Effects of binder on molding properties of HATO-based explosives

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Abstract: The safety performance of HATO explosives coated by Fluororubber and energetic thermoplastic elastomer ETPE were discussed, and it was analyzed that the influence of pressure and temperature on the moldability of HATO-based explosives with different binders. The results showed: the mechanical sensitivity of HATO explosives coated by binder were low, which improved the safety of HATO explosives to a certain extent; Pressure and temperature have a greater impact on the mold-ability of HATO-based mixed explosives containing Fluororubber or ETPE binder, and the mold-ability of HATO-based mixed explosives containing ETPE binder is better, which relative density can reach more than 98% at room temperature.

1. Introduction

The rapid development of modern weapons not only requires more and more energy of ammunition, but also less and less sensitivity to external stimuli. In order to improve currently the survivability of weapons and ammunition, the development focus is on high-energy and low-vulnerability (LOVA) ammunition. In the research of these ammunition formulas, binder research is the core and the key. Using the energetic polymers binders was the current trend of the development of explosives and had received widespread attention from countries of the world [1]. In recent years, energetic thermoplastic elastomers (ETPE) had received great attentions as a new type of adhesive, it plays an important role in solving the problems of high energy, low vulnerability, safety and environmental protection of propellants [2-4].

1,1′-dihydroxy-5,5′-bitetrazole dihydroxylamine (HATO, or TKX-50), which was different from conventional CHNO covalent compound explosives was a ionic salt of multi-nitrogen element [5-6], and had some advantages: crystal density of 1.879 g·cm⁻³, the thermal decomposition temperature was 249.1°C and the thermal stability was better than RDX, the vacuum stability was good, the explosion speed was high (the calculated detonation speed is 9998 m·s⁻¹, the tested detonation speed is 8509 m/s, which was higher than RDX and HMX), it had good processability. Therefore, HATO is a new type of energetic material. At present, the synthesis process of HATO is relatively mature, but there are no reports on the basic and application of HATO in explosive formulations in domestic and foreign
literature. Therefore, in order to study the basic application of HATO in explosives, these studies carried out the influence of different binders on the mechanical sensitivity of HATO explosives, and discussed the moldability of binders to HATO. This will provide a reference for the development and application of HATO explosives formulations.

2. Experimental

2.1. Materials
HATO (grinding pretreatment, $D_{50}$ was 97.981 $\mu$m, developed by Xi'an Modern Chemical Research Institute), Fluorinerubber (produced by Zhonghao Group Chenguang Chemical Research Institute), Thermoplastic elastomer ETPE (molecular weight was 18,000, developed by Xi'an Modern Chemical Research Institute), Solvent ethyl acetate (analytical grade, Shaanxi Hengzhi Fine Chemical Co., Ltd.).

2.2. Preparation of explosives
Sample was prepared by the "direct method" process. HATO-based explosive formulations with different binders (Fluororubber, ETPE) were designed, and the formula mass ratio was: HATO / binder = 95/5.

2.3. Characterizations
2.3.1. Impact Sensitivity. According to the GJB772A.97 standard 601.1 test method, the H3.5-10W drop hammer impact sensitivity meter was used to determine the explosive percentage of samples. Mass of falling weight: 10kg; Mass of samples : (50 ± 1) mg. There are 25 rounds in each group with a total of 50 rounds. Note: The impact sensitivity of explosives is ≤40%.

2.3.2. Friction Sensitivity. According to the GJB772A.97 standard 602.1 test method, the DM-l friction sensitivity meter was used to determine the explosion percentage of samples. Gauge pressure: 3.92 MPa; Swing angle: (90 ± 1) o; Mass of samples: (50 ± 1) mg. There are 25 rounds in each group with a total of 50 rounds. Note: The friction sensitivity of explosives is ≤40%.

2.3.3. Formability. The HATO explosive powder containing different binders was filled into a mold (Φ20mm), and the 63T precision press pressed it into a certain size of pellets under different pressures or different temperature conditions, and 3 pellets were pressed under each condition. The average relative molding density of the three pellets was taken as the molding density of the pellets under this condition.

3. Results and Discussion

3.1. The mechanical sensitivity
Table 1 shows the mechanical sensitivity data of HATO-based explosives with different binders. According to the data, when azide binders (ETPE) or Fluororubber binders to are added to HATO explosives, the impact sensitivity and friction sensitivity of mixed explosives were slightly lower than that of HATO explosives, it improved the safety of HATO explosives to a certain extent.
Table 1. Mechanical sensitivity data of HATO explosives with different binders.

| Samples          | Impact sensitivity, % | Friction sensitivity, % |
|------------------|-----------------------|-------------------------|
| HATO             | 38                    | 40                      |
| HATO / Fluororubber | 28                   | 24                      |
| HATO / ETPE      | 32                    | 30                      |

Such a result may be caused by: azide-based binder (ETPE) or Fluororubber binder coating HATO explosives, filling the voids of HATO explosives, these would cause the voids between the explosive particles to decrease. When HATO explosive was subjected to external mechanical shock, the relative movement rate of the binder in the explosive particles is lower than that of the HATO explosive particles, and the internal force of the explosive is not easy to concentrate on a small area or a certain point, resulting in fewer hot spots during impact and friction. In the end, the mechanical sensitivity of mixed explosives is slightly lower than that of HATO explosives.

3.2. Formability
The press molding process of explosives is essentially a process in which explosive powders are distorted, embedded, and compacted under pressure to reduce pores and eventually produce elastoplastic deformation. Due to the sliding ability and mechanical properties of explosive particles, there are differences in compressible and density distribution. The purpose of adding polymer binder to the explosive is to improve the mechanical properties and facilitate the processing and molding of the mixed explosive.

Based on this principle, Fluororubber and ETPE (energy-containing azide binder) with higher adhesion work and spread coefficient are preferred as binders, these were discussed the mold-ability of HATO-based explosives with different binders.

3.2.1. Forming pressure. Under normal temperature conditions, six pressure points of 50, 100, 150, 200, 250 and 300 MPa were selected to suppress the explosive pellets with Ф20mm × 20mm shape. The relative pressure on the relative forming density was shown in figure 1.
As can be seen from figure 1 that: the relative forming density of HATO-based explosives containing Fluorinerubber or ETPE binders increased with increasing of the pressed pressure under the condition of constant temperature (normal temperature, 25℃), which indicate that the pressing temperature is constant, the higher the pressure, the denser the pellet, the smaller the internal void ratio, and the higher the forming density. The HATO explosive containing thermoplastic elastomer ETPE has better mold-ability. ETPE which has good flexibility and elasticity is used as an azide-based energetic thermoplastic elastomer binder [7], it is easy to deform after being coated with HATO explosive particles, and easy to move between explosive particles and ETPE molecules, made the porosity between explosive particles decreased, resulting in an increase in the relative density of the pellet, which improves the mold-ability of the pellet; However, Fluororubber is a synthetic polymer elastomer containing fluorine atoms on the carbon atoms of the main or side chain, which has excellent oil resistance, high temperature resistance, acid and alkali resistance, high vacuum resistance and other properties, but there are defects such as poor fluidity and easy compression deformation [8]. Compared with ETPE binder, when Fluororubber coated HATO explosives, the particles are not easy to deform, it is difficult to move between the explosive particles and the Fluororubber molecules, the porosity of the pellets is increased, and the molding density is lower than that of HATO explosives contained ETPE.

Based on results, the curve of pressure on the relative density of HATO-based explosives containing ETPE or Fluorinerubber were fitted [9]. From figure 2 and table 2, knew that the fitted curve were in good agreement with the testing results.
Figure 2. The Fitting curves of pressure on relative density of HATO-based explosives with different binders.

It can be seen from figure 2 that the relative density of mixed explosives increased rapidly with increasing pressure from 0 to 150 MPa. The growth rate of relative densities slowed down above 150 MPa. At 250 MPa, the relative density of mixed explosives containing ETPE could reach approach (98%) , which is higher than that of HATO explosives with Fluorinerubber (97%). These results indicate that as the molding pressure increases, the porosity between the particles of mixed explosive containing ETPE decreases, the molecular spacing decreases, the inter molecular force gradually increases, the inter particle adhesion force increases, and the relative forming density of the pellet is high.

Table 2. The fitting equation of pressure on relative density of HATO-based explosives with different binders.

| Sample composition | The fitting equation | R²    | Note                                      |
|--------------------|----------------------|-------|-------------------------------------------|
| HATO+ETPE          | y=2.667 Ln(x)+82.55  | R²=0.9820 | Where: Y is the relative density; x is forming pressure; R is the correlation coefficient |
| HATO+Fluorinerubber| y=2.629 Ln(x)+82.02  | R²=0.9830 |                                           |

Figure 2 also showed that HATO-based explosive particles with different binders were displaced and deformed after compression, as the forming pressure increased, the relative forming density of particles took on changed regularly: (1) due to the effect of forming pressure, the explosives particles shifted and filled the gaps in the range of 0MPa -150MPa, as the pressure increased, the density increased rapidly, but the friction, shear and extrusion effects between the particles are relatively weak, called the sliding phase; (2) In the range of 150 MPa -250MPa, as the particles gap decreased, the particles appeared a certain compression resistance, and continue to increase the pressure, the increase in the compaction density slowed down, at this time the particles displacement was greatly reduced. At this stage, the strengthening of the extrusion and shearing between the particles, it was mainly the crushing phase of the particles; (3) Above 250MPa pressure, because the particles were in a relatively balanced state, the particle interstitial was basically completed, and the porosity between the particles was difficult continue to decrease, the increase of density was small. Therefore, when the pressure reached 250 MPa or more, the method of improving the explosives forming density by increasing the
forming pressure is not desirable.

3.2.2. Temperature. Under the condition of 200 MPa pressing pressure, six temperatures of 25 °C, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C were selected, the explosive powder and the mold were heated under different temperature conditions for 2 hours, and then suppressed the explosive pellets with a size of \( \Phi 20 \text{mm} \times 20 \text{mm} \). The change trend of temperature on the relative molding density of the explosive were shown in figure 3.

![Figure 3](image)

**Figure 3.** Effect of temperature on relative density of HATO-based explosives with different binders.

Figure 3 was the change trend of temperature on the forming density of HATO-based explosives containing Fluorine-rubber and ETPE binder under the forming pressure of 200 MPa. It can be seen that, temperature had a great influence on the forming density of HATO-based explosives with different binders. The relative density of mixed explosives increased with increasing temperature, and the relative density of mixed explosives decreased when the temperature was higher than 70 °C; In addition, the relative density of HATO-based explosives with ETPE binder was higher than that of HATO-based explosives with Fluororubber binder. Therefore, under the same pressure condition, increasing the temperature can effectively increase the forming density and make the forming effect of the explosive better. These results is mainly due to the lower melting temperature of the thermoplastic elastomer ETPE, which increases the fluidity of the thermoplastic elastomer molecules, resulting in a decrease in the porosity of the explosive particles. The more the plastic deformation and filling of the adhesive, the stronger the adhesion, the higher the forming density of mixed explosive sample.

![Figure 4](image)

**Figure 4.** The Fitting curves of temperature on relative density of HATO-based explosives with different binders.
The curve of temperature on the relative density of HATO-based explosives containing ETPE or Fluorinerubber were fitted, there results were shown in figure 4 and table 3. From figure 4 and table 3, the fitted curves were in good agreement with the testing results.

**Table 3.** The fitting equation of temperature on relative density of HATO-based explosives with different binders.

| Sample composition          | The fitting equation | $R^2$  | Note                                      |
|----------------------------|----------------------|--------|-------------------------------------------|
| HATO+ETPE                  | $y=1.21 \ln(x)+92.76$ | 0.9850 | Where: $Y$ is the relative density;       |
|                            |                      |        | x is temperature;                         |
| HATO+ Fluorinerubber       | $y=1.045 \ln(x)+93.21$ | 0.9860 | R is the correlation coefficient           |

It can also be seen from figure 4 that, the relative density of mixed explosives increased rapidly with increasing temperature at 25 °C to 40 °C; above range of 40 °C, the growth rate of relative density slowed down; the temperature could reach to 70°C, relative density of mixed explosives reaches 98%; the temperature continued to increase, the relative density of mixed explosives would decrease. It shows that, as the temperature increases, the porosity between HATO explosive particles contained ETPE (or Fluorinerubber) molecules decreases, the molecular distance decreases, the inter molecular force gradually increases, the inter particle adhesion force increases, the relative forming density is higher, and the relative density of HATO explosives containing ETPE is higher than that of HATO explosives containing Fluorinerubber. However, when the temperature is too high, the binder is excessively softened, which affects the bonding between particles, and leads to flow between particles blocked, which in turn affects the forming density of the pellet.

4. Conclusions

(1) After azide-based adhesive (ETPE) or Fluororubber adhesive coated HATO explosive, The safety of mixed explosives samples was studied. From the mechanical sensitivity data, it is known that the mechanical sensitivity of mixed explosives is reduced, which improves the safety of HATO explosives to a certain extent.

(2) It is analyzed the influence of pressure and temperature on the mold-ability of HATO-based explosives containing ETPE or Fluorinerubber binder, different pressures and temperatures have a greater impact on the formability of mixed explosives. HATO-based explosives containing ETPE binders have better formability, and relative density is more than 98%. Therefore, it is possible to design explosive formulas that meet specific requirements by adjusting the pressing pressure and temperature.

References

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