solid combustion products of HSRP, mainly Al_2O_3. To make the propellant more eco-friendly in the primary fumes classification it is necessary to decrease the concentration of aluminum. Aluminum is an energy supplement which helps in increasing the specific impulse of solid rocket propellants. Secondary smoke are these combustion products which condense in conditions of outflow from the nozzle and outside of the nozzle. Hydrogen chloride (HCl) is the precursor of secondary smoke. It is created during the combustion of propellants containing ammonium perchlorate, as a result of the decomposition of the oxidizer. In the air HCl undergoes a solvation by particles of steam, which causes the formation of white mark behind rocket. To make the HSRP more eco-friendly in the secondary fumes classification it is necessary to reduce the amount of ammonium perchlorate in composition by partly or complete replacement by other oxidizer or by using scavengers. Scavengers are compounds which neutralize HCl by chlorine binding during combustion. Chlorine binding is the reaction between HCl and ions of alkaline earth metals, introduced into composition for example as salts of nitric acid: sodium nitrate, potassium nitrate or as salts of carbonic acid: lithium carbonate, sodium carbonate [10-15]. Authors have decided to use sodium nitrate as a scavenger to make their propellants more eco-friendly.

2 Experimental

To prepare compositions substances mentioned and described below were used:

- α,ω-dihydroxylpolibutadiene (HTPB R45M) – *Island Pyrochemical Industries prod.*, binder,
- lecithin – *Sigma Aldrich prod.*, surfactant,
- catocene (BEFP) – *Neo Organics prod.*, burn rate modifier,
- dimeryl diisocyanate (DDI) – *Island Pyrochemical Industries prod.*, curing agent,
- aluminum powder (Al) – *Benda Lutz prod.*, energetic supplement,
- sodium nitrate (SN) – *VWR Chemicals prod.*, scavenger,
- ammonium perchlorate (AP) – *Island Pyrochemical Industries prod.*, fine-grained fraction (AP_{fg}, particle size 75 µm) and coarse-grained fraction (AP_{cg}, mixture of particles with sizes 250 µm:400 µm in 1:1 ratio), oxidizer.

2.1. Formulation

To examine the influence of Catocene on different properties of propellants, seven samples were prepared in NETZCH planetary mixer (Fig. 3) according to the following procedure:

- mixing liquid ingredients (except curing agent): HTPB R45M, lecithin and catocene under atmospheric pressure and then under reduced pressure,
- addition of aluminum powder and mixing under atmospheric pressure and ten under reduced pressure,
- addition of fine-grained ammonium perchlorate and mixing under atmospheric pressure and ten under reduced pressure,
- addition of coarse-grained ingredients: ammonium perchlorate, sodium nitrate and mixing under atmospheric pressure and ten under reduced pressure,
- addition DDI, and mixing under atmospheric pressure and ten under reduced pressure
- casting obtained suspension to mold,
- curing for 7 days in 70 °C.

Figure 3. Planetary mixer

The detailed compositions of obtained samples are presented in Tab. 1. The amount of catocene is increased while the amount of binder is decreased, amounts of solid ingredients do not change. Because of the liquid form of the burn rate modifier it is possible to replace the ingredient of distracting phase, then the viscosity of propellant suspension does not change significantly. In this case catocene is not only burn rate catalyst but also has a function of adhesive. Usually the concentration of the burn rate modifier is lower than 1%, in this work the amount of catocene was increased to 4.5%.

Table 1. Composition of prepellants.

Sample/ $\%_{mass}$	*P0*	P1	P2	*P3*	*P4*	*P5*	*P6*
HTPB	10,57	8.92	8.51	8.10	7.69	7.28	6.87
DDI	2.25	1.90	1.81	1.72	1.63	1.54	1.45
Lecithin	0.1	0.1	0.1	0.1	0.1	0.1	0.1
AP_{fg}	27.60	27.60	27.60	27.60	27.60	27.60	27.60
AP_{cg}	21.28	21.28	21.28	21.28	21.28	21.28	21.28
SN	26.20	26.20	26.20	26.20	26.20	26.20	26.20
Al	12	12	12	12	12	12	12
Catocene	0	2	2.5	3	3.5	4	4.5

2.2. Characterization metchods

After the curing process samples were subjected to:
- hardness measurement,
- heat of combustion measurement,
- thermal properties measurement,
- thermomechanical properties measurement,
- sensitivity to mechanical stimuli measurement,
- ballistic properties measurement.

Hardness is the ability of material to resist to hard material being driven into it. Hardness measurement consists in pressing the indenter into the tested material with adequate force and in determination of surface of the resulting deformation. The hardness of tested samples were determined with the hardener testing equipment Zwick/Roell HPE type A. The measurement was carried out in accordance with ASTM D 2240 [16]. The hardness of sample was the average value of 6 measurements.

Isochoric heat of combustion was measured in adiabatic calorimeter C4000 type. In each test there was 4,36 g of propellant examined and 1,44 g of standard gunpowder (with isochoric heat of combustion equal 4914 J/g) to ignite the sample. The heat of sample's combustion was the average value of at least 2 measurements.

Thermal properties of samples were determined with the use of differential thermal analysis and thermogravimetric analysis (DTA-TGA). Tests were carried out in Labsys^{TM} Evo apparatus. During the measurement sample (with mass (1,0 ÷ 1,5) mg) placed in aluminized measuring cell was heated from (30 ÷ 450) °C with the velocity of heating equal 5 °C/min in argon atmosphere. The test relies on the measurement of the difference temperature between cell with sample and reference vessel in function of time and temperature. For each exothermal decomposition of sample beginning of decomposition temperature (T_{onset}), maximum temperature (T_{max}) and mass loss (Δm) were determined.

Thermomechanical properties of propellants were define with the use of dynamic mechanical analysis (DMA) apparatus (DMA 242 E Artemis NETZSCH). Rectangular samples with dimensions 50 mm × 10 mm × 2 mm were placed in dual-cantilever handle, subjected to 1 Hz frequency vibrations at temperature range (-120 ÷ +100) °C in nitrogen atmosphere, the amplitude of deformation was equal to 20 μm. Thus it is possible to obtain three curves in E‘, E“ and tanδ dependency of temperature. According to STANAG 4540 it is better to determine the glass transition temperature (T_g) from the loss modulus (E”) on temperature dependence [17].

Sensitivity to mechanical stimuli is the ability of material to explosive decomposition caused by mechanical action. Sample’s sensitivity to friction and impact were determined as basic safeness designation. Measurements of sensitivity to impact and friction were carried out with the use of Kast’s hammer and Peter’s apparatus respectively. In both tests lower limit of sensitivity was determined, which is the lowest value of energy or friction force, which causes decomposition of sample in one of six trials.

Ballistic properties of obtained propellants were determined by combustion of rectangular sample (100 mm × 50 mm × 25 mm) in laboratory rocket motor (LRM). Method of determination of the dependence burning rate on the pressure of the combustion products assumes: ideal gas equation of state for combustion products, no changes in critical cross-section of the nozzle, one-dimensional and isentropic flow in the nozzle, layered combustion of propellant and constant burning rate in whole range of pressure. As a result of the combustion of the sample characteristics pressure in time ($p = f(t)$) are obtained. In accordance with methodology described in [5] the dependence of burning rate on pressure is determined. Before each test dimensions of sample and mass were measure. According to this the density of sample was determined.

3 Results and discussion

Fig. 4 is an example what dependences are obtained during one thermomechanical properties measurement. Obtain curves are typical for solid rocket propellants containing HTPB. For all tested samples there were similar dependences obtained, so in the Fig. 4 results of measurement of sample with 3.5% concentration of catocene are presented. X-axis is temperature and three Y-axes are loss modulus (E”), which is the ability of material to release the energy as heat, depends on viscous properties of material, elastic modulus (E’), which is the elastic answer of material to applied strength, and mechanical loss factor (tanδ), which is called dumpling and is the ratio of E”/E’. The elastic modulus decreases with the increasing temperature. On the loss modulus curve one peak can be seen, with maximum at -65.7 °C. There are two peaks on tanδ curve. Maximum of the first peak is at -57.2 °C and maximum of the second one is at +1.5 °C. Such phenomena is associated with the presence of hard and soft segments in polyurethane and propellant. The first peak is the glass transformation temperature of soft segment, which is the beginning or ending of segments of main chain of HTPB movement. The second peak is related to complex process because of superimposition of two mechanisms: interactions from polymer and interactions from heterogeneous material. It is the glass transition temperature of hard segments and/or soft segments, which mobility is significantly reduced by the presence of solid particles and interactions between binder and solid particles. Polyurethanes have a segmental structure: urethane groups (-N=C=O) are hard segments, while polybutadiene chain is soft segment [18].

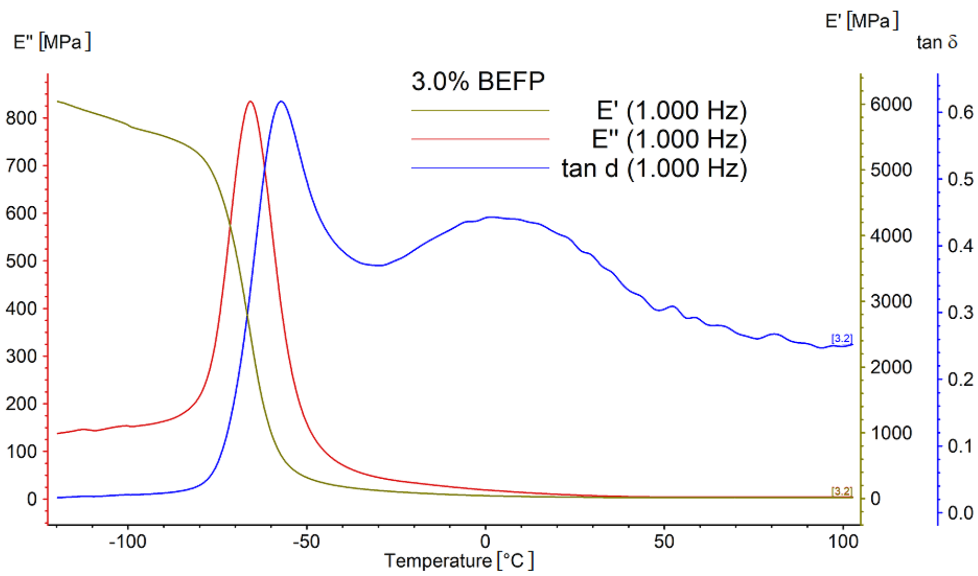

Figure 4. Loss modulus (E”), elastic modulus (E’) and mechanical loss factor (tanδ) in temperature function for propellant containing 3.0% of catocene.

Fig. 5 presents the dependence of the loss modulus (E”) on temperature for all samples. The glass transition is the maximum of the peak. The glass transition temperature is in the range (-66.5 ÷ -64.5) °C for propellants with catocene concentration in range (0 ÷ 3.5)%, above this range the glass transition temperature increases to -61°C. Graph is flat above 0 °C.

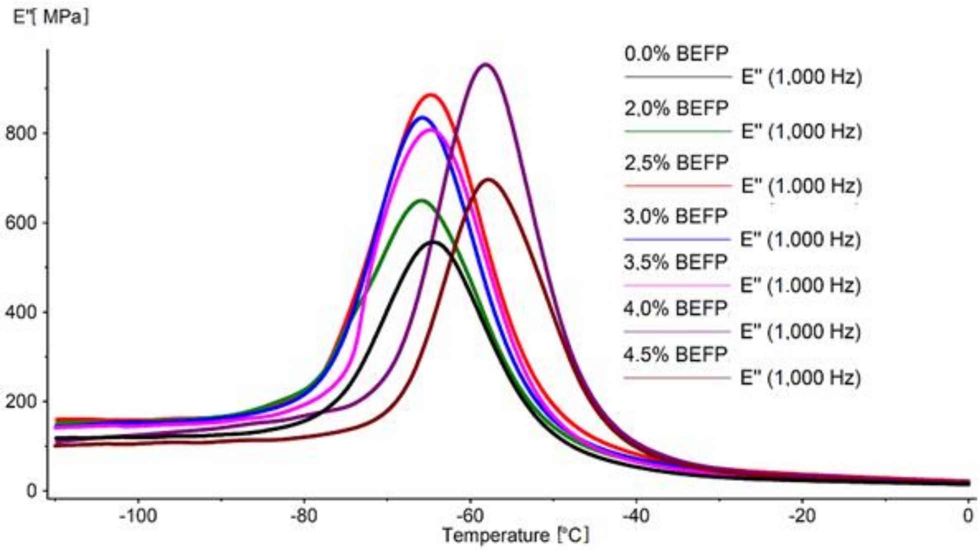

Figure 5. The loss modulus dependence on temperature.

In Fig. 6 DTA curve of P2 sample (2.5% of catocene) is presented as an example and is typical for propellants containing ammonium perchlorate as an oxidizer. At 240 °C there can be seen endothermic peak which is responsible for inter crystal transformation of ammonium perchlorate. Approximately at temperature 275 °C there is the decomposition beginning and the maximum of the peak lays at 279 °C. The decomposition process for all samples begins above 265 °C except sample 3.5% concentration of catocene, this propellant starts to decompose in 257 °C. This propellant is more sensitive to temperature action than other samples. The highest temperature of the begging of the decomposition has the propellants with no burn rate modifier. The temperature is equal 288 °C and is 15 °C higher than temperature of propellants with catocene. Mass loss during the decomposition does not depend significantly on catocene concentration and is in range (45 ÷ 65)% for propellants containing burn rate catalyst, sample P0 characterizes with the lowest mass loss which is 29% (Tab. 3).

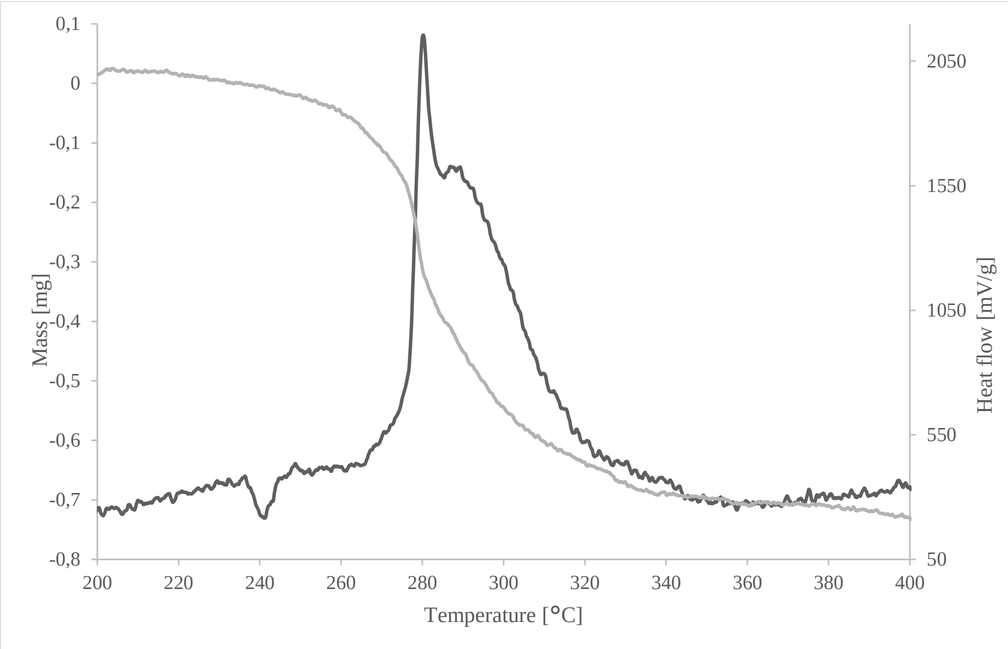

Figure 6. DTA curve for P2 sample.

Properties (hardness, heat of combustion, sensitivity to mechanical stimuli, glass transition temperature, onset temperature, maximum temperature and mass loss) of obtained propellants are presented in Tab. 2.

Table 2. Properties of propellants.

Sample/ property	*Hardness [°Sh, A]*	*Heat [J/g]*	*Friction sensitivity [N]*	*Impact sensitivity [J]*	T_g *[°C]*	T_{onset} *[°C]*	T_{max} *[°C]*	*Δm [%]*
P0	69	6001	160	7,5	-64.5	288	294	29
P1	59	6284	120	10	-66.6	270	276	51
P2	60	6314	160	10	-65.0	275	279	45
P3	60	6276	80	10	-65,9	265	287	50
P4	59	6067	120	7,5	-65.0	257	279	67
P5	44	6151	120	7,5	-61.3	274	296	61
P6	50	6177	120	10	-60.8	272	293	47

Hardness of propellants is in range (44 ÷ 69) °Sh (A). Samples with higher content of catocene are softer.

The isochoric heat of combustion increases with the increase of catocene amount for samples P0-P2 then decreases with increase of catocene concentration, except sample P4 with 3.5%

content of burn rate modifier. P4 sample generates the lowest amount of heat during combustion from all propellants with catocene.

Propellant with 3.0% of catocene has the highest sensitivity to friction. Under the influence of a force 80 N sample decomposed. Propellants with no catocene and with 2.5% of catocene have the lowest sensitivity to friction from all examined samples. Sensitivity to impact is 7.5 J for three compositions and 10 J for four compositions. Catocene does not extremely change sensitivity to mechanical stimuli.

Tab. 3 presents values of the coefficients from Equation 1 at define range of pressures. In addition the density of all samples are presented, which means the ratio mass to volume of sample. The higher concentration of catocene the higher density of the sample.

Table 3. Density and ballistic properties of propellants.

Sample/ property	*Density [g/cm³]*	*Pressure range [MPa]*	*A [cm/s]*	*n*	*R^2*
P0	1.814	4.5÷9.6	0.37	0.37	0.9867
P1	1.815	6.0÷17.7	1.15	0.15	0.9892
P2	1.826	6.0÷17.6	1.12	0.14	0.9877
P3	1.834	5.9÷17.4	1.48	0.12	0.9955
P4	1.871	4.2÷20.5	1.44	0.15	0.9934
P5	1.843	3.7÷17.4	1.36	0.18	0.9976
P6	1.852	3.6÷19.8	1.32	0.22	0.9980

As it is seen in Fig. 7, addition and the increment of catocene concentration to basic composition leads to an increase in the burning rate. Figure 8 shows the dependence of burn rate on catocene concentration. The curve is an illustration of expotentiall Equation 2 appointed at 10.2 MPa.

$$r = 2.79\text{-}1.93A\times\exp(-0.25\times x_{BEFP}) \qquad R^2=0.9918 \qquad (2)$$

where: r – burning rate, x_{BEFP} – catocene concentration.

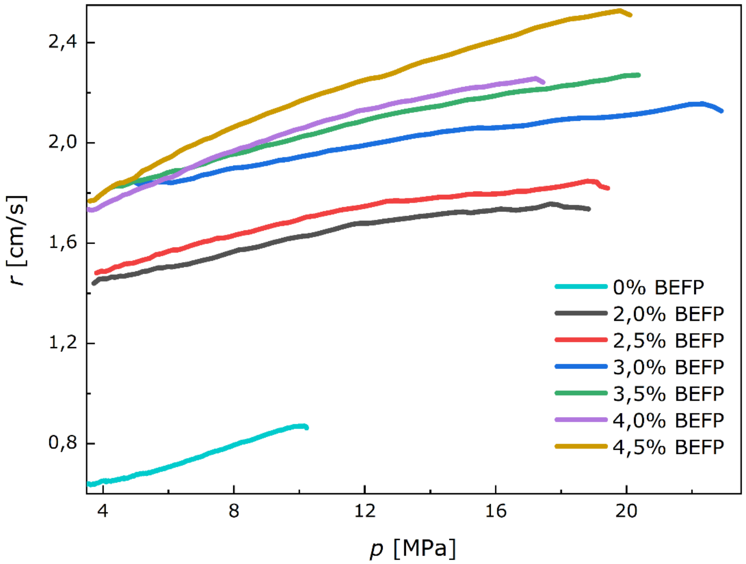

Figure 7. The burning rate (r) dependence on pressure (p) for obtained propellants.

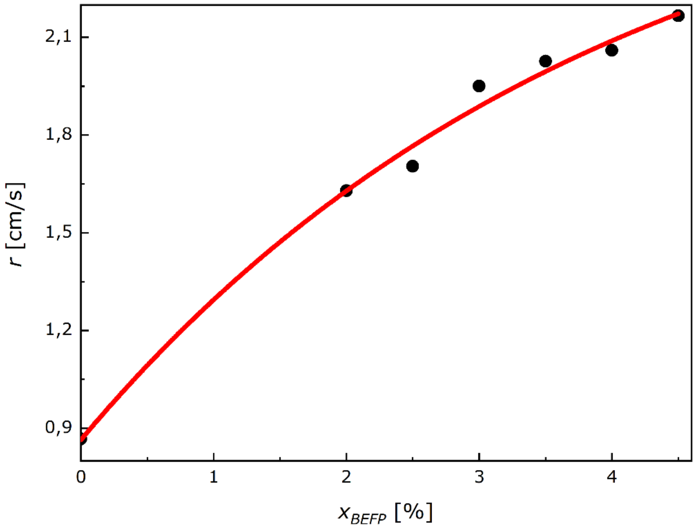

Figure 8. The burning rate (r) dependence on catocene concentration (x_{BEFP}) for obtained propellants.

4 Conclusions

Seven samples of propellants containing HCl scavenger (sodium nitrate) and commonly used burn rate modifier (catocene) were obtained. On the basis of the conducted measurements the influence of the burn rate catalyst on physicochemical, termomechanical and ballistic properties of propellants with reduced amount of HCl in combustion products.

Catocene concentration in range (2.0 ÷ 3.5)% does not signifacantlly change the glass transition temperature, increase of catocene concentration to 4.5% cuases the increase of T_g by about 4 °C. Burn rate catalyst lowers the initial decomposition temperature by minimum 15 °C relative to initial decomposition temperature of sample with no burn rate modifier but on the other hand increases mass loss by minimum 15% during the decomposition. Propellants with catocene concentration in range (2.0 ÷ 3.0)% show the highest value of isochoric heat of combustion (about 6300 J/g). The lowest value of sensitivity to impact and friction for all tested samples is equal 7.5 J and 80 N respectively.

As expected the higher catocene concentration the higher the burning rate of propellant. The dependence of the burning rate on catocene content (0.0 ÷ 4.5)% was described by expotential equation.

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