Full Paper

Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.201800299

The Detonation Properties Research on TKX-50 in High Explosives

Xiaoling Xing,[a] Shengxiang Zhao,[a] Xiaofeng Wang,[a] Weipeng Zhang,[a] Xiaoqiang Diao,[a] Wei Fang,[a] and W. X. Li[a]

Abstract: The mechanical sensitivity of TKX-50 under different preparation conditions and its preparation process to explosive samples were examined. The detonation properties of TKX-50 based samples were determined. The results show that the column density can reach 1.80-1.81 g cm^{-3} under the specific pressure of 3000. Different column diameters with different detonation velocities show the obvious scale effect of TKX-50 based explosives. The critical initiation pressure of TKX-50 based explosives is much higher than HMX and CL-20 based explosives, which means a much lower shock sensitivity. The determined explosion heat value of TKX-50 based explosiveis 4650 J g^{-1}, which is also much lower than HMX and CL-20 based explosives.

Keywords: TKX-50 · sample preparation · detonation properties · shock sensitivity

1 Introduction

Research on TKX-50 (5,5′-bistetrazole-1,1′-dioxide) is developing very fast since it has been synthesized in 2012 [1–5]. The main results show that TKX-50 has a high calculated detonation velocity of 9698 m/s, which is even higher than CL-20; it is also reported that the impact and friction sensitivities are lower than CL-20 or even RDX. These related characteristics of TKX-50 attracted more and more researchers and crystal structure modeling [6], thermal behavior and energetic properties were obtained accordingly [7–11]. The synthesizing methods are also discussed and optimized by all feasible ways. The main aim is to realize TKX-50 more clearly and accurately, and to release potential for its application in the energetic material field. The main superiority of TKX-50 are the cleaner detonation products, regarded as environmentally friendly energetic materials compared to ammonium nitrite explosives.

Although research on TKX-50 is popular recently [12], experiments on application of it in explosives are very rare. The energy level and source of TKX-50 cannot be described by the model prediction alone, and much experimental design must be carried out for verification and conformation because of its different structure and constitution from ammonium nitritelike materials. In this article, the proper raw TKX-50 was applied by our institute and prepared to explosive samples with very little binder by compression-molding process, the detonation properties were studied intensively, and interesting information on TKX-50 was obtained, correspondingly.

2 Experimental Section and Modeling

Pre-treatment process of TKX-50: different pretreatment times by ball milling method were carried out to find the proper conditions.

Simulation: The COMPASS of Materials Studio method was applied to study the binder force between the TKX-50 and the different binders, respectively.

Preparation of explosive samples: The selected binder was solved and the TKX-50 and other components were mixed with the solvent. The mixture was stirred for solvent evaporation. Then the residuals were screened by sifter with mesh number of 10 and put into a vacuum oven at 50 °C for 24 h.

Sample molding: The powders were placed in the certain mould with cylindrical bore and the sample molding condition was defined according to the sample density values.

3 Results and Discussion

3.1 The Pre-treatment of Raw TKX-50

According to the mechanical sensitivity results of TKX-50 samples by different crystallization method, the TKX-50 sample with the lowest mechanical sensitivity was selected as raw material. The main problem of TKX-50 was that the press molding density cannot be improved to acceptable level without pre-treatment, so the raw TKX-50 was pre-

[a] X. Xing, S. Zhao, X. Wang, W. Zhang, X. Diao, W. Fang, W. X. Li
Xi'an Modern Chemistry Research Institute, Xi'an, 710065, China

treated by ball mill. After the milling process, the particle distributions of TKX-50 were changed (Figure 1) after the pre-treating process.

From Figure 1, the particle distributions of TKX-50 do not vary much after the milling process of 1.5 h. The SEM also showed the shapes and surfaces of the TKX-50 in Table 1, correspondingly. From which one can see that the status does not change much after the milling process of 2 h. The verities of the mechanical sensitivity were measured and the results show that the mechanical sensitivity of TKX-50 is lowered (impact sensitivity from 56 to 50 and friction sensitivity 50 to 40, respectively). The ball milling pretreatment is beneficial to the lower sensitivity.

3.2 Simulation and the Binder Choice

The COMPASS of Materials Studio method was applied to study the binder force between the TKX-50 and four different binders. Fluroelastomer, EVA, EPDM and ETPE were supposed as binders and the mass fraction was to be 4%, the chemical affinities between TKX-50 and binders were simulated. The calculated results are shown in Table 2.

The chemical affinities can reflect the interfacial strength of TKX-50 and binders. The higher the chemical affinity is, the greater strength has the system. The greater interfacial strength can be beneficial to the molding density. According to the data in Table 2, the ETPE was selected as the most suitable explosive binder for the following preparation of explosive samples.

3.3 Preparation of Explosive Samples

The constituents of the explosive were

TKX-50 95.5%

ETPE 3%

Graphite and other materials 1.5%.

ETPE was dispersed in dichloromethane and the mixture kept in at 45 °C in a water bath until ETPE was completely dissolved. The pre-weighed TKX-50 and graphite etal were premixed directly before slowly adding the ETPE solution. Proper stirring is needed for the solvent evaporation. The residuals were screened by sifter with mesh number of 10 and placed into the vacuum oven of 50 °C for 24 h. Then the TKX-50 based explosive molding particles were obtained successfully.

The TKX-50 based explosive molding particles were pressed under different specific pressures to form $\Phi 20 \times 20$ mm columns of different densities. Figure 2 shows the relationship between the densities and specific pressures.

From Figure 2, the density of the columns increases with higher specific pressure. The increasing value is only 0.006 g cm^{-3} when the specific pressure is increased from 3000 to 3500, so the specific pressure of 3000 is a suitable value for the column molding process.

All explosive columns with different diameters were prepared under the specific pressure of 3000 conditions. The values of the densities are 1.80–1.81 g cm^{-3}.

3.4 Properties

3.4.1 Detonation Velocity

The detonation velocities of TKX-50 based explosives with different diameters were determined by probe (copper) method. The results are shown in Table 3.

The detonation velocities of TKX-50 based explosives increased with increasing diameter. The more obvious variation amplitude appears from the area of $\Phi 30$ mm $\times$ 30 mm to $\Phi 40$ mm $\times$ 40 mm, which shows the scale effect of TKX-50 based explosives. Perhaps a steady detonation cannot

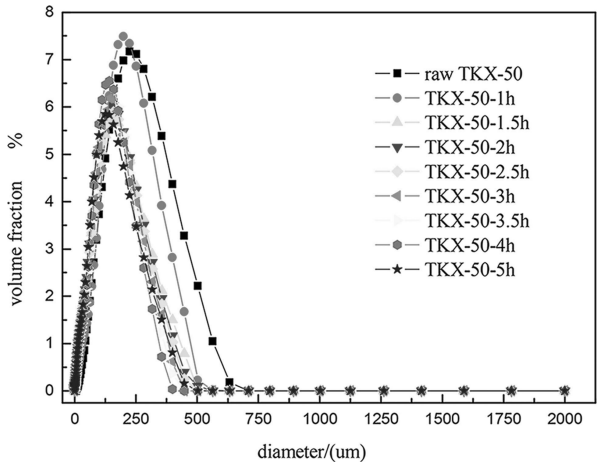

Figure 1. The particle distributions of TKX-50 after different mill pretreating duration.

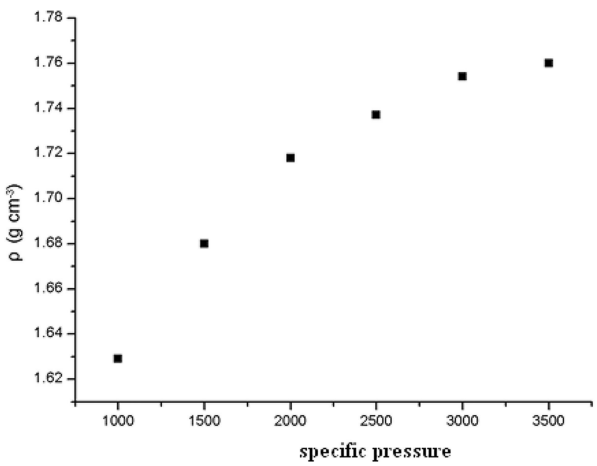

Figure 2. The relationship between the densities and specific pressures.

Table 1. The SEM of TKX-50 after different milling time durations.

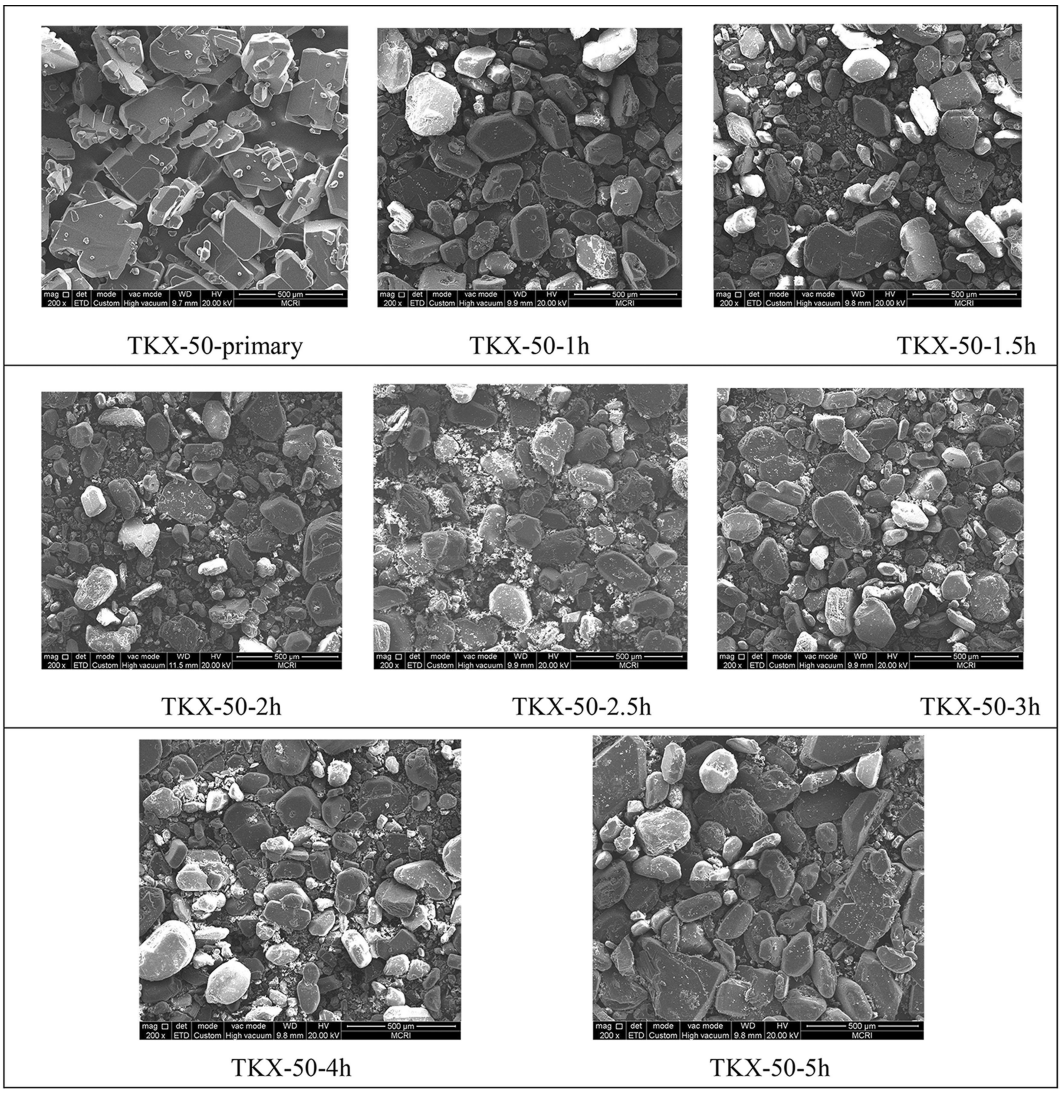

Table 2. The chemical affinities between TKX-50 and different binders.

	(0 0 1)	(0 1 0)	(1 0 0)	Average values
TKX-50/F26	100.01	41.85	33.14	58.33
TKX-50/EVA	28.34	60.41	47.40	45.38
TKX-50/EPDM	18.70	23.83	34.83	25.79
TKX-50/ETPE	113.52	132.94	86.84	111.10

happen when the column diameters are smaller than 30 mm.

Samples of TKX-50 based explosives with different densities were also examined, the results are shown in Table 4.

The relationship of the densities and the detonation velocities are shown as Eq. (1). r is the correlation coefficient, D is the detonation velocity, and ρ is the density.

Table 3. Detonation velocities of TKX-50 based explosives with different diameters.

Samples	Standards, mm	Density, g cm^{-3}	Detonation velocity, m s^{-1}
TKX-50/ binder = 95.5/4.5	Φ20 mm × 20 mm	1.79	8699
	Φ30 mm × 30 mm	1.80	8774
	Φ40 mm × 40 mm	1.80	8994
	Φ50 mm × 50 mm	1.81	8996
	Φ60 mm × 60 mm	1.80	9037

$$D = 499 + 4814\rho \qquad r^2 = 0.9925 \tag{1}$$

The characteristic detonation velocity of TKX-50 deduced by Urizar formula is 9432 m s^{-1}, much higher than RDX (8800 m s^{-1}) and HMX (9150 m s^{-1}).

Table 4. The detonation velocities of TKX-50 based explosives with different densities.

density/g cm^{-3}	1.555 (φ30)	1.606 (φ30)	1.658 (φ30)	1.697 (φ30)	1.702 (φ30)	1.740 (φ30)
Detonation velocity, m s^{-1}	7976	8248	8472	8716	—	8904

3.4.2 The Shock Sensitivities of TKX-50 Based Explosives

Generally, the shock sensitivity of explosives is measured by gap test method. The thickness of the clap board when 50% explosive explodes is regarded as the expression of the shock sensitivity.

The pressure decay process of shock waves in organic glass was determined by assembling test point severy 10 mm over the whole length of a 55 mm gap. The relationship of initiation pressure and thickness is shown in Figure 3.

The decay tendency of shock waves pressure in dense medium can be expressed by exponential equation. The relationship between the imitation pressure and gap thickness of organic glass is fitted as Equation 2:

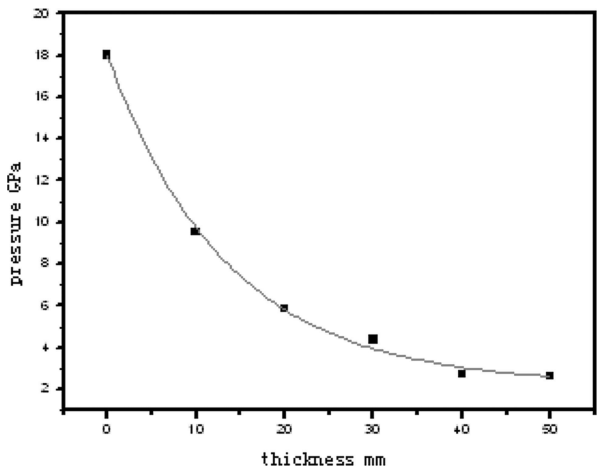

Figure 3. The relationship between the imitation pressure and gap thickness of organic glass.

Table 5. The thickness of the organic glass gap and the correspondingly pressure of shock wave values of TKX-50, HMX and CL-20 based explosives.

explosives	thickness (mm)	pressure (GPa)
TKX-50 based	18.45	6.24
HMX based	40.50	3.02
CL-20 based	49.51	2.64

$$p = 2.243 + 15.72 \exp\left(\frac{-x}{13.48}\right) \quad (2)$$

Where p is the pressure of shock waves in the organic glass, x is the thickness of the organic glass gap.

The thickness of the organic glass gap and the correspondingly pressure of shock wave values of different explosives are shown in Table 5.

The obtained pressure of shock wave values can be regard as the critical initiation pressures of TKX-50, HMX and CL-20 based explosives. The different values represent the shock sensitivity differences of different explosives. From Table 4, one can see that the critical initiation pressure of TKX-50 based explosive is much higher than HMX and CL-20 based explosives, which means that the shock sensitivity of TKX-50 based explosive is apparently lower than other two explosives.

3.4.3 Explosion Heat

The TKX-50 based explosive molding particles were also pressed to determine the explosion heat according to Chinese national military standard method. The value 4650 J g^{-1} is much lower than the calculation because of the oxygen-deficit of TKX-50.

4 Conclusion

1) TKX-50 based explosive molding particles were prepared and their molding properties were researched. The values of the column densities can reach 1.80–1.81 g cm^{-3} under the specific pressure of 3000 conditions.
2) The detonation velocities with different diameters of TKX-50 based explosive columns were obtained, and it shows obvious scale effect. The steady detonation perhaps cannot happen when the column diameters are smaller than 30 mm.
3) The critical initiation pressure of TKX-50 based explosive is much higher than HMX and CL-20 based explosives.
4) The determined explosion heat value of TKX-50 based explosive is 4650 J/g according to Chinese national military standard method.

Acknowledgements

The test support and useful discussion from Ms. Yao L. N. and Mr. Yang J. G. are greatly appreciated for our research.

References

[1] D. Fischer, T. M. Klapötke, M. Reymann, P. C. Schmid, J. Stierstorfer, M. Sućeska, Synthesis of 5-(1h-tetrazolyl)-1-hydroxy-tet-

razole & energetically relevant nitrogen-rich ionic derivatives, *Propel. Explos. Pyrotech.* **2014**, *39*, 550–557.
[2] T. M. Klapötke, R. D. Chapman, TKX-50, *New Trends in Research of Energetic Materials*, Czech Republic, **2013**.
[3] M. Göbel, T. M. Klapötke, J. Stierstorfer, High-nitrogen & high-oxygen explosives as possible replacements for RDX, *New Trends in Research of Energetic Materials*, **2011**.
[4] N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Pushing the limits of energetic materials – the synthesis & characterization of dihydroxylammonium 5,5-bistetrazole-1,1-diolate, *J. Mater. Chem.* **2012**, 22, 20418.
[5] V. K. Golubev, T. M. Klapötke, Comparative analysis of shock wave action of TKX-50 & other explosives on various barriers, *New Trends in Research of Energetic Materials*, Czech Republic, **2014**.
[6] Q. An, T. Cheng, W. A. Goddard, S. V. Zybin, Anisotropic impact sensitivity & shock induced plasticity of TKX-50 single crystal: From large scale molecular dynamics simulations, *J. Physic Chem.* **2015**, *119*, 2195-2207.
[7] H. F. Huang, Y. M. Shi, J. Yang, Thermal characterization of the promising energetic material TKX-50, *J. Thermal Analysis & Calorim* **2015**, *121*, 705-709.
[8] Z. Lu, Q. Zeng, X. Xue, Z. Zhang, F. Nie, C. Zhang, Does pressure increasing always accelerate the condensed material decay initiated through bimolecular reactions? A case of the thermal decomposition of TKX-50 at high pressures, *Phys. Chem. Chem. Phys.* **2017**, *19*, 23309-23317.
[9] Z. Lu, X. Xue, L. Meng, Q. Zeng, Y. Chi, G. Fan, Heat induced solid-solid phase transformation of TKX-50, *J. Phys. Chem. C* **2017**, *121*, 8262-8271.
[10] L. Meng, Z. Lu, X. Wei, X. Xue, Y. Ma, Q. Zeng, Two sided effects of strong hydrogen bonding on the stability of TKX-50, *Cryst. Eng. Comm.* **2016**, *18*, 2258-2267.
[11] V. P. Sinditskii, S. A. Filatov, V. I. Kolesov, K. O. Kapranov, A. F. Asachenko, M. S. Nechaev, V. V. Lunin, N. I. Shishov, Combustion behavior & physic-chemical properties of TKX-50, *Thermochimica Acta* **2015**, *614*, 85-92.
[12] L. Glasser, H. Donald, B. Jenkins, T. M. Klapötke, Is the Volume-Based Thermodynamics (VBT) approach valid for the estimation of the lattice enthalpy of salts containing the 5,5′-(Tetrazolate-1N-oxide)-dianion?, *ZAAC* **2014**, *640*, 1297–1299.

Manuscript received: October 1, 2018
Revised manuscript received: October 1, 2018
Version of record online: February 11, 2019

