



Preparation and Performance of a Novel Water Gel Explosive Containing Expired Propellant Grains

Peng WANG*, Xiaoan XEI and Weidong HE*

*School of Chemical Engineering,
Nanjing University of Science and Technology,
Nanjing, Jiangsu, 210094, China*

**E-mail: wangpeng0541@163.com; hewedong@mail.njust.edu.cn*

Abstract: Novel water gel explosives containing expired single base and double base propellant grains were prepared by using a new gelling agent and a simple process. The shock wave overpressures and underwater output energies of the explosives were measured. The detonation performances of the explosives were also investigated. As the particle size of the propellant was increased, the detonation velocity, peak overpressure and underwater energy of the explosive containing single base propellant (NCP) were gradually reduced. Double base propellant (DBP) had low detonation sensitivity due to its thermoplasticity. When it was mixed with the appropriate quantity of NCP, DBP could also be reused. NCP acted as the sensitizer and energy source in the explosive containing both DBP and NCP. So the detonation velocity, peak overpressure and underwater energy of the explosive increased with the increase in ω_{NCP} . With excellent detonation performance, these two kinds of water gel explosives can be used as opencast blasting agents.

Keywords: expired propellant, detonation performance, reuse, water gel explosive

Introduction

The quantity of expired or demilitarized smokeless gun propellants is at present over several thousand tons per year in many countries. The traditional ways of disposing of demilitarized propellants include landfill, open burning, and open detonation *etc.* [1]. These methods lead to environmental and health

problems as well as concern over safety regulations. Moreover, the expired propellants, which are a useful energy resource, are wasted in these processes. In recent years, some methods have been adopted to recycle, recover and reuse these demilitarized propellant sources [2, 3]. The idea of reusing expired propellants as ingredients in commercial explosives is both practical and attractive. After the expired propellants have been crushed or reduced in size, the propellant powders or small propellant grains can be mixed with ammonium nitrate and other additives to make powdery explosives. They can also be incorporated into ordinary water gel explosives, emulsion explosives or ANFOs (ammonium nitrate-fuel oil) as sensitizer ingredients [4-9]. These mixed explosives usually contain 20-35% propellant. However, the propellants must be crushed into small particles before reuse, thus increasing the production cost and leading to safety problems. A type of water gel explosive containing about 60% of large-grain single base or triple base propellants can be produced by filling the spaces of the propellant grains with an oxidizer solution, which can then gradually become gelled [10, 11]. In this method, the hazardous process of grinding the propellants is avoided. Compared with the above traditional methods, it is simpler and further more suitable for disposing of large quantities of expired propellant. This water gel explosive has excellent detonation performance with a detonation velocity above 6000 m/s. However, the solution becomes gelled too quickly (within 10 min of infusion) when a gelling agent (modified cellulose or guar gum) is present. Whether double base propellants could be reused by the same method has not been reported.

In order to extend the infusion time and to make it suitable for industrial production, a new gelling agent and process have been studied. We improved the method for the reuse of double base propellants (DBP) by using the appropriate proportion of single base propellant as a sensitizer. In order to describe the power effect and working capability, the shock wave overpressures and underwater output energies of the explosives were measured through the air explosion and underwater blast respectively. In addition, we have studied the effects of the particle size of the propellant and its mass fraction on the detonation performances of the explosives containing NCP. The effect of the mass fraction of NCP on the performances of explosives containing both DBP and NCP were also investigated.

Materials and Methods

Explosive sample preparation

Three different types of single base propellant (NCP) were used in this study. The shapes and sizes of the propellants are shown in Table 1. The single

base propellants all had porous structures contained about 95% nitrocellulose. The double base propellant (DBP) was in the form of single tubes with diameter 5.6 mm, bore 2.2 mm and cut lengths of about 10 mm. The DBP was composed of 56% nitrocellulose, 26.5% nitroglycerine, 9% dinitrotoluene, 4.5% dibutyl phthalate and 4% modifiers.

Table 1. Sizes of single base propellant used

Type of NCP	Number of perforations	Shape size	
		Outer diameter (mm)	Length (mm)
1	7	2.5	3.4
2	14	5.2	9.0
3	7	7.8	16.0

The manufacturing process for these novel water gel explosives was relatively simple and had three basic steps. Firstly, the required mass of propellant grains was added to a cylindrical plastic cartridge. The propellant grains were randomly distributed. Secondly, an oxidizer solution containing ammonium nitrate, sodium nitrate and urea was prepared. With the addition of sodium nitrate, the crystallization point of the solution was reduced. Urea was useful for improving the frost resistance at low temperatures. Then, an organic monomer, a cross-linking agent, an initiator and a polymerization inhibitor were added and dissolved in the solution. The mixed solution had a density of $1.38 \text{ g}\cdot\text{cm}^{-3}$ at 298.15 K with an oxygen balance of 15.4%. Finally, the solution was poured into the cartridge containing the propellant until the spaces among the propellant grains were completely filled and the top surface of the propellant was just immersed. After a time, the monomer and cross-linking agent in the solution had become cross-linked to form a copolymer as a 3D gel network under the action of the initiator.

Three different sizes of NCP propellant were reused in the water gel explosive according to the method mentioned above. The DBP propellant had a similar size to NCP-2. The two different types of propellant grains were mixed in a revolving drum to distribute the grains as uniformly as possible.

Detonation performance test

Detonation performance of the water gel explosive was measured using the witness plate test. The explosive was placed in contact with a 10 mm thick witness plate made of Q235 carbon steel. The explosive was detonated by a detonator and a 40 g booster of desensitized hexogen (RDX/wax 95/5). The

degree of completeness of the explosion can be observed from the damage to the steel plate. The relative brisance can be also obtained from the depth of the dent. The detonation velocity of the explosive with diameter 60 mm was evaluated using the time required for the detonation wave to transit through three 70 mm long sections.

Underwater energy test

The experiment was carried out in an 8 m deep explosion water pool with a diameter of 8 m. The explosive sample was placed at a height of 4.25 m below the water surface. The pressure histories were captured and recorded by a piezoelectric sensor (PCB138M124), a signal disposal instrument (PCB482A16) and a data collector (JOVIAN 5200). The mass of the explosive was 400 g with diameter 60 mm. Every type of sample was tested three times in parallel. The scheme for the experimental arrangement is shown in Figure 1. The calculation method of the under output energy was described by Li Zhang [12].

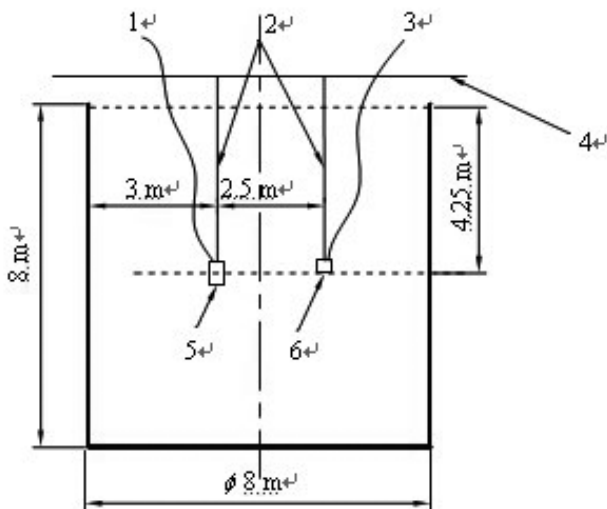


Figure 1. Scheme for underwater blast experimental arrangement: 1 – ignition cable; 2 – load rope; 3 – transmission cable; 4 – experimental holder; 5 – test device; 6 – gauge.

Air blast peak overpressure test

The center of the explosive sample was 40 cm above the ground. The distances of the test points to the center of the explosion were 1.5, 2, 2.5, 3, 3.75

and 4.5 m. The mass of the explosive was 800 g with diameter 85 mm. Each sample was tested three times in parallel. The pressure histories were captured and recorded by a pressure sensor (PCB113B), a signal disposal instrument (PCB482A20) and a data collector (VXI-1115).

Results and Discussion

Effect of concentration of polymerization inhibitor on the time

Figure 2 shows that the time required for the solution polymerization to form water gel can be adjusted from 5 min to about 1 hour through changing the concentration of the polymerization inhibitor.

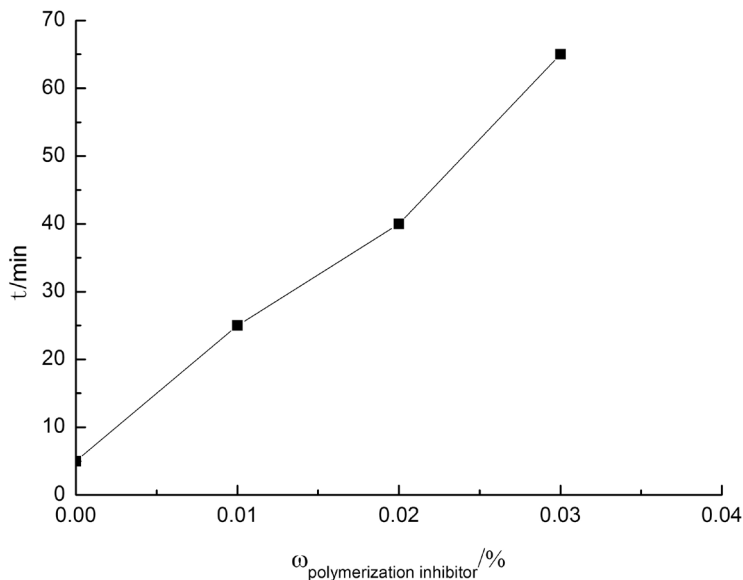


Figure 2. The effect of concentration of polymerization inhibitor on the starting time of polymerization.

The reaction is a radical polymerization, and the polymerization inhibitor can delay chain initiation. So the starting time of polymerization could be easily controlled by using the new gelling agent. It would be useful for the industrial scale production of the explosives if the infusion time were above 30 min.

Results of witness plate test and detonation velocity

The results of the witness plate test and the detonation velocity test are provided in Table 2.

Table 2. Results of witness plate tests and detonation velocities of explosives studied

Type of propellant	$\rho/(g \cdot cm^{-3})$	$\omega_P / \%$	Dent of steel plant	VOD/(m·s ⁻¹)
NCP-1	1.46	67	perforated, 59 mm hole diameter	6450
NCP-2	1.43	58	perforated, 54 mm hole diameter	6379
NCP-3	1.42	56	perforated, 53 mm hole diameter	6230
DBP	1.42	57	no dent	–
DBP/NCP-2 70/30	1.42	58	no dent	–
DBP/NCP-2 60/40	1.42	58	perforated, 38 mm hole diameter	–
DBP/NCP-2 50/50	1.42	58	perforated, 53 mm hole diameter	6193
DBP/NCP-2 40/60	1.42	58	perforated, 57 mm hole diameter	6235

ω_P : mass fraction of propellant in the explosive.

As the particle size and aspect ratio of the propellant increases, the spaces between the particles decrease in the water gel explosive containing NCP. Therefore, the mass fraction of NCP and the density of the explosive were both gradually reduced. The detonation velocities, which were all above 6200 m/s, were also slowly decreased. Because NCP contains about 95% nitrocellulose, NCP has a high sensitivity towards shock initiation.

The explosive containing only DBP grains could not be detonated. Therefore, to increase the detonation sensitivity, NCP was added and mixed with the DBP grains. When the ω_{NCP} in the mixed propellant grains of NCP and DBP was 30%, the explosive would still not detonate. As ω_{NCP} was increased to 40%, 50% and 60%, the steel witness plates were all perforated, and the diameter of the perforation gradually increased. The detonation velocity was also increased by the increase in ω_{NCP} . As the DBP contains 9% dinitrotoluene and 4.5% dibutyl phthalate, it is thermoplastic with a low glass transition temperature of 329.15 K and a softening temperature of 393.9 K. DBP would therefore become

plasticized after absorbing heat and became a viscous state under the action of the shock wave generated by the booster, causing the reaction to be unsustainable. Consequently the explosive containing only DBP was difficult to detonate. As a sensitizer and energy source, NCP causes the explosive containing DBP and NCP to detonate more readily and enhances the detonation velocity.

Underwater energy test

The underwater output energies of the explosives are provided in Table 3.

Table 3. Underwater explosion energies of explosives studied

Type of propellant	ω_{NCP} %	ω ($\text{g}\cdot\text{cm}^{-3}$)	e_s (kJ/g)	e_b (kJ/g)	e_t (kJ/g)	Q_v (kJ/g)	e_t/Q_v %
NCP-1	67	1.46	1.385	1.980	3.418	3.457	98.9
NCP-2	58	1.43	1.313	1.796	3.157	3.195	98.8
NCP-3	56	1.42	1.117	1.538	2.675	3.161	84.6
DBP/NCP-2 50/50	29	1.42	0.776	1.402	2.207	2.904	75.9
DBP/NCP-2 40/60	34	1.42	1.018	1.500	2.568	2.960	86.8
DBP/NCP-2 30/70	40	1.42	1.048	1.613	2.719	3.016	90.2
Cast TNT		1.56	1.630	2.420	4.250	4.270	99.5
1 [#] rock emulsion explosive		1.15	0.653	3.105	3.758	-	-
2 [#] rock emulsion explosive		1.15	0.613	2.798	3.411	-	-

ω_{NCP} : mass fraction of single base propellant in the explosive;

e_s : specific shock wave energy; e_b : specific bubble energy; e_t : specific total energy; values for 1[#] and 2[#] rock emulsion explosives as cited in [13].

Since the single base propellant had a high energy and a high heat of explosion (>3.5 kJ/g), this was the main energy source in the water gel explosives containing NCP. Therefore, as ω_{NCP} was increased, the shock wave energy and the bubble energy both gradually increased. The results also showed that the surface area of the propellant grains had an incidental effect on the output energy.

The shock wave energy, bubble energy and total energy of the explosive also increased with the increase in ω_{NCP} in the water gel explosive containing both DBP and NCP. There was a nonlinear relationship between the energies and ω_{NCP} , and the growth rate of the energies gradually decreased.

For the explosives containing NCP, their total energy accounted for about

90% of the theoretical heat of explosion. For the explosives containing both NCP and DBP, the percentage of the theoretical heat of explosion increased from 76% to 90% with the increase in ω_{NCP} . So the addition of NCP was also beneficial in completely releasing the energy during detonation. Compared with rock emulsion explosives [13], the total energies of these two kinds of water gel explosives were lower, but the shock wave energies were much higher. As the water gel explosives have negative oxygen balances (about -14%), they would be suitable for use as opencast blasting agents, with a large diameter (over 50 mm) for hard rock blasting.

Blast peak overpressure test

The peak blast overpressures of the two kinds of water gel explosives at different scaled-distances are shown in Figures 3 and 4.

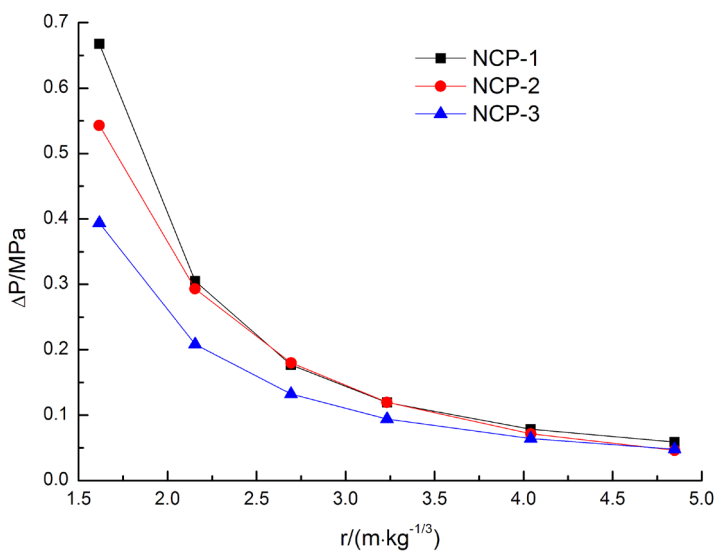


Figure 3. Curves of peak overpressure and scaled distance for the explosives containing NCP.

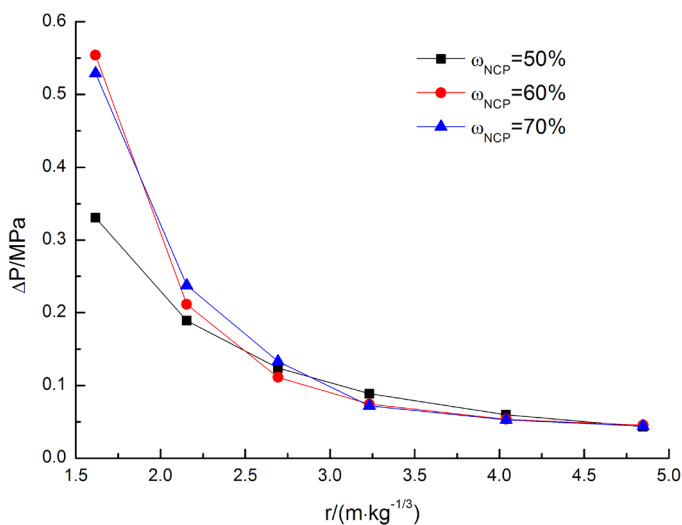


Figure 4. Curves of peak overpressure and scaled distance for the explosives containing both BDP and NCP.

The peak overpressure of the explosive containing NCP rose significantly with the increase in ω_{NCP} at the first and second measurement distances. The peak overpressure of the explosive respectively containing NCP-1 and NCP-2 showed almost no change over the last four measurement distances. In the explosives containing both NCP and DBP, the same variation of the overpressure value with the increase in ω_{NCP} was also obtained at the first measurement distance. However the rising rate of overpressure was not obvious when ω_{NCP} was increased from 60% to 70%.

The fitting equation for overpressure and scaled distance complied with the similar law for explosions in air. The equations are as follows:

$$\Delta P = \frac{A_1}{r} + \frac{A_2}{r^2} + \frac{A_3}{r^3} \quad (1)$$

$$r = r_0 / \sqrt[3]{m} \quad (2)$$

where: r_0 , m and ΔP are respectively the distance between the test point and the explosion center, the mass of the explosive and the peak overpressure; A_1 , A_2 and A_3 are undetermined coefficients; r is the scaled-distance.

TNT test data and the fitting curve for TNT are shown in Figure 5. As this figure shows, the fitting curve for the experimental data for TNT were consistent

with the results obtained by Zhong Q. *et al.* [14].

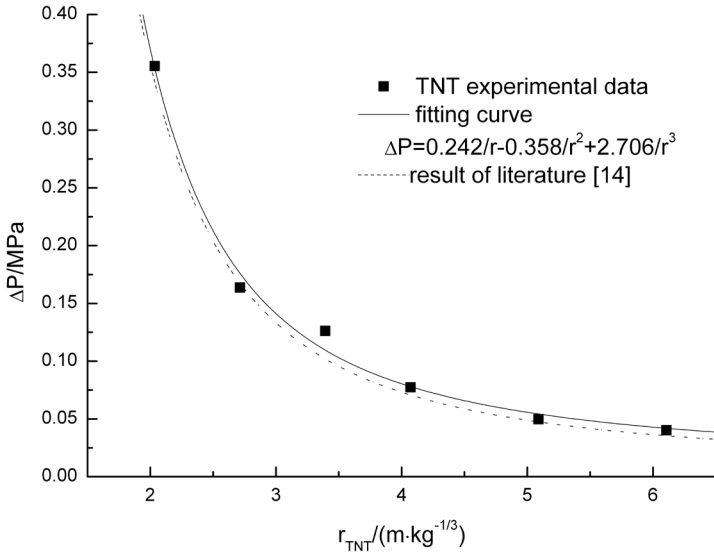


Figure 5. Fitting curve of peak overpressure and scaled-distance for TNT.

The TNT equivalence of the explosive is given by:

$$E_q = \frac{W_{TNT}}{W_{EX}} = \left(\frac{r_{EX}}{r_{TNT}} \right)^3 \tag{3}$$

where: W_{TNT} and W_{EX} are respectively the mass of TNT and the water gel explosive containing propellant grains; r_{EX} and r_{TNT} are respectively the scaled-distance for TNT and the water gel explosive at the same overpressure.

Fitting formulae for overpressure and scaled-distance of the explosives are given in Table 4 and the TNT equivalents for the overpressure were also calculated.

Table 4. Fitting formulae for overpressure and TNT equivalents of explosives containing propellant grains

Type of propellant	Fitting formula	TNT equivalent
NCP-1	$\Delta P = \frac{0.285}{r} - \frac{0.636}{r^2} + \frac{3.098}{r^3}$	0.887
NCP-2	$\Delta P = -\frac{0.099}{r} + \frac{1.561}{r^2} - \frac{0.027}{r^3}$	0.826
NCP-3	$\Delta P = \frac{0.150}{r} + \frac{0.213}{r^2} + \frac{0.925}{r^3}$	0.738
DBP/NCP-2 50/50	$\Delta P = \frac{0.0676}{r} + \frac{0.661}{r^2} + \frac{0.151}{r^3}$	0.531
DBP/NCP-2 40/60	$\Delta P = \frac{0.480}{r} - \frac{2.225}{r^2} + \frac{4.680}{r^3}$	0.627
DBP/NCP-2 30/70	$\Delta P = \frac{0.164}{r} - \frac{0.428}{r^2} + \frac{2.501}{r^3}$	0.638

Within the range of the scaled-distances ($1.61\text{--}4.8 \text{ m}\cdot\text{kg}^{-1/3}$) in the tests, the TNT equivalents of the explosive containing NCP slowly decreased due to the effect of ω_{NCP} and the particle size. The TNT equivalents of the explosive containing both DBP and NCP increased with the increase in ω_{NCP} .

The TNT equivalent of the explosive containing NCP was close to the value of an emulsion explosive, which was approximated to 1 by Simoens *et al.* [15]. However the TNT equivalent of the explosive containing both DBP and NCP grains was lower (about 0.6). Perhaps its energy of explosion was not completely released.

Conclusions

The starting time, when the monomer begins to be polymerized in the oxidizer solution, can be effectively extended by changing the concentration of the polymerization inhibitor. This would be useful in the industrial scale production of the water gel explosive.

In the water gel explosive containing NCP, as the particle size of the

propellant increases and ω_{NCP} is decreased, the detonation velocity, peak blast overpressure and underwater energy are gradually reduced. DBP has low detonation sensitivity due to it being thermoplastic. When it is mixed with an appropriate proportion of NCP, it also can be reused by the same process. NCP functions as a sensitizer and energy source in the explosive containing both DBP and NCP. Therefore, the detonation velocity, peak blast overpressure and underwater energy gradually increase with the increase in ω_{NCP} .

The detonation velocities of the two kinds of water gel explosives containing propellant grains were both more than 6000 m/s. The shock wave energies of the explosives were higher than those of rock emulsion explosives. They could therefore be used as opencast blasting agents for hard rock blasting.

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