

Effects of TKX-50 on the properties of HTPB-based composite solid propellant

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Abstract

Several industrial- and research-type hydroxyl terminated polybutadiene (HTPB) composite solid rocket propellants, containing dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) particles and, featuring the same nominal composition, were prepared. The energetic properties of composite propellants containing different mass fractions of TKX-50 particles were theoretically computed and experimentally evaluated. The effects of different mass fractions of TKX-50 on the rheological properties of both TKX-50/HTPB binder slurries and AP/HTPB/Al propellant slurries were investigated. The strand burning rates, the associated combustion flame structures, and the hazardous properties of the resulting propellants were experimentally analyzed. All of the properties mentioned above were also compared to those of the reference propellant without TKX-50. The results show that the prepared TKX-50 particles can sufficiently be dispersed in the HTPB binder plasticized by di-2-ethylhexyl sebacate (DOS). The propellant formulations containing different mass fractions of TKX-50 are insensitive to impact and friction, differently for the reference propellant without TKX-50. Moreover, over the explored pressure range, TKX-50 can affect the combustion behavior and decrease the burning rate as well as pressure exponent of composite solid propellants compared with the reference formulation.

1. Introduction

High-energy solid propellant formulations play an essential role in propulsion for space exploration. The gravimetric specific impulse and/or density specific impulse of propellants can be increased by the inclusion of certain highly energetic ingredients^[1-4]. However, energetic materials (EM) with increased energy content are needed that also have decreased sensitivity toward external stimuli of heating, friction, and impact. In this respect, many efforts are ongoing to design and synthesize new explosives with improved performance. Promising candidates among the new EMs are nitrogen-rich heterocycles. Tetrazole derivatives are among these compounds. In order to improve the energetic properties of the tetrazoles, N-oxides were proposed in several studies as providing even higher densities and stabilities, lower sensitivities and better oxygen balances^[5-7]. A new explosive, dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50), which belongs to this chemical class, was recently synthesized^[8]. According to published data, the explosive performance of TKX-50 exceeds that of RDX and is comparable to that of CL-20. At the same time, it features good thermal stability, low toxicity, and handling safety comparable to that of RDX. It was reported^[9-11] that the detonation velocity of TKX-50 ($9698\text{m}\cdot\text{s}^{-1}$), calculated at the maximum density of $1.918\text{g}\cdot\text{cm}^{-3}$ (at 100 K), is higher than that of β -HMX ($9221\text{m}\cdot\text{s}^{-1}$) and also of ϵ -CL-20 ($9455\text{m}\cdot\text{s}^{-1}$). At room temperature (298 K), the density of TKX-50 is $1.887\text{g}\cdot\text{cm}^{-3}$. Next to its impressive performance, the impact sensitivity of TKX-50 is 20 J, which is much lower than the sensitivities of RDX, HMX, and CL-20, ranging from 4 to 7.5 J. Friction sensitivity of TKX-50 with 120 N is comparable to or lower than that of RDX, HMX or CL-20. TKX-50 has an electrostatic sensitivity of 0.1 J, which is far higher than what the human body can generate (0.025 J). Finally, the thermal stability of TKX-50 with a decomposition onset of 221°C is comparable to that of RDX.

It is obvious that the highly energetic characteristics of TKX-50 are primarily due to its high enthalpy of formation. Highly energetic performance along with high safety allows considering TKX-50 as not only a powerful explosive^[5,12], but also as a promising ingredient for propulsion, which could result in superior propellant compositions. Calculations have shown that TKX-50 is a better replacement of RDX in composite modified double-base (CMDB) propellants^[8,9]. Substitution of HMX by TKX-50 in NEPE propellants results in a 2 - 5 s increase of gravimetric specific impulse. At the same time, neither the combustion behavior nor the combustion mechanism of TKX-50 has been studied up to date. Thus, the purpose of this work is to study the characteristics of the in-house prepared TKX-50 particles and compare with those of the commonly employed AP by using scanning electron

microscope (SEM) and laser granulated analysis diagnostic techniques. Six solid propellant compositions with different mass fractions of TKX-50 particles were produced. The focus of this paper is on how they affect the combustion properties, placing emphasis on the investigation of the hazardous properties, which could be used for solid rocket nozzle motor applications.

2. Experimental

2.1. Materials and specimen

The binder system is composed of hydroxylterminated polybutadiene (HTPB) plasticized with di-2-ethylhexyl sebacate (DOS, $\geq 99.4\%$), and cured with 2,4-toluene diisocyanate (TDI). Micron-sized aluminum powder, whose mass fraction is 18% in the formulation (Al, $5\mu\text{m}$) were used as high-energy fuel of the manufactured composite solid rocket propellant. Tri-modal ammonium perchlorate (AP) was utilized in the propellant formulation. The first mode consisted of pure research grade ($>99\%$ pure) AP with an average particle size of $105\text{--}147\mu\text{m}$. The second AP mode had an average particle size of $178\text{--}250\mu\text{m}$. The third AP mode was made by grinding ammonium perchlorate ($>99\%$ pure) to an average particle size of around $1\text{--}5\mu\text{m}$ in a fluid energy mill. TKX-50 particles were well dried before use. Part of AP mass fraction was replaced by TKX-50 in six propellant formulations, and TKX-50 mass fraction of the samples thus prepared ranges from zero up to 40% in PHT-1 (0%), PHT-2 (5%), PHT-3 (10%), PHT-4 (20%), PHT-5 (30%) and PHT-6 (40%), respectively. Except where otherwise stated, all propellants were manufactured, processed, and tested at Xi'an Modern Chemistry Research Institute under identical conditions and using identical procedures.

2.2 Preparation of propellants

All propellant formulations were mixed in 500 g batches using a vertical planetary mixer of 2 dm^3 capacity. Batches were mixed and cast under vacuum by a slurry cast technique. Propellant was cured at $50\text{ }^\circ\text{C}$ for 120 h in a water jacketed oven.

2.3. Characterization Methods of Ingredients and Propellants

2.3.1 SEM and particle size distribution experiments

Particle size and its distribution were measured by a Master Sizer Instrument. The morphologies of oxidizers were examined by a scanning electron microscope (SEM) technology. The measured specific surface area values refer to the particle size distribution determined by the Malvern MasterSizer.

2.3.2 Rheological experiment

Different particles were mixed with HTPB binder in the mass ratio of 1/1. The viscosity of the propellant slurry was determined using a HAAKE cylindrical rotational rheometer RS300. The samples were tested in the coaxial cylinder sensor system at a temperature of about $50\text{ }^\circ\text{C}$.

2.3.3 Burning rate test method

The measured apparatus is fully described in references ^[14,15]. Propellant samples were placed vertically on the combustion rack of a sealed chamber which was filled with a nitrogen atmosphere. A metal fine wire (0.1 mm in diameter) was threaded through the top of the strand with an alternating voltage of 100 V to ignite the propellant strands (diameter = 5–6 mm, length=140 mm) at an initial temperature of $20\text{ }^\circ\text{C}$.

2.3.4 Hazardous properties test

The hazardous properties of the tested propellant compositions to impact stimuli were determined by applying the fall hammer method (2 kg drop weight) in a Bruceton staircase apparatus ^[16] and results are given in terms of statistically obtained 50% probability of explosion (H_{50}). Friction sensitivity was measured on a Julius Peter apparatus ^[17] by incrementally increasing the load from 0.2 to 36 kg, until no ignition was noted in five consecutive test samples.

2.3.5 Heat of explosion test

The theoretical heat of explosion was obtained by using "Ideal Gauss Law", It can be calculated according to the equation (1) as follows.

$$H_u = x_1 H_{u1} + x_2 H_{u2} + \dots + x_n H_{un} \quad (1)$$

where H_u is theoretical heat of explosion, $\text{J}\cdot\text{g}^{-1}$; x_1 is mass fraction of the first ingredient; H_{u1} is theoretical heat of explosion of the first ingredient, $\text{J}\cdot\text{g}^{-1}$; x_2 is mass fraction of the second ingredient; H_{u2} is theoretical heat of explosion of the second ingredient, $\text{J}\cdot\text{g}^{-1}$; x_n is mass fraction of the n -th ingredient; H_{un} is theoretical heat of explosion the n -th ingredient, $\text{J}\cdot\text{g}^{-1}$.

The measured heat of combustion values can be experimentally verified by means of an isothermal method. A definite mass of propellant sample was put into a calorimetric oxygen bomb, which is surrounded by a fixed mass of water. The propellant was ignited in the bomb and the heat of explosion of the sample was calculated according to equation (2) after the value of the water temperature increase was measured.

$$Q_v = (C\Delta T - q_1)/m \quad (2)$$

where Q_v is heat of explosion, $J \cdot g^{-1}$; C is thermal capacity of the calorimeter, J/K ; ΔT is the value of the water temperature increase after the propellant combustion, K ; q_1 is heat of explosion of the initiation wire, joule (J); m is mass of sample, gram (g).

2.3.6 Density test

The density measurements were carried out with a Model AG 104 METTLER TOLEDO balance with rectangular shaped samples of $30 \text{ mm} \times 30 \text{ mm} \times 10 \text{ mm}$, which were steeped in a liquid paraffin medium at the temperature of $20 \pm 2 \text{ }^\circ\text{C}$.

2.3.7 Mechanical properties

Mechanical characteristics of the tested propellant compositions were determined by an Instron 4505 tensile tester. Cured propellants were cut into slices, from which JANNAF dog - bones were stamped. Tests were carried out at $+20^\circ\text{C}$ temperature with 100 mm min^{-1} cross-head speed.

3 Results and Discussion

3.1 SEM and grain size distribution analysis

Detailed morphology information concerning the powder was collected by running a series of advanced diagnostic techniques, including BET, scanning electron microscope (SEM) and grain size distribution. The well-dried TKX-50 particles were free of fluid, their microstructures and grain size distributions, compared with AP I (first mode) are shown in Figs. 1 and Table 1, respectively.

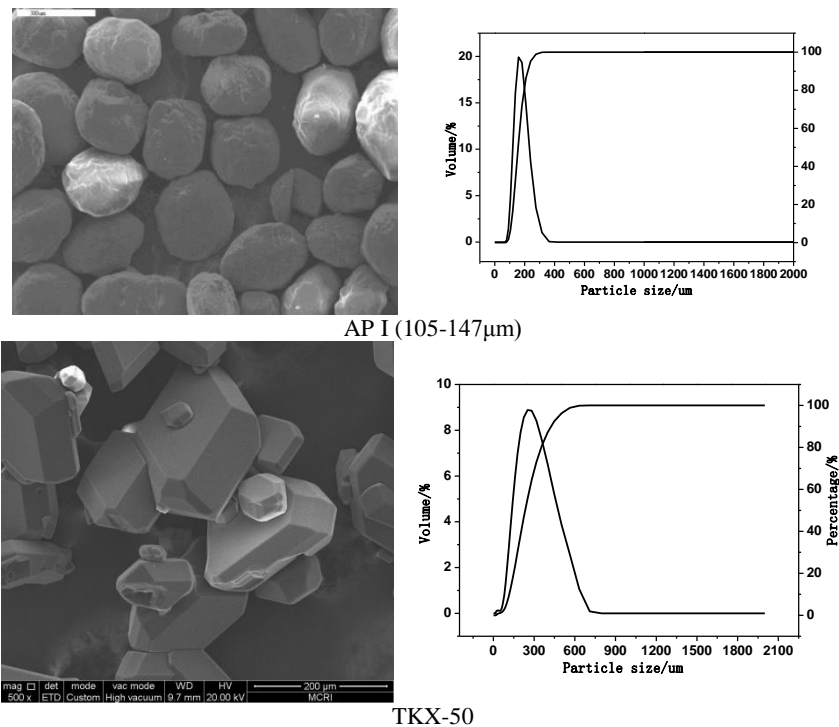


Figure 1. SEM images and grain size distribution of tested particles (High magnification ($\times 500$))

Table 1. Characteristics of AP and TKX-50 particles

Items	unit	AP (105-147 μm)	TKX-50
d_{10}	μm	111.5	116.9
d_{50}	μm	155.8	233.7
d_{90}	μm	218.4	423.2
Width	-	0.686	1.31
Density	$\text{kg m}^{-3}, \times 10^3$	1.94	1.88
Relative atomic mass	-	117.5	236.15

Specific surface area (SSA)	$\text{m}^2 \text{g}^{-1}$	1.13	0.03
Oxygen balance	%	34.04	-27.10

In the table, d_{10} : particle diameter corresponding to 10% of the cumulative undersize distribution, μm ; d_{50} : median particle diameter, μm ; d_{90} : particle diameter corresponding to 90% of the cumulative undersize distribution, μm ; width = $(d_{90}-d_{10})/d_{50}$; and specific surface area refers to the particle size distribution determined by Malvern Mastersizer. It should be note that the numbers showed in the table is not much reliable for non- spherical particles.

It can be seen from that the microstructure of the tested TKX-50 particles presents an irregular shape, which are different from those of the near spherical AP used as a reference oxidizer. The d_{50} of TKX-50 particles is 233.7 μm , which is much larger than that of the common AP particles and the particle size distribution curve is coarser than that of the common AP. The width of TKX-50 particles is 1.31, which is much higher than that of AP particles (0.686). Corresponding to the higher values of d_{50} , the specific surface area of TKX-50 is $0.03 \text{ m}^2 \text{ g}^{-1}$, which is much lower than that of AP ($1.13 \text{ m}^2 \text{ g}^{-1}$).

3.2 Thermo-chemical and hazardous properties of tested propellants

3.2.1 Ideal Energetic properties

The energetic properties of composite solid propellants with and without TKX-50 particles were calculated by means of “Energy Calculation Star (ECS)” software^[12], which was developed by Xi’an Modern Chemistry Research Institute based on the fundamental thermodynamics principle of minimum free - energy program. Material density plays an important role in developing high - energy materials. The data obtained are listed in Table 2, and the curve of ideal specific impulse vs. TKX-50 mass fractions is shown in Figure 2.

Table 2. Ideal energetic properties of composite propellants with and without TKX-50 particles (7MPa)

Samples	I_{sp}/s	$C^*/\text{m}\cdot\text{s}^{-1}$	T_c/K	O/F
PHT-1	265.4	1589.8	3393.5	0.527
PHT-2	266.3	1595.2	3333.7	0.497
PHT-3	266.7	1596.8	3261.4	0.468
PHT-4	261.4	1573.3	3042.9	0.413
PHT-5	256.7	1525.5	2698.1	0.361
PHT-6	255.2	1517.5	2648.2	0.313

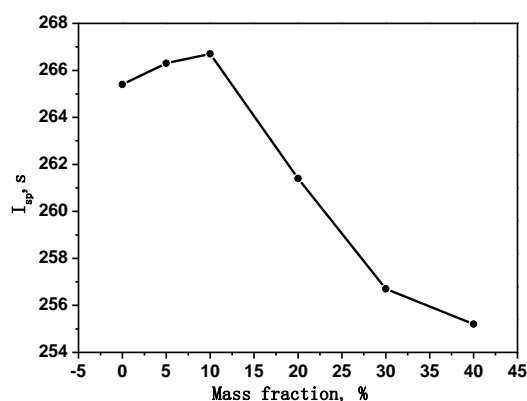


Figure 2. The curve of specific impulse with mass fraction of TKX-50 particles in the propellants

It can be seen that the gravimetric specific impulse (I_{sp}) and characteristic velocity of propellants loaded with TKX-50 particles first increase with an increase in the mass fraction of TKX-50 particles in the formulations and then decrease, showing a peak at 10 % TKX-50. On the contrary, the adiabatic flame temperature (T_c) decreases with an increase in the mass fraction of TKX-50. The density of TKX-50 particles (1.88 g cm^{-3}) is lower than that of AP (1.94 g cm^{-3}), resulting in a lower density of the corresponding propellants. The gravimetric specific impulse and characteristic velocity of propellants with different TKX-50 mass fractions decrease in the following order: [PHT-3] > [PHT-2] > [PHT-1] > [PHT-4] > [PHT-5] > [PHT-6], while the adiabatic flame temperature (T_c) decrease monotonically in the order: [PHT-1] > [PHT-2] > [PHT-3] > [PHT-4] > [PHT-5] > [PHT-6].

3.2.2 Energetic properties (density and heat of explosion)

Densities and heat of explosion measurements were conducted for each propellant and the results were compared with the theoretical data. Table 3 summarizes the findings of these tests.

Table 3. Effect of different mass fraction of TKX-50 on the energetic properties for composite solid propellants

Sample	Heat of explosion/ $\text{J}\cdot\text{g}^{-1}$	Heat of	Density/ $\text{kg}\cdot\text{m}^{-3}$ ($\times 10^3$)	Density
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s	Theoretical l	Measured	explosion efficiency/%	Theoretical	Measured	efficiency/%
PHT-1	6609	6528	98.77	1.767	1.762	99.72
PHT-2	6497	6441	99.14	1.764	1.760	99.77
PHT-3	6364	6312	99.18	1.761	1.756	99.72
PHT-4	6026	5838	96.88	1.756	1.750	99.66
PHT-5	5775	5531	95.78	1.750	1.740	99.43
PHT-6	5437	5158	94.87	1.744	1.734	99.42

It can be seen from the results in Table 3 that the density of composite propellants containing TKX-50 is in the range of 1.734-1.760 g·cm⁻³, which is lower than that of the propellant without TKX-50 (1.762g·cm⁻³). The density of TKX-50 is lower than that of AP, and when parts of AP in the propellant formulation are replaced by TKX-50 particles this leads to a decreasing propellant density. Moreover, increasing the high density materials and fine particle percentages leads to an increase in propellant density, which may be due to better powder packing during the manufacturing process. The measured heat of explosion of composite propellant PHT-1 is 6528 J·g⁻¹, which is higher than that of all propellants containing TKX-50 (ranging from 5158 J·g⁻¹ to 6441J·g⁻¹). This may be attributed to the lower heat of formation of TKX-50 (446.6 kJ mol⁻¹), which results in a lower heat of explosion of the corresponding propellants. Moreover, the values of the measured heat of explosions being lower than that of the theoretical ones, which may be attributed to the difference combustion efficiency of different mass fractions of TKX-50 powders. However, there is a peak in the heat of explosion efficiency for 10 % mass fraction of TKX-50 in the propellant formulation. This result agrees with the ideal calculated data. The sequence of the measured heat of explosion and density for the propellants with different TKX-50 mass fractions is the same and is as follows: [PHT-6] < [PHT-5] < [PHT-4] < [PHT-3] < [PHT-2] < [PHT-1].

One must be note that without going into discussion on the calculation methods, we note that the present value of the enthalpy of formation of TKX-50 is highly questionable. Indeed, a simple sum of enthalpies of formation of TKX-50 constituents-hydroxylamine (-27.3 kcal/mol^[18]) and 5,5'-bis (2-hydroxytetrazole) (-115 kcal/mol, estimation based on enthalpy of formation of 5,5'- bistetrazole^[19]) gives a much lower value of ~60.5kJ mol⁻¹. The heat of reaction between an acid and a base, the so-called heat of salt formation, is the difference between enthalpy of formation of salt and sum of enthalpies of formation of salt constituents. Based on comparison of enthalpies of formation of hydroxylammonium perchlorate, hydroxylammonium nitrate, liquid perchloric and nitric acids, and hydroxylamine, the heat of salt formation for hydroxylamine salts averages 16 kcal per one mole of hydroxylamine^[18,19]. Taking into account the heat of salt formation for two hydroxylamine molecules (~32 kcal, estimation), the enthalpy of formation of TKX-50 can be calculated as 28.4 kJ mol⁻¹, that is more than three times less than the value reported in Ref.[8].

3.2.3 Hazardous properties

TKX-50 particles, as one of the most popular high-energy density materials, are very insensitive. Results of the hazardous properties experiments are shown in Table 4.

Table 4. Hazardous properties of composite solid propellants with different mass fraction of TKX-50 particles

Samples	Friction (P)/%	Confidence level of 95% believe level	Impact/N·m	Standard deviation S (logarithmic value)
PHT-1	92	(74%, 99%)	4.29	0.04
PHT-2	84	(64%, 96%)	4.71	0.12
PHT-3	80	(59%, 93%)	5.39	0.10
PHT-4	80	(59%, 93%)	11.55	0.11
PHT-5	76	(55%, 91%)	20.05	0.04
PHT-6	72	(51%, 88%)	24.68	0.08

It can be seen that all the propellant formulations containing TKX-50 were insensitive to impact and friction except the reference one without TKX-50, which is more sensitive to friction as compared to the other compositions. The insensitiveness may be attributed to the low specific surface area and mechanical insensitivity of TKX-50 particles in contrast with AP particles, especially for UFAP. The result reveals that the use of the prepared TKX-50 powder in solid propellant leads to a decrease in the sensitivities of friction and impact for the composite solid propellant, making feasible and safe its application in the propellants, whereas, the compositions with different particle size and size distribution of TKX-50 need to be investigated in future.

3.3 Effects of different mass fraction of TKX-50 particles on the composite solid propellant slurries

The viscosities of the composite solid propellant with different mass fraction of TKX-50 were determined and the rheological results of the propellant slurry in one hour are shown in Table 5.

Table 5. Effect of different mass fraction of TKX-50 particles on the rheological properties for composite propellants

Samples	Viscosity/Pa·s	Yield stress/Pa	Flowing properties of propellant slurry ^{a)}
PHT-1	224.4	56.2	A
PHT-2	231.8	58.3	A
PHT-3	254.2	62.4	A
PHT-4	318.8	70.1	B
PHT-5	357.1	79.7	B
PHT-6	389.4	87.2	C

^{a)} A-D represents that the flowing properties of a propellant slurry suspension is from good to bad in turn.

It can be found that the rheological properties of the propellant slurry show a behavior of pseudo-plastic, non-Newtonian fluids. TKX-50 particles, when added to the composite solid propellant, increase the viscosity of the slurry insignificantly. The viscosity and yield stress of the reference propellant slurries without TKX-50 (sample PHT-1) were slightly lower than those of propellant slurry containing TKX-50. The characteristics of the viscosity and yield stress for the reference propellant slurries lead to improvement of process properties and pot life ^[20].

In order to analyze the physical structures of composite solid propellants containing different mass fraction of TKX-50, the microstructures of propellants were analyzed and the results are shown in Figure 3.

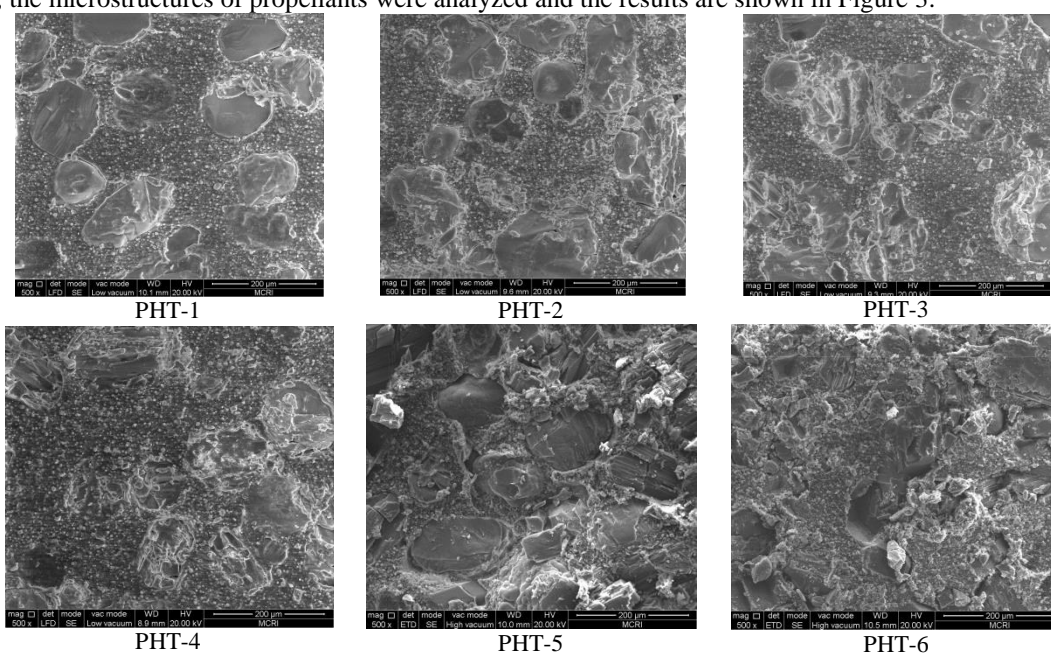


Figure 3. Microstructure surface of composite propellants containing different mass fraction of TKX-50 particles (High magnification ($\times 500$))

Figures 3 indicate that there are many granulated particles on the surface of cured composite propellants. The prepared TKX-50 particles are compatible with the ingredients of composite solid propellant systems, and the granulated particles with smaller diameters can fill into the spaces between the larger grains sufficiently well.

3.4 Effects of TKX-50 mass fraction on the combustion properties of composite propellants

3.4.1 Burning rate and pressure exponent

Propellant burning rates determine the rate of gas generation, which determines the pressure inside the motor and the overall thrust. Burning rates herein are obtained experimentally by burning small propellant strands and measuring the surface regression versus time. Various factors like the particle diameter, oxidizing species, pressure, and temperature may affect the burning rate of propellants. The burning rate data of propellants containing TKX-50 were obtained under different pressures and are shown in Fig.4. Table 6 shows the burning rate trend at 7.0 MPa of composite propellants containing different mass fractions of TKX-50.

Table 6. Burning rate trend for composite propellants with different mass fraction of TKX-50 particles

Samples	PTH-1	PTH-2	PTH-3	PTH-4	PTH-5	PTH-6
Burning rate ($\text{mm}\cdot\text{s}^{-1}$ at 7.0 MPa)	8.69	8.41	8.47	8.33	8.28	7.67

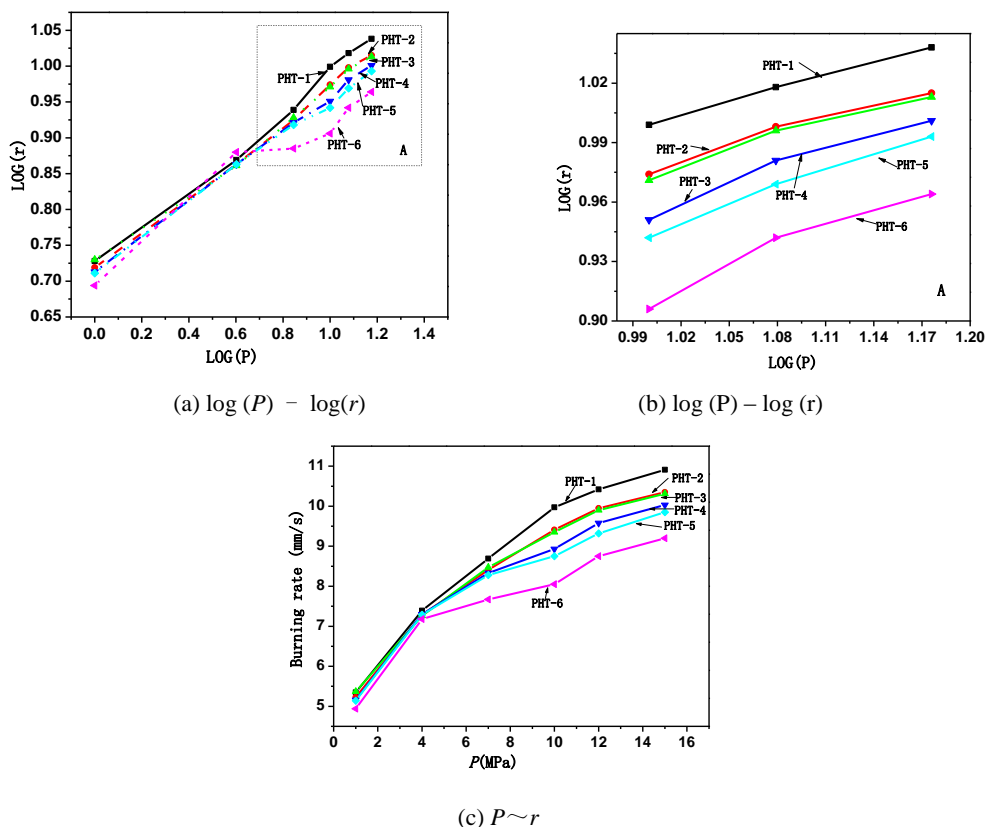


Figure 4. Burning rate of composite solid propellant containing different mass fractions of TKX-50 particles at various pressures. Fig. 5 (b) is the enlarged figure of dotted portion in figure 5 (a).

It can be seen in Fig.4 that TKX-50 additives can affect the combustion behavior and change the burning rate of composite solid propellant. The burning rates of all tested samples increase with increasing pressures, and the increasing extent for PHT-6 samples in the pressure range of 1-15 MPa is obviously less than those the other tested samples. The average pressure exponent of PHT-6 sample is 0.245 (1-15 MPa), which is the lowest one among all tested formulations. The reasons of addition TKX-50 particles to the composition decrease the burning rate maybe as follows: from the view point of heat transfer, the addition of TKX-50 powder to the propellant can decrease the heat adsorption in the combustion process to some extent; from the view of dynamics, TKX-50 powder cannot get in contact with polymer binder and gaseous reactants because of their high insensitivity and relative small specific surface area. Also, the releasing heats and heat transmission at the combustion surface for TKX-50 are lower than those of AP at tested pressure range.

In order to analyze the effect of TKX-50 on the combustion mechanism, the thermal decomposition of composite propellant containing TKX-50 were combined, and the curves shown in Fig.5.

The thermal behavior of TKX-50 and the kinetics of its thermal decomposition were studied using differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) in non-isothermal condition only^[21,22], the decomposition mechanism of TKX-50 remains unknown. By applying multiple heating rate of DSC measurements and Ozawa's iso-conversional model free method the activation energy of 32.4 kcal/mol, and pre-exponential factor of $1.99 \times 10^{12} \text{ s}^{-1}$ were calculated from DSC peak maximum temperature vs. heating rate relationship^[21]. The thermal decomposition of TKX-50 studied by TG-DTA with help of Ozawa's and Kissinger's methods gives close kinetics parameters: 35.21 kcal mol⁻¹ and $10^{12.91} \text{ s}^{-1}$, respectively^[23]. The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction obtained by DSC measurements and Kissinger's method in^[22] are significantly different: 56.8 kcal mol⁻¹ and $10^{23.89} \text{ s}^{-1}$. It can be seen from Fig. 5 that the decomposition of composite solid propellants with TKX-50 particles show three exothermic decomposition processes. The first decomposition peak is the main decomposition stage, and there is a little decomposition process affiliated to the first one, the mass loss of thermal decomposition is about 35%, which maybe the decomposition of TKX-50 particles.

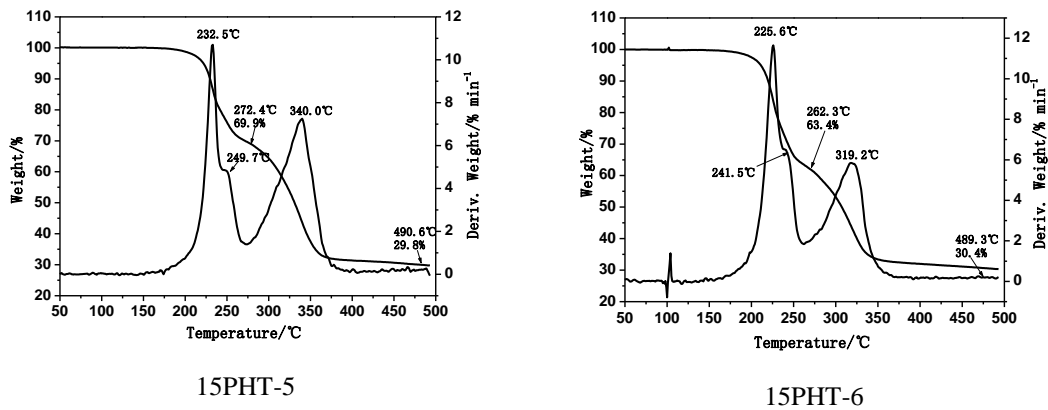


Fig. 5 Thermal decomposition of composite propellant containing different mass fraction of TKX-50 particles
 3.4.2 Combustion flame structures

TKX-50, as one of the high-energy insensitive materials, has significant influence not only to the burning rate but also to the pressure exponent, which obviously have much effects on the combustion mechanism (such as: combustion flame structure, etc.) of composite solid propellants. In order to understand the effects of TKX-50 on the flame structure of the composite propellant, the flames of composite propellant with different mass fractions of TKX-50 at 1 MPa and 3 MPa are shown in Figure 6.

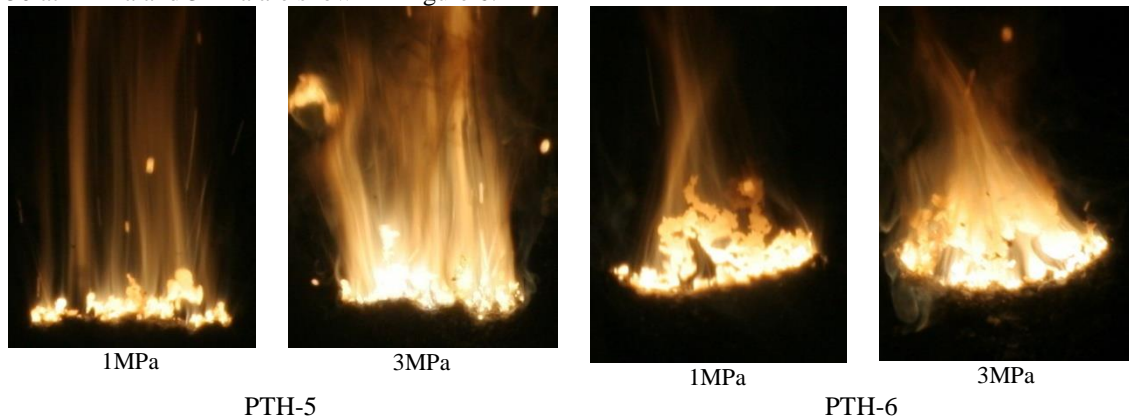


Fig. 6 Combustion flame structures of composite solid propellants with different mass fraction of TKX-50 particles
 From the results of Figure 6, it can be seen that the combustion of composite propellants with and without TKX-50 particles present multi-flame structures. There are many sparks on the propellant surface during the combustion process, which can be attributed to the addition of the aluminium metal fuels to the propellant formulations. Also, there are many flakes near the burning surface of the propellants, which can be related to the aggregation/agglomeration phenomenon of aluminium powder in the propellant. Although the metal oxidation process follows a common set of events, aggregation/agglomeration phenomena near the burning surface are noticeably different depending on the enforced operating conditions and details of the solid propellant formulations.

3.5 Mechanical properties of composite propellants with and without TKX-50 particles

Six different series of propellant compositions with and without TKX-50 were tested. The mechanical properties were tested according to the GJB 772A -1997, 413.1 standards and the results are shown in Table 7.

Table 7. The mechanical properties of dual oxidizer composite solid propellants

Samples	Mechanical properties (+20°C)		
	σ_m /MPa	ε_m /%	E/MPa
PHT-1	1.08	25.4	6.24
PHT-2	1.10	23.8	6.12
PHT-3	1.14	23.6	5.82
PHT-4	1.19	23.5	5.67
PHT-5	1.29	22.4	5.44
PHT-6	1.34	21.5	5.28

The maximum tensile strength and elastic modulus of AP-based composition (1.08 MPa and 6.24 MPa, respectively) are lower than those of the propellants containing TKX-50 particles, which are in the range of 1.10-1.34 MPa and 5.28-6.12 MPa, respectively. Whereas, the elongation of the referenced propellant (25.4 %) is higher than that of propellants loaded with TKX-50 particles, which is in the range of 21.5 %-23.8 %.

4 Conclusions

(1) The TKX-50 prepared particles could be dispersed in the HTPB binder effectively, and their application in the composite propellants, which can be casted in vacuum and cured, is feasible.

(2) The TKX-50 particles could be used as the energetic components which would improve the combustion properties of the composite propellant. The addition of TKX-50 particles can decrease the burning rates compared to the reference propellant. Also the pressure exponent of the propellants containing TKX-50 particles decrease compared to the reference one (PHT-1 sample).

(3) One must be note that without going into discussion on the calculation methods, we note that the present value of the enthalpy of formation of TKX-50 is highly questionable. It maybe should be investigated further.

References

- [1] Price E W. 1984. Combustion of Metallized Propellants. In Kuo K K, Summerfield M, eds. *Fundamentals of Solid Propellants Combustion*, Vol.90, Chapter 9. AIAA Progress in Aeronautics and Astronautics.
- [2] Babuk V A, Vasilyev V A, Sviridov V V. Formation of condensed combustion products at the burning surface of solid rocket propellant. In: Yang V, Brill T B, Ren W Z, eds. 2000. *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics*, Progress in Aeronautics and Astronautics, AIAA. Reston, va, 749-776.
- [3] Reydellet D. 1986. Performance of Rocket Motors with Metallized Propellants in AGARD Advisory Report AR-230. AGARD, Paris, France, AGARD PEP WG-17.
- [4] Prajakta R. Patil, V.N. Krishnamurthy, Satyawati S. Joshi, 2006. Differential scanning calorimetric study of HTPB based composite propellants in Presence of nano-ferric oxide, *Propellants, Explosives, Pyrotechnics*, 31.
- [5] Churakov A.M., Tartakovsky V.A. Progress in 1,2,3,4-tetrazine chemistry, *Chem. Rev.*, 2004, 104, pp. 2601-2616.
- [6] Gobel M., Karaghiosoff K., Klapotke T.M., Piercey D.G., Stierstorfer J. Nitrotetrazolate-1N-oxides and the strategy of N-oxide introduction, *J. Am. Chem. Soc.*, 2010, 132, pp. 17216-17226.
- [7] Klapotke T.M., Piercey D.G., Stierstorfer J. Taming of CN7-ANION, *Chem.-Eur. J.*, 2011, 17, pp. 13068-13077.
- [8] Fischer N., Fischer D., Klapotke T.M., Piercey D.G., Stierstorfer J. Pushing the limits of energetic materials-the synthesis and characterization of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate, *J. Mater. Chem.*, 2012, Vol 22, 20418-20422.
- [9] R Fischer N., Fischer D., Klapotke T.M., Piercey D.G., Stierstorfer J. Pushing the limits of energetic materials - the synthesis and characterization of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate, *J. Mater. Chem.*, 2012, 22, 20418-20422.
- [10] Mayer R., Kohler J., Homburg A. *Explosives*, 5th Edn, Wiley VCH, Weinheim, 2002, pp. 237-239.
- [11] Bircher H.R., Mdaeder P., Mathieu, J. Properties of CL-20 based high explosives, *Proc. 29th Inter. Annual Conf. ICT*, 1998, paper 94.1-94.14.
- [12] Bi Fu-qiang, Fan Xue-zhong, Fu Xiao-long, et al. Interaction of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate with CMDB propellant components [J]. *J. Solid Rocket Technology*, 2014, 512 (2): 214 -218.
- [13] Li Meng, Zhao Feng-qi, Luo Yang, et al. Energetic characteristics computation of propellants containing dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) [J]. *Chinese J. Energetic Materials*, 2014, 22(3): 286-290.
- [14] Huang Haifeng, Shi Yameng, Yang Jun, et al. Compatibility study of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) with some energetic materials and inert materials [J]. *J. Energ. Materials*, 2015, Vol. 33(1), pp. 66-72.
- [15] Fischer N., Klapotke T.M., Stierstorfer J., Wiedemann C. 1-Nitrateoethyl-5-nitriminotetrazole derivatives-shaping future high explosives [J]. *Polyhedron*, 2011, Vol. 30, pp. 2374-2386.
- [16] Zhu Zhou-shuo, Jiang Zhen-min, Wang Peng-cheng, Lu Ming, Shu Qiang, Yu Xian-han. Synthesis and properties of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate [J]. *Chinese J. Energetic Materials*, 2014, Vol. 22(3), pp. 332-336.
- [17] Wang Jun-feng, Yang Yun-feng, Zhang Chun-yuan, Wang Xiao-jun, Zhang Xiao-peng. Thermal decomposition reaction kinetics of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate [J]. *Chinese J. Expl. & Propel.*, 2015, No. 2.

- [18] An Q., Liu W.G., Goddard W.A., Cheng T., Zybin S.V., Xiao H. Initial steps of thermal decomposition of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate crystals from quantum mechanics[J]. *J.Phys.Chem.C*, 2014, Vol. 118(46), pp.27175-27181.
- [19] Fogelzang A.E., Egorshv V.Yu., Sinditskii V.P., Dutov M.D. Combustion of nitroderivatives of azidobenzenes and benzofuroxans[J]. *Comb. Flame*, 1991, Vol.87, pp.123-135.
- [20] Xu Pei-xian. The rheology of polymer and its applications[M]. Beijing: Chemical Industry Press, 2003.
- [21] Nazin G.N., Manelis G.B., Rubtsov Y.I., Strumin V.A. Thermal decomposition and combustion of explosives and propellants[J]. Taylor & Francis Group, CRC Press, Boca Raton, 2003.
- [22] Sinditskii V.P., Egorshv V.Yu., Serushkin V.V., Levshenkov A.I. Berezin M.V., Filatov S.A.. Combustion of energetic materials governed by reactions in the condensed phase[J]. *Inter. J. Ener. Materials and Chemical Propulsion*, 2010, 9(2):147-192.
- [23] Sinditskii V.P., Egorshv V.Yu., Serushkin V.V., Levshenkov A.I. Berezin M.V., Filatov S.A., Smirnov S.P. Evaluation of decomposition kinetics of energetic materials in the combustion wave[J]. *Thermochim. Acta*, 2009, 496(1-2):1-12.