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Studies of the Influence of Nano Iron(III) Oxide on Selected Properties of Solid Heterogeneous Propellants Based on HTPB

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Abstract: This paper presents the results of investigations into the use of 56 nm nano iron(III) oxide as a combustion rate modifier in a solid heterogeneous rocket propellant (SHRP). A series of solid heterogeneous rocket propellants based on HTPB and ammonium perchlorate with different nano iron(III) oxide contents in the propellant composition were prepared and investigated. The ballistic parameters of the examined propellants were determined by combustion in a laboratory rocket motor (LRM). The ballistic properties were evaluated in the pressure range 5-10 MPa. It was found that the linear burning rate at 7 MPa was increased by 15% for 1% nano iron(III) oxide content in comparison to 0.2% content. Determination of the sensitivity to friction and impact, the calorific value, hardness and decomposition temperature of the derived propellants were also investigated.

Keywords: combustion rate modifier, nano iron(III) oxide, solid heterogeneous rocket propellant, HTPB, LRM

1 Introduction

Solid propellants are widely used as propulsion systems in rocket technology. Within this group of specific use materials two main classes of solid propellants

may be distinguished: homogeneous and heterogeneous. Homogeneous solid propellants are single-base propellants – containing mainly NC, and the double-base propellants – containing NC and NG as the two main components. There are also known compositions of the *composite-modified double-base propellant* (CMDB) type, containing the additives ammonium perchlorate (AP) and aluminium (Al) [1]. Solid heterogeneous rocket propellants (SHRP) are also composite systems consisting of an inorganic oxidizer, usually ammonium perchlorate, metal particles, for example aluminum, and processing additives such as plasticizers, *e.g*. dioctyl adipate (DOA), binders, antioxidants, and combustion rate modifiers, bonded in a polymeric matrix [2, 3]. The matrix is formed by curing a prepolymer in the final stage of the SHRP preparation. The most commonly used synthetic prepolymer is a polybutadiene rubber HTPB (hydroxy terminated polybutadiene), which undergoes chemical curing using di-isocyanates such as dimeryl di-isocyanate (DDI), forming the above mentioned matrix. HTPB is used because of the very good mechanical properties of the propellant obtained, moderate production cost, broad compatibility and the ability to prepare NHTPB (nitrated hydroxy-terminated polybutadiene) or Butacene® [4]. An SHRP is formed by the uniform dispersion of solid and liquid fractions when stirred at elevated temperature in the liquid polymeric matrix, which undergoes chemical curing after casting. This leads to a solid composite with specific physical, mechanical and ballistic properties. The physicochemical and physicomechanical properties are determined by all of the components forming the heterogeneous solid rocket propellant [5], while the ballistic properties are mainly determined by the combustion rate modifier content, which is added in amounts of about 1%. Inorganic and organic iron compounds are widely used as combustion rate modifiers in SHRP technology [6]. Ferrocene and its derivatives [7], catocene and butacene belong to the group of organic combustion rate modifiers. The use of ferrocene in solid heterogeneous rocket propellants is associated with the problematic migration of the particles of this compound in the mass of the propellant, resulting in the formation of regions in which an elevated content of the iron compound is observed. In the case of catocene, this effect is minimized due to the expanded spatial structure of the molecule. With Butacene®, ferrocene being indirectly substituted onto the HTPB chain, this phenomenon does not exist because the formation of the Butacene® binding chains is a part of the SHRP polymeric matrix development. Inorganic combustion rate modifiers include iron oxides, especially Fe_2O_3 [8], which are characterized by high stability and chemical inertness. During combustion of an SHRP, the combustion rate modifiers based on iron compounds form very small particles of iron oxides in the combustion zone, with a high specific surface area

and also a large contact area with crystals of NH_4ClO_4. It therefore seemed to be reasonable to use nano iron(III) oxide (nFe_2O_3) as a burn rate modifier [9-12]. The aim of this paper is to present the results of a study of the influence of nano iron(III) oxide on selected properties of solid heterogeneous rocket propellants based on HTPB. In this study, the observed influence of nano iron(III) oxide on the rate of curing of the SHRP suspension, as well as on the sensitivity to impact and friction, the calorific value, hardness, the decomposition temperature and the linear speed of combustion of the obtained propellants are presented.

2 Experimental

2.1 Sample preparation

Five compositions of solid heterogeneous propellants (P1-P5) with different nFe_2O_3 contents were prepared for the investigations. The compositions of the propellants obtained are summarized in Table 1.

Table 1. Composition of the propellants obtained

Component [%]	P1	P2	P3	P4	P5
HTPB	9.03	9.03	9.03	9.03	9.03
nFe_2O_3	0.2	0.4	0.6	0.8	1.0
Al	16	16	16	16	16
AP	70.4	70.2	70.0	69.8	69.6
Additives*	4.37	4.37	4.37	4.37	4.37

*DDI, DOA, Lecithin, Tepanol

The propellants mentioned above were obtained using HTPB R45M (IPI), ammonium perchlorate (IPI) with two levels of porosity (diameter) 200 μm and 50 μm, aluminum powder of diameter 32 μm (Benda Lutz), dioctyl adipate (Boryszew Erg SA) as the plasticizer, DDI (IPI) as the curing agent, and lecithin and tepanol as technological additives. Nano iron(III) oxide was used as the combustion rate modifier with medium diameter 56 nm and was obtained by the combustion method (MUT). The forming of the propellant mass was carried out using a laboratory planetary mixer NETZSCH, nano iron(III) oxide was added to the suspension of the propellant in the form of a homogeneous suspension in the plasticizer (DOA) to prevent agglomerate formation of the nano iron(III) oxide particles, reducing the effect of nanocrystalline form. The propellant samples were cast into shaped molds and cured at 65 °C for 7 days. The slurry samples

for rheological testing were taken prior to casting into the molds. For laboratory testing, samples of the prepared propellants were subjected to grinding to form cubes with an approx. 2 mm side (Figure 1).

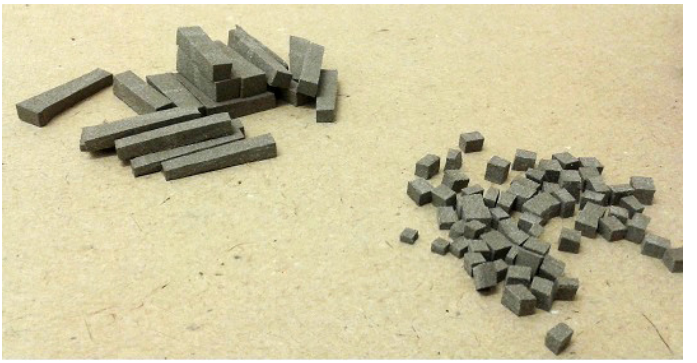

Figure 1. A sample of the shredded propellant.

2.2 Test methods

To determine the influence of nano iron(III) oxide on the curing process of the SHRPs, the viscosity measurement was performed during curing of the slurry propellant. For this purpose a reoviscosimeter HA DV-II+ Pro with adapter device Helipath, spindle T-D and thermostat TC-550 SD from Brookfield, were used. The measurements were performed at 65 °C, the curing temperature of the propellant slurry.

An adiabatic calorimeter IKA C 4000F was used for measurement of the isochoric heat of combustion (calorific value, Q) of the propellants. Its calorimetric constant was determined using standard gunpowder with a known calorific value of 4922 J/g. The results of the calorific values obtained are the mean of two different measurements, differing from each other by a maximum of 25 J/g; the sample mass of the tested propellant was 5.8 g.

In order to determine the sensitivity to mechanical stimuli, the standard Kast's hammer and Peters' apparatus, in accordance with the procedure described in more detail in [13], were used.

To determine the Shore A hardness of the propellants obtained, the hardener testing equipment Zwick/Roell HPE type A was used. The size of the penetration of the intender into the flat surface of the examined propellant, during 3 s under a pressure of 12.5 N, was measured and converted into °Sh A. Six measurements were performed with an accuracy of 0.1 °Sh A for each propellant tested, which lead to the calculation of the mean value.

The decomposition temperature of the investigated propellants was examined

by two independent methods: Wood's alloy heating, described precisely in [14, 15] and thermal analysis DSC/TG. A differential scanning calorimeter with simultaneous mass loss registration, a NETZSCH STA 449F1, was used for DSC/TG analysis. The measurement was performed from 40 °C to 400 °C at a heating rate of 10 °/min, in an inert atmosphere (N). Samples of mass between 0.8 mg and 1.1 mg, in aluminum crucibles (without a pin hole) were used.

The ballistic tests of the propellants obtained were conducted in an LRM system fully described in [16, 17]. The rectangular shaped SHRP were subjected to combustion at ambient temperature using a nozzle of 7 mm diameter.

3 Results and Discussion

3.1 Rheological studies

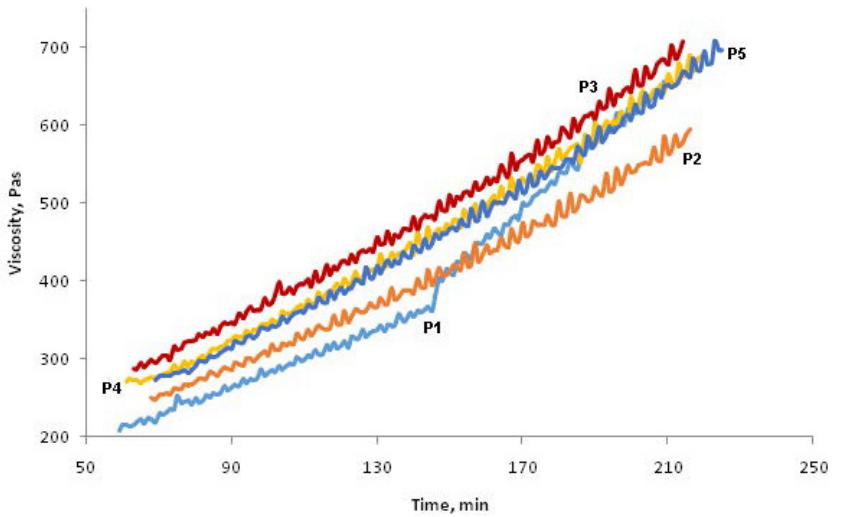

Figure 2. The set of viscosity curves for particular suspensions of the propellants.

On the basis of the curves obtaining for the different propellants (Figure 2), the rate constant for slurry curing was determined based on regression analysis (Table 2) according to the equation [18, 19]:

$$\eta = \eta_0 e^{kt}$$

where:
η – viscosity [Pas],
η_0 – viscosity [Pas] at $t = 0$,

k – rate constant for the curing reaction,
t – time [min].

Table 2. Rate constants for curing of the corresponding suspensions of the propellants

No. of suspension	$k \cdot 10^2$ [min^{-1}]	R^2
P1	0.77	0.9913
P2	0.55	0.9961
P3	0.57	0.9950
P4	0.59	0.9971
P5	0.62	0.9973

It was found that the rate constant for the curing reaction for all of the propellant suspensions obtained does not significantly change on increasing the nFe_2O_3 content in the suspension, indicating that the life time of the suspensions is relatively long.

3.2 The calorific value

The calorific values obtained are presented in Table 3.

Table 3. Calorific values of the propellants examined

Propellant	Calorific value [J/g]
P1	6600
P2	6595
P3	6557
P4	6525
P5	6523

Based on the above data, it can be concluded that the calorific value of the tested propellants decreases slightly with increasing nFe_2O_3 content in the propellant composition.

3.3 Sensitivity to friction and impact

Table 4 summarizes the values obtained for sensitivity to friction and impact measured for the different propellant samples.

Table 4. Sensitivity to mechanical stimuli of the propellants investigated

Composition	Sensitivity	
	Friction [N]	Impact [J]
P1	80	7.5
P2	80	15
P3	80	15
P4	120	10
P5	120	10

It may be inferred from the data obtained that the sensitivity to friction for the propellants examined decreases for higher nFe_2O_3 content in the compositions (P4, P5). However, the results obtained for sensitivity to impact do not show a clear dependence on the nFe_2O_3 content in the compositions.

3.4 Hardness

The hardness values obtained for the tested propellants are summarized in Table 5.

Table 5. Hardness values of the tested propellants

Propellant	Hardness [°Sh A]
P1	73
P2	71
P3	68
P4	68
P5	68

From the results obtained, propellant P1 with the lowest nFe_2O_3 content has the highest hardness. Increasing the combustion rate modifier content causes the hardness to decrease slightly and stabilizes at 68 °Sh A.

3.5 Thermal studies

Table 6 presents the results of the decomposition temperature determinations during heating of samples in a glass tube in Wood's alloy, and the onset temperatures from DSC measurements and mass losses from TG determinations.

During the measurements from heating in Wood's alloy, all samples decomposed rapidly by deflagration. According to the data collated in Table 6, the temperature distribution of the propellants tested decreased slightly with increasing nFe_2O_3 content in the propellant compositions.

Table 6. Decomposition temperatures and mass losses of the propellants examined using the method of heating in Wood's alloy and DSC/TG measurements

Propellant	Decomposition temperature, [°C] on heating in Wood's alloy	Decomposition temperature, [°C] T_{onset} DSC, first step	Mass loss by TG [%]
P1	259	264.7	65.87
P2	258	267.4	75.21
P3	256	269.8	68.15
P4	253	268.9	73.61
P5	250	267.2	80.83

In the case of the DSC/TG analysis (Figure 3), the maximum of the main decomposition peak for all propellant samples occurred at a temperature of approx. 355 °C.

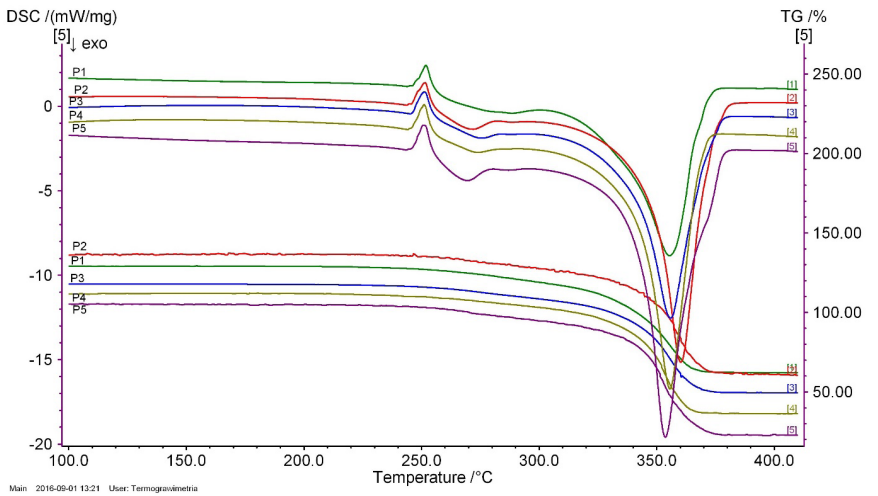

Figure 3. DSC/TG curves of the propellants examined.

There is a difference between the decomposition temperature measured by static and dynamic methods. The heating rate in DSC/TG shown in the Figure 3 was 10 °C/min and the temperature of decomposition measured by this method was shifted in comparison to the decomposition temperature obtained by the static method. But as can be seen on the DSC/TG curve, the thermal decomposition of the propellant is a complex process with several steps. The

first step of decomposition (small exotherm, soon after the phase transition of ammonium perchlorate) is above 250 °C (onset temperature is 267.2 °C). Table 6 gives the decomposition temperatures (T_{onset}) for the first step of decomposition of the samples examined. There are no other significant visible differences in the thermoanalytical curves for the propellants with different nFe_2O_3 contents and no tendency towards a decrease in temperature with increasing amounts of nFe_2O_3. The results from the TG measurements show that the addition of more nFe_2O_3 causes a greater mass loss during decomposition. But here there is a need to take into consideration that the propellants examined are heterogeneous and for the small amount of sample taken for these measurements, certain differences may occur.

3.6 Ballistic examination

Ballistic properties of propellants are characterized, among others, by the linear burn rate (*r*), and its dependence on pressure. The indirect determination of the combustion rate of the compositions investigated was performed by using a laboratory rocket motor system (LRM) [16, 17]. The method described in [16], that is based on tests performed in an LRM, was adopted. The pressure courses registered during combustion of the propellant samples in the form of cubes are shown in Figure 4. The characteristic values obtained for the combustion process of each propellant are presented in Table 7.

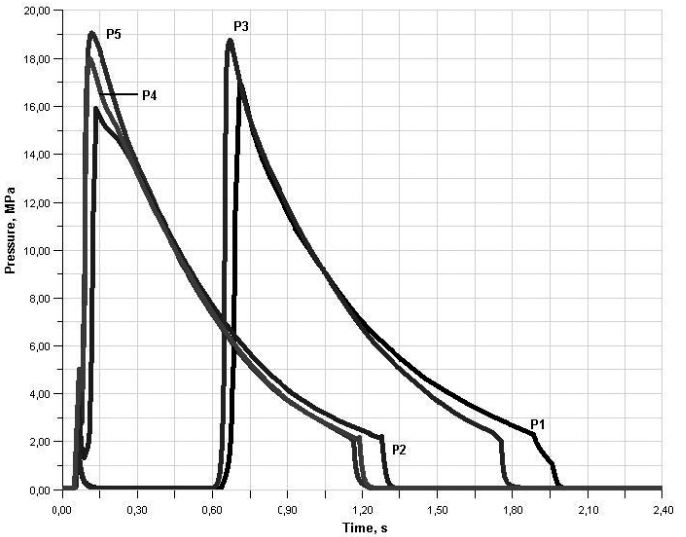

Figure 4. $p = f(t)$ curves for the propellants examined.

Table 7. Combustion time and maximum gas pressure (P_{max}) for the propellants examined

Propellant	Time [s]	P_{max} [MPa]
P1	1.33	16.962
P2	1.19	15.838
P3	1.15	18.821
P4	1.12	17.967
P5	1.09	19.044

From the records obtained it may be observed that the engine run time becomes shorter with increasing nFe_2O_3 content in the composition. A non-linear increase in the maximum gas pressure in the LRM chamber (P_{max}) with increasing nFe_2O_3 content in the propellant was observed.

The calculation of the linear burn rate and its pressure dependence were performed according to the method described in [16]. Numerical evaluation based on integration of the registered $p = f(t)$ dependence was performed by the use of Wolfram Mathematica® 10 software. The $r = f(p)$ curves obtained are presented in Figure 5, while the linear burn rate values for selected engine operating pressures are shown in Table 8.

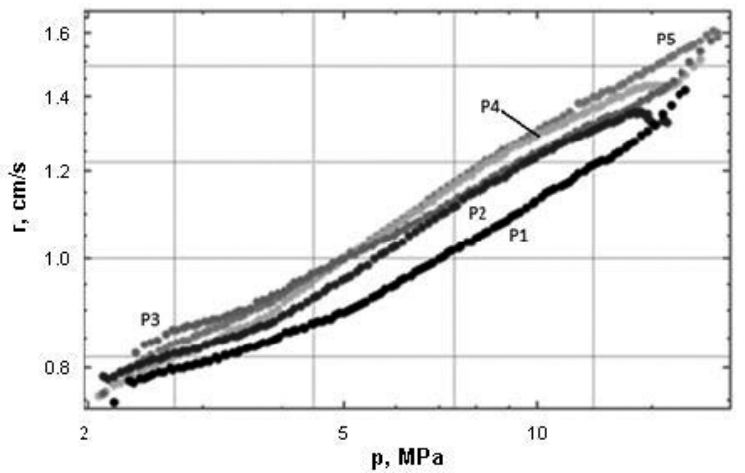

Figure 5. Dependence of $r = f(p)$ for the propellants examined.

Table 8. Linear burn rate of the propellants examined estimated for the working pressures of the LRM

Propellant	Linear burn rate for		
	5 MPa [cm/s]	7 MPa [cm/s]	10 MPa [cm/s]
P1	0.90	1.00	1.13
P2	0.96	1.09	1.23
P3	1.00	1.11	1.25
P4	1.00	1.14	1.29
P5	1.00	1.15	1.31

The results indicate a catalytic effect of nFe_2O_3 on the linear burn rate values for the propellants examined. In the case of low pressure operation of the engine, the characteristics of combustion are close to each other, but for pressures exceeding 7 MPa, an increase in linear burn rate is visible for propellants P2-P5 in comparison to P1. In the case of P2 it is 9% increase, while for P5 it attains an increase of 15%. In higher pressure ranges the effect remains constant.

4 Conclusions

This study has demonstrated the influence of nano iron(III) oxide as a modifier of linear burn rate on selected properties of the solid heterogeneous rocket propellant HTPB/DOA/AP/Al. In order to avoid the formation of agglomerates of nano iron(III) oxide, this material was introduced into the propellant in the form of a uniform suspension in the plasticizer. It was found that nFe_2O_3 does not have a major influence for solid heterogeneous rocket propellants on such properties as calorific value, hardness and sensitivity to friction and impact.

The results from DSC/TG analysis demonstrated that the decomposition process is complex and has at least two steps. With increasing nFe_2O_3 content in the SHRP there are some changes in the peak of the first stage of decomposition. The onset temperature of the decomposition peak was between 264-269 °C. The mass loss during decomposition increased with increasing amounts of nFe_2O_3, from 65% to 80%. Some differences can be attributed to the inhomogeneity of the propellants examined and the small samples taken for the DSC measurement. The determination of the decomposition temperature using the method of heating in Wood's alloy indicated that the minimum temperature of decomposition is slightly decreased by increasing the nFe_2O_3 content in the SHRP.

In the rheological study, no negative effects of nFe_2O_3 on the curing process

and the technological lifetime of the propellant suspensions obtained were observed. Through the determination of the curing rate constant of the propellant suspensions containing nFe_2O_3, no significant effects of this compound were observed on the acceleration of the curing process.

As a result of the ballistic tests conducted in an LRM system, an increase in gas pressure in the LRM chamber as well as a reduction in the combustion time of the propellant was observed with increasing nFe_2O_3 content in the SHRP, indicating its influence on the rate of combustion of the propellant. From the determination of the $r = f(p)$ relationship, it was observed that the increase in the linear burn rate for propellants based on nano iron(III) oxide depended on its content, the increase being about 15% for P5 in relation to P1.

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