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Effect of Nitrate Ester on the Combustion Characteristics of PET/HMX-based Propellants

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ABSTRACT

The effect of nitrate ester NG/TEGDN on the combustion characteristics of PET/HMX-based propellants has been experimentally investigated using of high-speed photography technique and scanning electron microscopy. It is indicated that the increase of NG/TEGDN content has little impact on the propellant burning rates at the same pressure. Furthermore, propellant can not be self-sustaining combustion at low pressure (≤1 MPa). The increase of NG/TEGDN content does not affect the flame structure of propellant, but it plays an important role in condensed phase reaction zone. The flame structure of propellant is estimated. The thermal decomposition products in different combustion zones are also discussed. Scanning electron microscopy examination of quenched sample indicates that a liquified layer forms during combustion of these propellants. Numerous gas bubbles are present. Especially, the burning surface of propellant with low NG/TEGDN content shows signs of crystallization. The thickness of condensed phase reaction zone, by cross-section examination of propellant burning surface, has also been investigated. The results show that the thickness of condensed phase reaction zone increases with NG/TEGDN content increasing. These observations suggest that the condensed phase zone plays significant role in propellant combustion.

Keywords: Nitrate ester, combustion characteristics, PET/HMX-based propellants

1. INTRODUCTION

Ethylene oxide-tetrahydrofuran copolyether (PET), as a polymer binder and cyclotetramethylenetetranitramine (HMX) as an oxidiser are the major components of nitrate ester plasticised polyether (NEPE) propellants. Over the past several years, advances in energetic materials have been made in many types of propellant ingredients, including binders, oxidisers, and metal additives. Numerous literatures studies describe how to decrease the burning rate pressure exponent of NEPE propellants or how to enhance its combustion performance[1-3]. However, few data are available regarding the effect of nitrate ester nitroglycerine/triethylene glycol dinitrate (NG/TEGDN) on combustion characteristics of propellants, so the present paper is efforts to increase our knowledge in interpreting the combustion characteristics of PET/HMX-based propellants with different NG/TEGDN contents.

Plasticiser is a key ingredient of high-energetic solid propellant and plays a vital role in controlling the solid propellant property. Extensive studies for plasticiser concentrate on thermodynamic, structural, mechanical, ballistic implication and sensitivity in high energy propellant[4-8]. Literature survey reveals that few studies have been conducted on the effect of nitrate ester NG/TEGDN on the combustion characteristics of PET/HMX-based propellants.

The primary objective of this study is to characterise and compare the combustion behaviour of PET/HMX based solid propellants with different NG/TEGDN contents. It is hoped that this work would be useful in providing a clearer understanding of high performance energetic solid propellant studies.

2. EXPERIMENTAL

2.1 Propellant Formulations

The propellant samples (E-1 and E-2) investigated in this study consist of HMX particles with PET as a binder and NG/TEGDN as plasticisers. The particle size of HMX is 5-80 μm. Their main compositions are shown in Table 1.

Table 1. Propellant compositions

Sample	Propellant compositions (wt %)	
	PET/NG/TEGDN	HMX
E-1	1:0.25:0.25	70
E-2	1:1:1	70

2.2 Burning Rate Measurement

A high-pressure optical strand burner (Fig. 1) was used to measure the burning rates of the samples between 1-3 MPa. The propellant strands were burned under constant-

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pressure condition and the burning rates were deduced from video images recorded using a CCD camera, and the pressure exponent was calculated according to Vieile $r=aP^n$. In this investigation, nitrogen was used as the purge gas.

2.3 Flame Images of Propellants

The experimental set-up used for flame image consists of a combustion chamber, fitted with two quartz side windows (Fig.1). Propellant sample size was 2×4×15 mm. The sample was ignited by a hot nickel-chrome wire. The flame picture was obtained by CCD.

2.4 SEM Measurement

To study the effect of NG/TEGDN on the quenched surface, the experiment was carried out for E-1 and E-2 propellants. The quenched surfaces of propellants were acquired by slack water. The quenched surface images were observed by scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1 Effect of Nitrate Ester NG/TEGDN on the Burning Characteristics of PET/HMX-based Propellants

The burning rates and burning rate pressure index of propellants E-1 and E-2 are shown in Table 2. As shown in Table 2, E-1 and E-2 propellants can not be self-sustaining combustion at 1MPa. Increasing the pressure to 2 MPa, the burning rates of both propellants were nearly the same. While at 3MPa, the burning rate of E-2 propellant was slightly higher than that of E-1 propellant, but the difference was not obvious. It is clear that the content of NG/TEGDN has little impact on the burning rates of PET/HMX-based propellants at the same pressure. The burning rates of both propellants were increased with the pressure increasing. The burning rate pressure index of E-1and E-2 propellants was 0.8417 and 0.8917, respectively. This result is similar to Y. Wang[9], *et.al.* They reported that the burning rate pressure index of only binder/HMX was 0.96. The high HMX or nitrate ester content is the root cause of high burning rate pressure index of propellant[10].

It is well known that the burning rate is determined by the heat generated at the burning surface and the heat transferred back from the gas phase to the burning surface. In other words, the heat feedback from the exothermic reactions occurring in the gas phase along with the condensed-phase heat release sustains the combustion process. The specific processes in the condensed and gas phases depend on the particular ingredient under consideration.

At 1MPa, the flame stands-off relatively farther from the burning surface. This causes a reduction in the heat

Table 2. The burning rates for propellants E-1 and E-2 at different N_2 pressure

Samples	Burning rate(mm/s)			Burning rate pressure index
	1MPa	2MPa	3MPa	
E-1	self-extinguished	1.025	1.442	0.8417
E-2	self-extinguished	1.065	1.529	0.8917

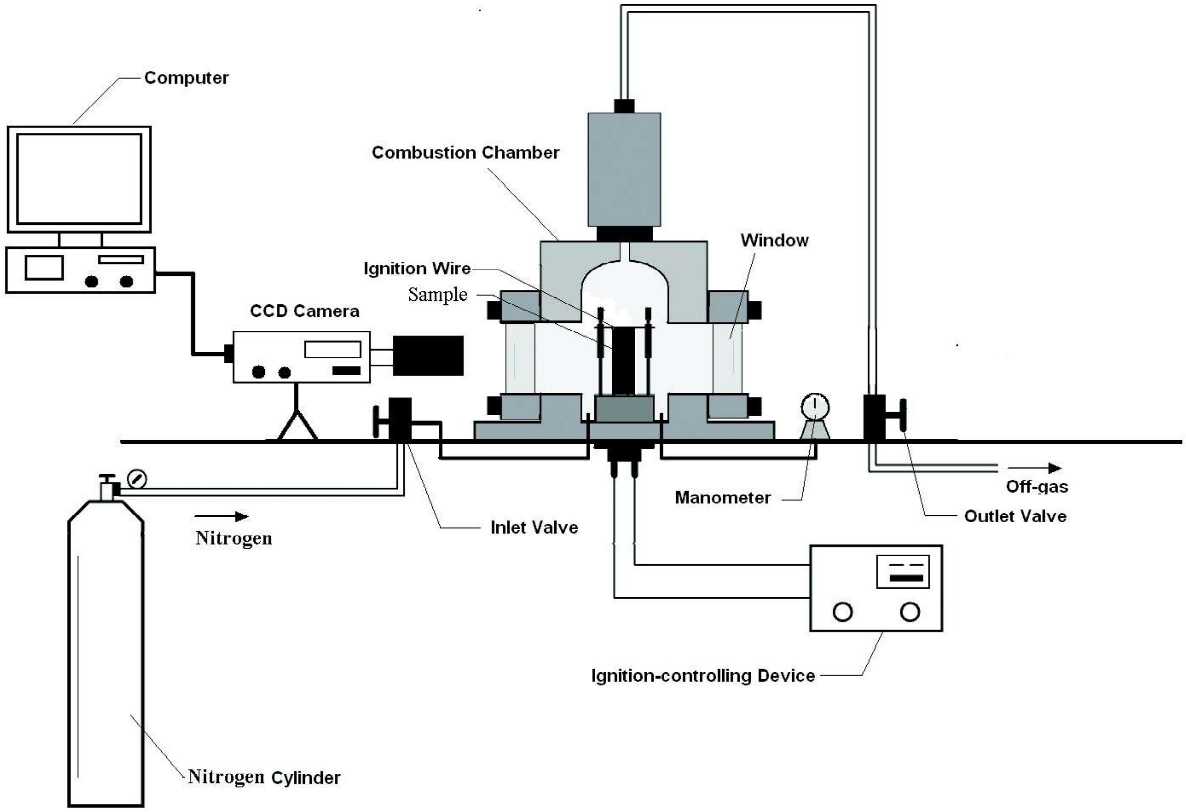


Figure 1. Schematic of the high-pressure optical strand burner experimental set-up.

flux to the propellant surface, and the net heat flux at the burning surface is insufficient to sustain the decomposition of HMX in the condensed phase. Also, PET binder forms a melt layer on the burning surface. The heat, which is transfered back from the gas phase to the burning surface is absorbed by the melt layer. Thus, HMX oxidiser can not get enough heat to sustain the combustion process. So the propellants can not be self-sustaining combustion and take place self-extinguished phenomena. When the pressure increases, the flame may be close to the burning surface and the heat feedback from the gas phase to the condensed phase may increase. This increase accelerates the decomposition of melt PET binder, and causes the thickness of melt layer to become thin. The net heat flux at the burning surface is sufficient to sustain the decomposition of HMX in the condensed phase, so the propellants can be self-sustaining combustion. However, NG/TEGDN content increase can not modify the burning rate as expected. As shown in Table 2, the changes of burning rate are not obvious at the same pressure. This may have relations to the decomposition of HMX and nitrate ester in the following.

Oxidiser HMX is characterised by-$N\text{-}NO_2$ chemical bonds that are attached to hydrocarbon structures. The bond breakage of $N–N$ produces NO_2, which acts as an oxidiser. The remaining hydrocarbon fragments act as fuel components.

The total initial decomposition reaction of HMX is as follows[11-13]:

$$3(CH_2NNO_2)_4 \rightarrow 4NO_2 + 4N_2O + 6N_2 + 12CH_2O \qquad (1)$$

Since formaldehyde reacts quite rapidly with nitrogen dioxide[14], the gas phase reaction is as follows:

$$7NO_2 + 5CH_2O \rightarrow 7NO + 3CO + 2CO_2 + 5H_2O \qquad (2)$$

It is probably the dominating reaction[15]. This reaction determines the burning rate of the propellant. The reaction between NO_2 and CH_2O releases a large amount of heat, and the reaction rate is much faster than other reactions.

Plasticiser NG/TEGDN is characterised by-$O\text{-}NO_2$ chemical bonds. The bond breakage of $O\text{-}N$ produces NO_2, which acts as an oxidiser. The remaining hydrocarbon fragments act as fuel components.

The decomposition of nitrate ester is as follows:

$$RNO_2 \rightarrow NO_2 + \text{organic molecules (mainly aldehydes)} \qquad (3)$$

Then,

$$NO_2 + \text{organic products of (3)} \rightarrow NO + H_2,\ CO,\ CO_2,\ H_2O, \text{ etc.} \qquad (4)$$

It can be seen from that HMX oxidiser and NG/TEGDN plasticisers all contain elements C,H,O,N, and the decomposition products are nearly the same. The contents of NO_2 and aldehyde increase as the nitrate ester content increases, while the ratio of NO_2/aldehyde shows a little change. Thus, the decomposition of NG/TEGDN does not obviously accelerate the HMX reaction, and the change of NG/TEGDN content does not apparently increase the burning rate of PET/HMX-based propellants. This leads to small difference of both propellant burning rates at the same pressure.

3.2 Characteristics of Combustion Flame

Typical flame images of PET/HMX-based propellants containing NG/TEGDN are shown in Figs 2 and 3 as a function of pressure. It is evident that the flame presents dark zone. Furthermore, the combustion process presents a lot of smoke. When the pressure is 1MPa, the flame of E-1 propellant is very weak, and the luminous flame will be blown away from the burning surface, as shown in Fig. 2. The flame zone approaches the burning surface as pressure increases[16]. Moreover, the flame intensity increases and dark zone becomes thin due to increasing pressure.

For E-2 propellant, a thin luminous flame sheet stands-off some distance from the burning surface and a reddish flame was produced above this luminous flame zone, as shown in Fig.3. The flame also presents dark zone. The thickness of dark zone changes as the pressure increases, especially for the pressure between 1MPa and 2MPa. The flame intensity of E-2 propellant increases compared to that of E-1 propellant. Furthermore, the quantity of smoke involved in the combustion process was greatly reduced, so it can be concluded that the combustion of E-2 propellant is more complete than that of E-1 propellant as NG/TEGDN content increases.

Figure 2. Flame photographs of E-1 propellant at three different pressures.

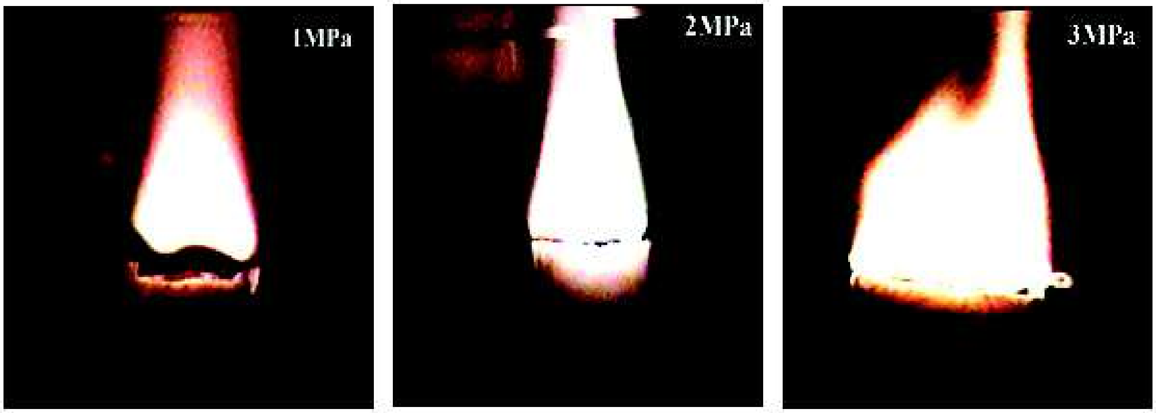


Figure 3. Flame photographs of E-2 propellant at three different pressures.

From the comparisons between the flame photographs of E-1 and E-2 propellants, it can be found that the increase of NG/TEGDN content does not affect the flame image but only enhances the flame intensity. The flame structures of E-1 and E-2 propellants are similar to HMX-CMDB combustion model. It is reported that the flame structures of both propellants belong to premix flame structure[17], so the diffusion flame between HMX and PET/NG/TEGDN was not found. Since HMX is a stoichiometrically balanced crystalline material, no diffusion flamelets were formed above the burning surface. The gaseous decomposition of the HMX particles diffuse and mix with the gaseous decomposition products of the base matrix and form a reactive homogeneous gas, which reacts to produce a pre-mixed flame above the burning surface. As in the case of double-base propellants, the luminous flame is distended from the burning surface for both HMX-CMDB propellants. Furthermore, the flame stand-off distances decrease as the pressure increases because of the increase in the reactant concentrations and gas densities, which in turn increase the reaction rate and reduce the transport velocity.

Photographic observations of the flame are useful to understand the overall combustion characteristics of propellants. The flame characterisation must be controlled by inherent factors in both condensed phase and gas phase. To make it clearer as to how the inherent factors affect the flame characterisation of PET/HMX-based propellants which contain different NG/TEGDN contents, the combustion process was simulated by the flame schematic (Fig. 4).

The condensed phase zone, as shown in Fig. 4, is the thermal-chemical reaction layer, where many changes take place such as crystal transformation, melting, thermal decomposition, sublimation, and vapourisation. The burning surface that contacts the condensed phase and gas phase is gas/liquid interface at low pressure, where most of the thermolysis products are released and parts of HMX, NG

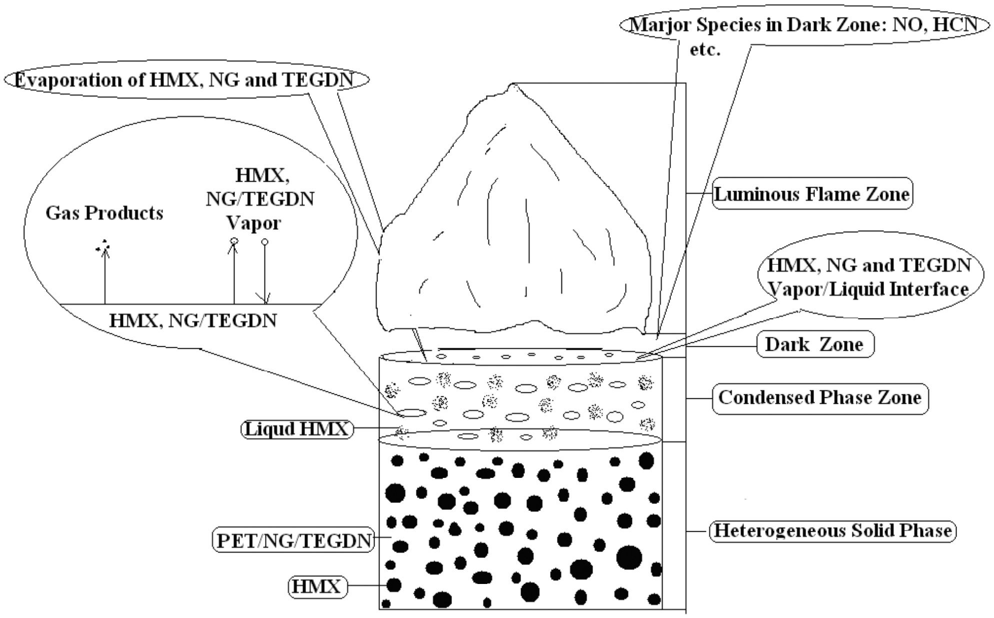


Figure 4. The flame model of PET/HMX-based propellants.

and TEGDN are evaporated. The dark zone is a nonluminous region which separates the primary reaction zone near the propellant surface from the luminous secondary flame zone. As discussed above, the decomposed species are expelled and transported away from the burning surface via both diffusion and convection. Subsequent reactions occur among the decomposed products, and produce intermediate species such as HCN, NO, CO, and N_2O in the dark zone.

The -NO_2 contents in the binder system directly influence the exothermic reaction between NO_2 and aldehydes, thus affecting the heat balance of burning surface and the average temperature of burning surface. According to the results in Section 3.1, in the condensed phase zone, NG/TEGDN decomposition produces NO_2 and organic molecules (mainly aldehydes). The concentration of NO_2 and aldehydes increases as the content of NG/TEGDN increases, thus the reaction rate of reaction 2 [(Eqn. 2)] increases. This increase can result in higher exothermal heat rate of the reaction 2 [(Eqn. 2)]. Then released thermal energy continuously accelerates the next reaction, so it can be found that the flame intensity of E-2 propellant is stronger than that of E-1 propellant at the same pressure.

3.3 Analysis of Quenched Surface

Information on the nature and importance of condensed phase reactions in propellant combustion is needed as input for modelling studies. This information is also expected to be very important in understanding combustion behaviour of propellants. To understand the nature and importance of condensed phase reactions in the combustion of PET/HMX-based propellant containing NG/TEGDN, the burning surface and cross-section of extinguished propellants were studied.

Figure 5 shows the SEM photographs of unburned surface of E-1 propellant. It could be seen found that the oxidiser HMX was homogeneously distributed among the propellant.

Typical SEM photograph of the extinguished surface of E-1 propellant is shown in Fig. 6 (a). The extinguished surface appears as a hole or crater. SEM examination reveals that the extinguished surface of E-1 sample contain numerous bubbles, which appear as holes on the surface. The phenomeon seems in agreement with the reports[18,19]. The diameters of these holes are 9~20μm. The very top layer of the surface usually appears relatively smoother with only occasional signs of crystallisation.

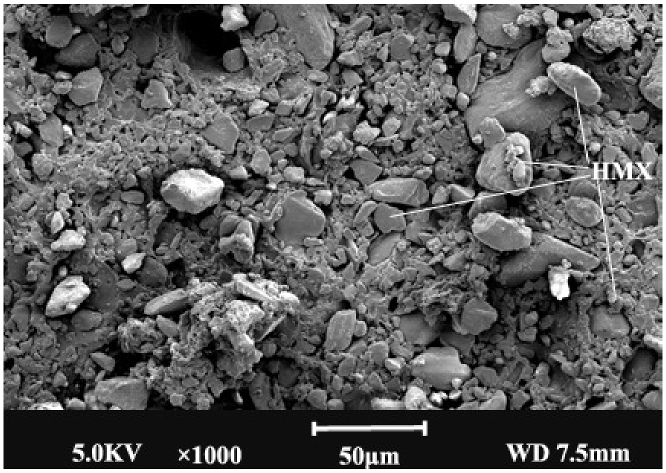
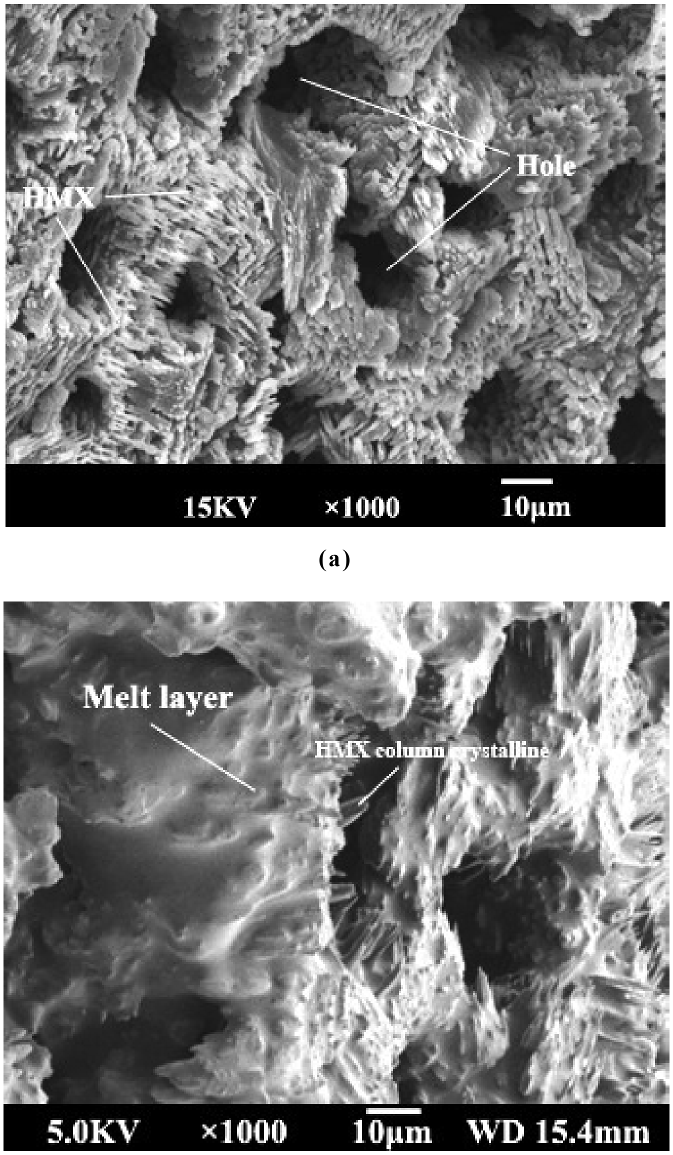


Figure 5. The unburned surface of propellant E-1.

It can be shown that the cross-section of burned surface of E-1 propellant presents a melt layer that covers the surface (Fig.6 (b)). The thickness of condensed phase reaction zone is ~120 to 190μm. Evidence of the melt layer includes numerous bubbles and the formations which appear to be columns crystalline material, especially in the area immediately close to the holes of the unburned propellant. This suggests that crystallisation may have been seeded by the HMX crystals in the unburned propellant, due to



(a)

(b)

Figure 6. (a) The extinguished surface and (b) the cross-section of burned surface of E-1 propellant.

the preponderance of HMX in the melt layer.

The extinguished surface of E-2 propellant appears relatively smoother, but cracked [(Fig. 7(a)]. It contains numerous holes on the extinguished surface, whose diameters are 11~34 μm. Compared with E-1 propellant, the extinguished surface near the hole is relatively smoother; with few signs of crystallisation, but there are globosity grains.

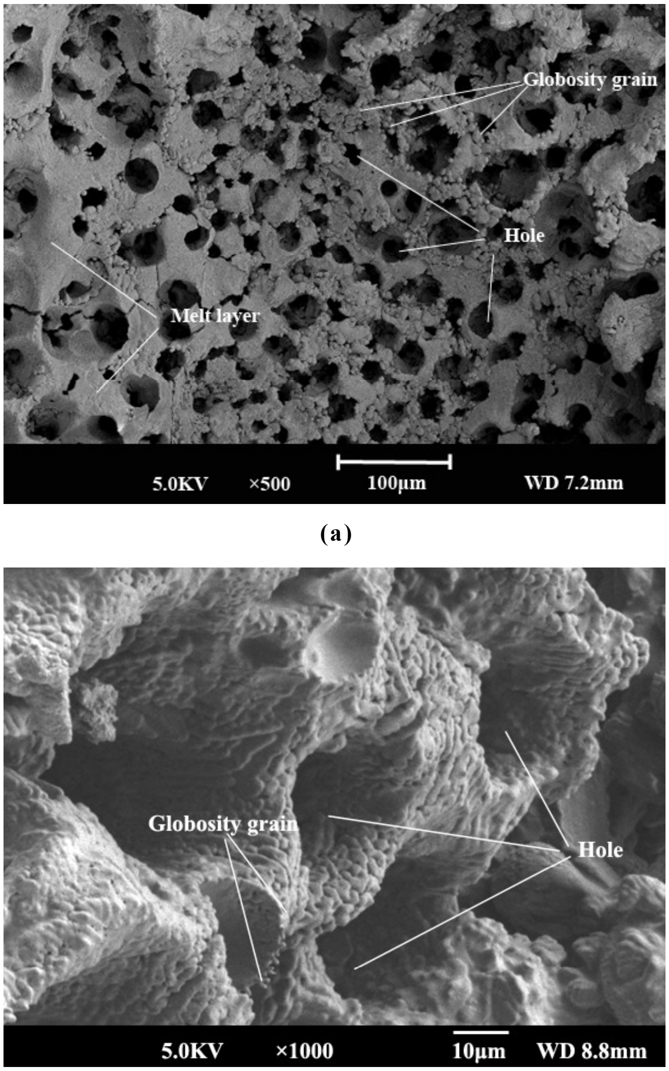
A comparison between the extinguished surfaces of E-1 and E-2 propellants reveals that the burning surface of E-1 propellant is rather rough, and with crystallisation near the holes. The burning surface of E-2 propellant near the hole is relatively smoother; with few signs of crystallisation, but there are some globosity grains. The difference of burning surface can be attributed to the content of NG/TEGDN.

With regard to the content of nitrate ester, it may play an important role in the quenched surface characteristics. E-1 propellant combustion generates lower heat release due to relatively lower NG/TEGDN content. According to E. W. Price's theory of surface disproportionation[20], under this condition, the PET binder with the lower activation energy will decompose more rapidly than oxidiser HMX (Table 3), leading to rising concentration of HMX and the ratio of O/F at the surface. Moreover, the melting and vapourisation being almost simultaneous (Table 3), the small HMX particle will melt, and then liquid HMX will be recrystallised on cooling after quenching. This results in evident sign of crystallisation for E-1 propellant. By the same reasoning for E-2 propellant, E-2 propellant combustion generates higher heat release than that of E-1 propellant due to higher NG/TEGDN content. The concentration profile of burning surface has to change with surface temperature, (and hence, burning rate), to satisfy the mass flux ratio $(O/F)_p$. The binder would tend to melt. The melt binder and its decomposition products tend to accumulate in the region just under the burning surface. The surface layers during combustion contain enhanced amount of the binder and/or its condensed-phase decomposition products[19], so the melt layer of the burning surface of E-2 propellant shows few signs of crystallisation.

Table 3. Activation energy, melting and decomposition temperatures of HMX[21] and PET[22]

Sample	Activation energy (kJ·mol-1)	Melting (°C)	Decomposition temperature (°C)
HMX	186±22	282	282
PET	26.16	---	170

Figure 7 (b) shows the cross-sections of the burned E-2 propellant. The burning surface is uneven. The thickness of condensed phase reaction zone is ~170 μm to 253 μm, which increases compared to that of E-1 propellant.



(a)

(b)

Figure 7. (a) The extinguished surface and (b) the cross-section of burned surface of E-2 propellant.

4. CONCLUSIONS

The increase of NG/TEGDN content has little impact on the burning rates of PET/HMX-based propellants at the same pressure. Furthermore, these propellants can not self-sustain combustion at lower pressure (≤1MPa). NG/TEGDN content does not affect the flame structure of PET/HMX-based propellants, but it plays an important role in condensed phase reaction zone. The flame structure is similar to HMX-CMDB combustion model, and belongs to premix flame structure.

The quenched surfaces of PET/HMX-based propellant are relatively even, and there are signs of bubbles. Moreover, the burning surface of propellant with lower NG/TEGDN content is relatively rough, and crystallisation is near the holes. The burning surface of propellant with higher NG/TEGDN content is relatively smooth; with few signs of crystallisation, but there are some globosity grains.

The cross-section of burned PET/HMX-based propellant indicates that the thickness of the condensed phase reaction zone increases as the NG/TEGDN content increases.

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REFERENCES

1. Cheng, F.T.; Tan, H.M.; Qin, W.L.; Luo, S.G.; Ying, Y.Q. & Luo, Y.J. Study on decreasing the burning rate pressure exponent of nepe propellant. *Chin. J. Solid Rock. Techn*., 1999, **22**(4), 31-34 (Chinese).
2. Liu,Y.F.; Yao, W.S; Li, X. M. & Tan, H.M. Combustion property of NEPE propellant. *Chin. J. Explos. Propell.*, 2003, **26**(4), 30-32 (Chinese).
3. Li, J.F. & Ming, F. Study on modification technology of the combustion property of the NEPE propellant. *Chin. J. Energ. Mater.,* 2002, **10**(1), 4-9 (Chinese).
4. Leach,C.; Flower, P.; Hollands, R.; Flynn, S.; Marshall, E. & Kendrick, J. Plasticisers in energetic materials formulations – A UK overview. *In* the 29th International Annual Conference of ICT, Karlsruhe, Germany, 1998, pp. 2-14.
5. Venkatesan, D.; Srinivasan, M.; Audisesha Reddy, K. & Pendse, V. V. The migration of plasticiser in solid propellant grains. *Polymer International*, 1993, **32**(4), 395-99.
6. Mohanrao, K.; Kanakaraju, P.; Reddy, K.A.; Athithan, S.K. & Kishore, K. Effect of hydrocarbon on the ageing behaviour of composite. *In* the 2nd International High Energy Materials Conference and Exhibits, IIT Madras, Chennai, 8-10 December, 1998.
7. Agrawal, J.P.; Khangaonkar, D.G. & Kulkarni, K.S. Migration of some plasticisers through cured novolac epoxy resin-polyamide hardener systems. *Ind. J. Eng. Mater. Sci.,* 1998, **5**(2), 58-64.
8. Jawalkar, S.N.; Mehilal, K. Ramesh; Radhakrishnan, K. K. & Bhattacharya, B. Studies on the effect of plasticiser and addition of toluene diisocyanate at different temperatures in composite propellant formulations. *J. Hazard. Mater.,* 2009, **164**(2-3), 549-54.
9. Wang, Y.; Sun, Z.H.; Zhao, F.Q.; Li, S.W. & Yuan, C. Study on combustion mechanism of NEPE propellant. *Chin. J. Explos. Propel*., 2004, **4**, 24-26 (Chinese).
10. Pang, A.M.; Wang, B.H. & Tian, D.Y. An analysis on the pressure index of high energy nitramine propellants. *Mod. Def. Technol.*, 2000, **24**(2), 34-38.
11. Duterque, J. & Lengelle, G. Combustion mechanisms of nitramine based propellants with additives. *J. Propul. Power,* 1990, **6**(6), 718-26.
12. Suryanarayana, B.; Graybush, R.J. & Antera, J.R. Thermal degradation of secondary nitramines: A nitrogen tracer study of HMX. *Chem. Indust.*, 1967, **52** (2), 2177-178.
13. Kimura, J. & Kubota, N. Thermal decomposition process of HMX. *Propell. Explos., Pyrotech.*, 1980, **5**(1), 1-8.
14. Hinshelwoo, C.N. The kinetics of chemical change, Oxford University Press, Oxford, 1950.
15. Miller, J.A. & Bowman, C.T. Mechanism and modeling of nitrogen chemistry in combustion. *Prog. Energy Combust. Sci*., 1989, **15**(4), 287-338.
16. Moskaleva, L.V. & Lin, M.C. The spin-conserved reaction CH+N!H+NCN: a major pathway to prompt NO studied by quantum/statistical theory calculations and kinetic modeling of rate constant. *Proc. Combust. Inst.*, 2000, **28**(2), 393-401.
17. Kubota, N. Propellants and explosives: Thermochemical aspects of combustion. Wiley-VCH, Germany, 2001. 236 p.
18. Schroender, M.A.; Fifer, R.A.; Miller, M.S.; Pescerodriguez, R.A.; Mcnesby, C.J.S. & Singh, G. Condensed-phase processes during combustion of solid gun propellants. I. nitrate ester propellants. *Combustion Flame*, 2001, **126**(1-2), 1569-576.
19. Schroender, M.A.; Fifer, R.A.; Miller, M.S.; Pescerodriguez, R.A.; Mcnesby, C.J.S.; Singh, G. & Widder, J.M. Condensed-phase processes during combustion of solid gun propellants-II. nitramine composite propellants, *Combustion Flame*, 2001, **126**(1-2), 1577-598.
20. Price, E.W.; Chakravarthy, S.R. & Sigman, R.K. Pressure dependence of burning rate of Ammonium Perchlorate-hydrocarbon binder solid propellants. *In* the 33rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Seattle, WA, 6-9 July, 1997.
21. Jiang, Z.; Li, S.F.; Zhao, F.Q.; Chen, P.; Yin, C.M. & Li, S.W. Effect of nano metal powder on the thermal decomposition characteristics of HMX. *J. Propul. Technol*., 2002, **23**(3), 258-261 (Chinese).
22. Sun, Y.L.; Dang, H.C.; Zhu, B.Z. & Li, S.F. Thermal decomposition characteristics of the Ethylene Oxide-Tetrahydrofuran copolyether binder. *In* the 2nd International Conference on Energy and Environment Technology, ChangSha, China, December 2010.

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