

DAMAGE OF A HIGH-ENERGY SOLID PROPELLANT AND ITS EFFECTS ON COMBUSTION

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ABSTRACT: In order to improve the safety of high-energy solid propellants, a study is carried out for the effects of damage on the combustion of the NEPE (Nitrate Ester Plasticized Polyether) propellant. The study includes: (1) to introduce damage into the propellants by means of a large-scale drop-weight apparatus; (2) to observe microstructural variations of the propellant with a scanning electron microscope (SEM) and then to characterize the damage with density measurements; (3) to investigate thermal decomposition; (4) to carry out closed-bomb tests. The NEPE propellant can be considered as a viscoelastic material. The matrices of damaged samples are severely degraded, but the particles are not. The results of the thermal decomposition and closed-bomb tests show that the microstructural damage in the propellant affects its decomposition and burn rate.

KEY WORDS: propellant, damage, thermal decomposition tests, closed-bomb tests, combustion

1 INTRODUCTION

In order to meet the stringent performance requirements (i.e. in range, payload, velocity) for the new generation solid rocket motors, the amount of nitramine additives will be increased in the proposed chemical formulations of propellants. The two most common nitramines used to enhance the propellant performance are 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetra-nitro-1,3,5,7-tetrazacyclooctane (HMX). Unfortunately, the presence of these high-energy additives presents a trade-off between the improved propulsion performance and the potential for an inadvertent explosion of rocket motors^[1].

Some previous results have shown that the deflagration-to-detonation transition (DDT) of high-energy solid propellants sometimes occurs with a ballistic malfunction, which can heavily damage propellants. Since the propellants have been consumed in a DDT, little is known about the nature of the damage (generated under the stress fields) which leads to the DDT. For instance, E. James and L. Green have reported the following result observed in a

155 mm gun test^[2]. DDT may occur after a primary shock of less than 1.0 GPa has passed through the original cross-linked, double-base (XLDB) propellant, leaving behind changed regions that may be reduced to a fractured rubble. The hot spot population and surface area are thereby increased. Secondary shocks passing through damaged propellants at levels as low as 70 MPa have initiated XLDBs.

Because of these problems and the evolution of safety regulations, it is now necessary to take safety issues into account at the very beginning of any project. Consequently, there is a need to develop laboratory techniques of small-scale tests to generate damaged propellant samples. These samples would be available for a variety of sensitivity and performance tests, such as for augmented burning rate, closed tube DDT behavior and shock sensitivity.

The pyrotechnic behavior of solid propellants can be cataloged according to their chemical decomposition forms. Propellants may exhibit three modes of decomposition: thermal decomposition, combustion and detonation. Thermal decomposition is the first stage of the combustion process, combustion is the slow decomposition mode of propellants and detonation is the fast decomposition mode. The aim of the present research is to examine and analyze the influences of damage on the combustion of the NEPE propellant. Therefore, the study consists of four parts: (1) to introduce damage in the propellants, (2) to observe the microstructural changes and to quantify the extent of damage, (3) to investigate if there is any difference in the thermal decomposition of the original and damaged propellants, (4) to investigate the combustion of the original and damaged propellants.

2 DAMAGE PRODUCTION

In order to reduce the vulnerability of rocket systems to low velocity projectile/fragment impact or drop during transport, a fundamental understanding of the intermediate strain-rate behavior of the NEPE propellants is important. So, the propellants were machined into cylindrical samples of 40 mm in diameter, 10 mm in thickness. A hammer of 400 kg mass in a large-scale drop-weight test was then dropped from a height of 0.25 m to impact the sample. The apparatus and the typical load-time curve are shown in Figs.1(a) and (b). In Fig.1(b), the peak pressure $p_m = 145$ MPa, average axial strain-rate $\dot{\epsilon} = v/L = \sqrt{2gH}/L \sim 10^2 \text{ s}^{-1}$. From the observed stress-time curve (Fig.1(b)), various deformation processes may occur. In Stage 1, extensive viscoelastic/plastic deformation occurs. In Stage 2, the sample was

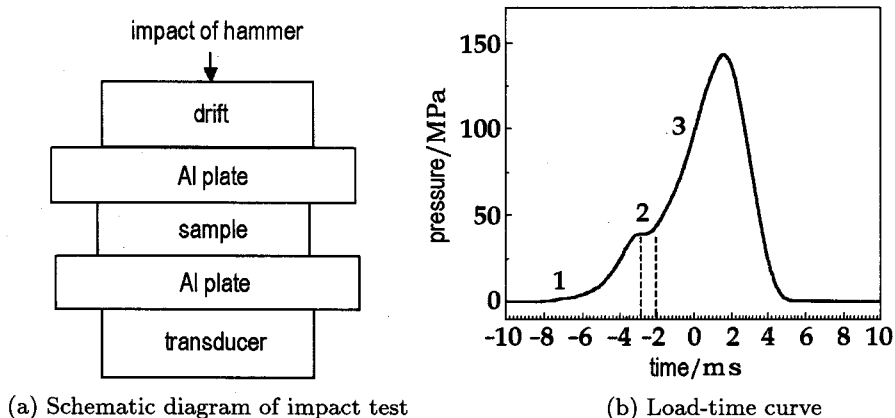


Fig.1

extensively crushed out and the pressure remained to be 39 MPa. In Stage 3, the pressure sharply increased. During impact, the sample underwent deformation so extensively that most of the sample was squeezed out from between the two Al plates and only a thin layer was left. After impact, the sample almost fully recovered, and cracks were not visible on the sample surface. This phenomenon implies that the propellant exhibits some characteristics of elastomeric polymers undergoing quasi-rubber-like deformation.

3 DAMAGE CHARACTERIZATION

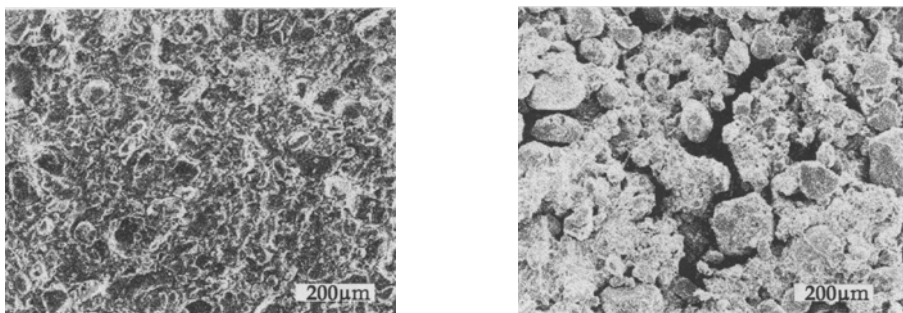
Damage in the samples subjected to the drop weight loading was evaluated by means of scanning electron microscopy and density measurements.

3.1 Scanning Electron Microscopy (SEM)

The samples did not exhibit visible cracks. So, the scanning electron microscopy (SEM) was used to examine the sections of the original and impacted samples in order to identify damage modes under the impact condition.

Firstly, we should keep the following facts in mind. The NEPE propellant is with an energetic composition containing oxidizers RDX, ammonium perchlorate (AP) and reducer aluminum (Al) powders of various particle sizes. Its matrix is made up from a great deal of energetic plasticizer nitrate ester (NG+BTTN) and polyurethane binder (PEG+N-100). The surface of an RDX crystal is inert so that RDX crystals in the propellant are weakly bonded to the matrix.

The SEM micrograph from a microtomed cross-section of the original sample is shown in Fig.2(a). The polyurethane binder was poorly adhered to the crystal surfaces of filled RDX particles. For instance, there appeared seams in the range of 1~10 μ m between RDX particles and the matrix. Thus, the bigger RDX particles easily went apart at the seams. In order to improve the adhesive properties of the matrix and the filled particles, a suitable binding agent should be used or the filled particles should be coated to restrain dewetting.



(a) 100 \times

(b) 100 \times

Fig.2 (a) the original sample; (b) the impacted sample

Compared to the original samples, the impacted samples show changes (see in Fig.2(b)) in two ways: (1) The matrix is torn. Between the bigger particles and the voids in the matrix, a great many microcracks form and propagate. (2) Bigger particles dewet. The bigger particles are separated from the matrix, but the particles themselves are not disrupted. At the same time, smaller particles are still coated with matrix.

3.2 Density Measurement

Owing to damage, the volume and the density of the sample are changed. The damage variable is expressed as^[3]

$$D_\rho = (1 - \rho_1/\rho_0)^{2/3} \quad (1)$$

Damage is defined here as a scalar quantity. D_ρ denotes the extent of damage in the impacted sample, $0 < D_\rho < 1$. $D_\rho = 0$ corresponds to the undamaged condition, whereas $D_\rho = 1$ corresponds to the complete material failure. ρ_0 and ρ_1 are the densities of the original and the impacted samples, respectively.

Based on Archimedes principle, the mass of the sample was weighed with a scale (precision 0.0001 g) in air and in liquid (paraffine oil). The densities of the original and impacted samples were 1.793 g/cm³ and 1.777 g/cm³, respectively. So, the damage variable D_ρ is 0.043.

4 THERMAL DECOMPOSITION

The combustion process includes several steps from condensed phase to gas phase, in which the condensed phase plays an important role. The reaction in the condensed phase is thermal decomposition. Thermal decomposition is the first step of combustion. Therefore, a thorough and detailed investigation of the thermal decomposition of the propellant should be performed as a basis of combustion.

The measurements were performed on a DSC 910 instrument, made by American TA Corp., at a heating rate of 10 K/min and with a nitrogen flow rate of about 40 cm³/min, and samples were weighed about 1~5 mg. The other measurements were carried out on a TGA 2950 instrument, made by American TA Corp., at a heating rate of 5 K/min and with a nitrogen flow rate of 60 cm³/min. 1~5 mg samples were put in an aluminum cell.

4.1 Original Sample

The typical DSC (Differential Scanning Calorimetry) and TG (Thermogravimetry) traces of the original sample are shown in Fig.3. Table 1 gives its decomposition peak temperature T_p and mass loss rate ΔG of the nitrate ester in the propellant.

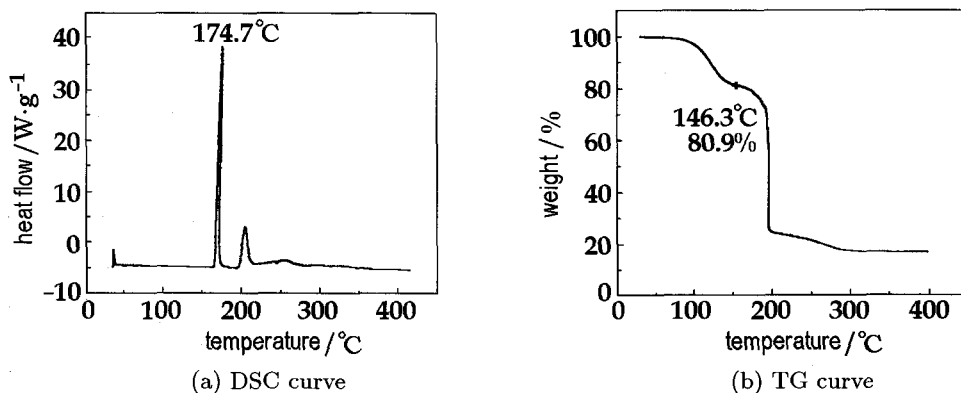


Fig.3 The original sample

On the DSC curve, there are three exothermic peaks, which have been assigned to three marked decomposition ranges. The first exothermic peak is decomposition of the nitrate ester, and emerges at about 170°C. The second is the oxidizer RDX's decomposition

and appears at about 200°C. The third is the oxidizer AP's decomposition at about 250°C.

The TG curve of the propellant is divided into three stages. The temperature range for the first mass loss stage is in the range of about 80°C ~ 150°C, and the mass loss percent (about 19.1%) is equal approximately to the mass of plasticizer nitrate ester(NG/BTTN). So, it is mainly the volatilization and decomposition of nitrate ester. When the temperature increases continuously, the RDX and a little of AP are decomposed. In addition, the mass loss rate increases quickly, and the decomposition is at about 200°C. In the third stage, a great deal of heat is released by the dissolved energetic components (NG+BTTN, RDX, AP). The degradation of polyurethane is initiated while the degradation promotes the decomposition of the surplus AP. The above analyses are supported by a previous published paper^[4]. The residues are mainly Al₂O₃, which are produced during the burning of Al powders.

4.2 Impacted Sample

The decomposition peak temperature and mass loss rate of the impacted sample are listed in Table 1. For the impacted sample, the decomposition process is approximately consistent with the observations for the original sample. Only a few minor differences were observed and they focus on T_p and ΔG of the nitrate ester. In contrast to the original sample, in DSC, the T_p of the nitrate ester of the impacted sample is shifted slightly to a lower temperature. It can be explained by the acceleration of the thermal conduction for the nitrate ester since a great many microcracks are formed. On the other hand, in TG, ΔG is increased. Likewise, this can be contributed to the acceleration of the thermal conduction. As shown in DSC and TG, the impacted sample is less thermally stable than the original sample.

5 CLOSED-BOMB TEST

Both original and impacted samples were cut into small cubes of the same size. Then, a 90.75 cm³ ($\Phi 34$ mm×10 mm) closed-bomb was used to burn the same amount of cubes with total weight of 18.9g for both samples, respectively. The ignition primer for these tests consisted of 1.1g NC (nitrocellulose), which was ignited via an electric fuse. The chamber pressure was monitored as a function of time with a 500 MPa quartz piezoelectric pressure gage, and charge-amplified signals were transmitted to a digital oscilloscope. The data of voltage versus time were stored on floppy diskettes and converted to ASCII format for burn property analysis.

In Table 2, t_m denotes the time reaching maximum pressure p_m and T denotes the time to reach maximum pressurization-rate $(dp/dt)_m$. Table 2 outlines the results of closed-bomb tests on the original and impacted samples. The curves for pressure-time ($p-t$) and pressurization-rate-time ($dp/dt-t$) are presented in Fig.4. The solid and dotted lines correspond to the experimental data of the impacted and original samples, respectively. In

Table 1 Results for thermal decomposition of the nitrate ester

Methods	DSC	TG
characteristic variables	$T_p/^\circ\text{C}$	$\Delta G/\%$
original sample	174.7	19.1
impacted sample	173.2	21.6

Table 2 Results for the closed-bomb tests

	p_m/MPa	t_m/ms	$(dp/dt)_m/\text{MPa}\cdot(\text{ms})^{-1}$	T/ms
original sample	315.4	8.1	86.5	5.4
impacted sample	312.7	7.0	80.1	3.9

comparison with the original sample, the combustion process of the impacted sample demonstrates distinct changes, see Fig.4(a) and Fig.4(b), namely, t_m and t of the impacted sample drop 13.6% and 27.8%, respectively. The results can be explained by the dependence of the burn rate on the ratio of surface-to-volume. In fact, the impact loading induced a great many microcracks in the microstructure of the sample. These microcracks can even be seen after unloading (Fig.2(b)) and serve to increase the ratio of surface to volume in the impacted sample.

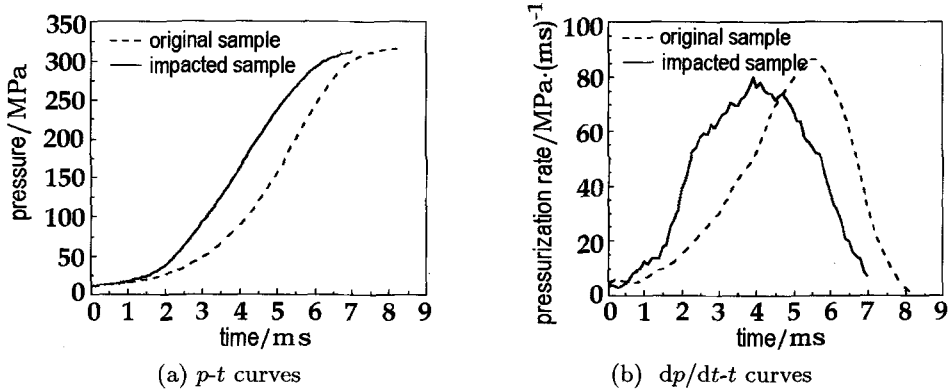


Fig.4 The original and impacted samples

6 CONCLUSIONS

- (1) This propellant can undergo extensive elastic deformation and is a viscoelastic material.
- (2) In comparison with the microstructure of the original sample, there are two kinds of changes in the impacted sample: matrix tearing and the bigger RDX particles dewetting. These changes greatly enhance surface area. Moreover, the changes of density can be used to quantify the damage.
- (3) The DSC tests verified that the destruction of nitrate ester accelerates the thermal conduction. Simultaneously, accelerating the thermal conduction can increase the mass loss in TG tests.
- (4) In closed-bomb tests, the apparent burn rate of impacted samples varies considerably. Namely, increasing the burning surface may increase its burn rate. The results suggest that the burn rate differences of the impacted sample are dependent on the surface area increase due to the damage.

The above results indicate that the damage induced by impact could result in an increase in the decomposition and burn rate. In the worst case, it is possible that the damage can lead to a deflagration-to-detonation transition (DDT). Further studies on the effects of damage on DDT will be reported in another paper.

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