Research on the Synthesis and Performance of a New Type of Neutral Polymer Bonding Agent

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Abstract. In order to improve the mechanical properties of nitrate ester plasticized polyether (NEPE) propellants, 3-allylic hydantoin was synthesized by hydantoin, potassium hydroxide and 3-bromopropene, and then a new type of intermediate polymer bonding agent (NPBA) was synthesized by 3-allylic hydantoin, acrylonitrile, hydroxyethyl acrylate and dimethylaminoethyl methacrylate. At the same time, two traditional neutral polymer bonding agents were synthesized for comparative study. Through the contact angle test, the bond performance prediction shows that: compared with the two traditional bond agents, the bond work between the new bond agent and oxidant (ammonium nitrate, ammonium perchlorate) is greater, indicating that the bond between the new bond agent and oxidant is stronger.

Keywords: 3-Allylhydantoin, Dimethylaminoethyl Methacrylate, Neutral Polymer Bonding Agent, Tensile Strength, Elongation at Break.

1. Introduction
Nitrate ester plasticized polyether (NEPE) propellant is composed of oxidizer (ammonium nitrate, ammonium perchlorate) and nitrates plasticized adhesive (polyether polyurethane), which has excellent energy properties [1]. Ammonium nitrate (oktobin, RDX) is slightly soluble in plasticizer, forming a soft interface layer on the surface, and oktobin (HMX), RDX, and AP are all non-reinforcing materials, which have poor adhesion with adhesive, resulting in poor mechanical properties of NEPE propellant [2]. Although the application of NPBA in NEPE propellant solves the problem of soft interface layer of ammonium nitrate, the problem of poor adhesion between HMX, RDX, AP and binder still exists, and the mechanical properties of propellant are difficult to meet the application requirements. Alkanolamine bonding agents have good bonding effect in AP based propellants [3], and hydantoin compounds play an efficient bonding role in ammonium nitrate based propellants [4]. In order to improve the mechanical properties of NEPE propellants, a new type of multi-functional bonding agent which can solve the problem of "dehumidification" of HMX, RDX and AP is proposed in this study.

Firstly, 3-allylhydantoin was synthesized from hydantoin, potassium hydroxide and 3-bromopropene. Then, NPBA-1 was synthesized by 3-allylhydantoin, acrylonitrile, hydroxyethyl acrylate and dimethylaminoethyl methacrylate, and two traditional bonding agents NPBA-2 and NPBA-3 were synthesized at the same time. NPBA-1, NPBA-2 and NPBA-3 were applied to a NEPE propellant formulation. After that, the mechanical properties of the propellant were studied, and the application effect of NPBA-1 in the propellant was tested.
2. Experiment

2.1 Reagents
Acrylonitrile, methyl acrylate, dimethylaminoethyl methacrylate, hydroxyethyl acrylate, azodiisobutyronitrile, acetone, potassium hydroxide, N, N-dimethylformamide (DMF), ethanol, n-hexane, acetic anhydride, all of which are analytical pure and purchased from Sinopharm Chemical Reagent Co., Ltd. Methylimidazole and β-mercaptoethanol are all analytical pure and purchased from Shanghai Yien Chemical Technology Co., Ltd. 3-bromopropene and hydantoin are chemically pure and purchased from Shanghai xianding Biotechnology Co., Ltd.

2.2 Synthesis

2.2.1 Synthesis of 3-allylhydantoin
Add 80 ml methanol, 200 ml distilled water, potassium hydroxide (0.40 mol) and hydantoin (40.03 g, 0.40 mol) to a 500 ml three port flask. The water bath is heated to 60 °C, and the reaction is heated and stirred for 0.5 h. Add 3-bromopropene (48.40 g, 0.40 mol) slowly, and then react for 4 h at 60 °C. The crude yellow product was obtained by rotating the reaction liquid. Recrystallization with n-hexane and filtration were carried out to obtain 34.27 g white crystal with a yield of 61.20%. The synthetic route of monomer is shown in Figure 1.

![Figure 1](https://via.placeholder.com/150)

Figure 1. Synthesis route of a monomer

2.2.2 Synthesis of neutral polymer bond

2.2.2.1 Synthesis of NPBA-1
Add 1.35 g of initiator azodiisobutyronitrile, 60 ml of acetone, 14 g of acrylonitrile, 4 g of 3-allylhydantoin, 4 g of dimethylaminoethyl methacrylate, 8 g of hydroxyethyl acrylate, and β-mercaptoethanol into 250 ml three port flask. Heat the flask in water bath to 60 °C and keep it warm for 7 h. The reaction product was precipitated in ethanol, washed three times, dried in a vacuum oven at 80 °C for 4 h, and then taken out and mashed to obtain a light yellow powder solid. The synthesis route of NPBA-1 is shown in Figure 2.

![Figure 2](https://via.placeholder.com/150)

Figure 2. NPBA-1 Synthesis routes

2.2.2.2 Synthesis of NPBA-2
Add 1.35 g of initiator azodiisobutyronitrile, 60 ml of acetone, 22 g of acrylonitrile, 8 g of hydroxyethyl acrylate, and β-mercaptoethanol into a 250 ml three port flask successively. Heat the flask in water bath to 60 °C for 7 hours. The reaction product was precipitated in ethanol, washed three
times, dried in a vacuum oven at 80 °C for 4h, and then crushed to get a yellow powder solid. The synthesis route of NPBA-2 is shown in Figure 3.

![Figure 3. NPBA-2 Synthesis routes](image)

### 2.2.2.3 NPBA-3 synthesis

Add 1.35 g of azo dibutyltrino, 60 ml acetone, 14 g acrylic, 8 g acrylic, 8 g acrylic, and beta-pyridine ethanol to 250 ml of three-mouth flask with a thermometer. The water bath heats up to 60 degrees C and the insulation reaction is 7h. The reaction product is precipitated in ethanol and washed 3 times, drying 4h in a vacuum drying chamber at 80 degrees C, removing and crushing, and obtaining a pale yellow powdered solid. The synthetic route of NPBA-3 is shown in Figure 4.

![Figure 4. NPBA-3 Synthesis routes](image)

### 2.2.3 Instruments and characterizations

#### 2.2.3.1 Infrared spectral characterization

The monomer products and NPBA-1 products were characterized by spectrum two Fourier transform infrared spectrometer of Perkin Elmer company. KBr method was used to determine the monomer products and NPBA-1 products. The wave number range was 4000-400cm-1.

#### 2.2.3.2 Mr. magnetic resonance characterization

The monomer was characterized by the advancedpx400 nuclear magnetic resonance instrument of Bruker company in Germany. Using CDCl3 containing TMS as solvent, the monomer was determined at room temperature.

#### 2.2.3.3 Molecular weight determination

The viscosity average molecular weight of NPBA was determined by Ubbelohde viscometer [5].

#### 2.2.3.4 Hydroxy value determination

Hydroxyl value of NPBA was determined by acetic anhydride methylimidazole DMF method [6].

### 2.2.4 Mechanical performance testing

First, prepare the sample, take 1g from each of the three NPBA, and press the tablet on the tablet press, the pressure is 16MPa, and press for 20min. The contact angles of glycerin, glycol, trimethylbenzene phosphate, formamide and aniline on the surface of three kinds of bonding agents were measured by contact angle measuring instrument at 20 °C, and the average value was taken for 5 times in parallel.

### 3. Results and Discussions

#### 3.1 Infrared Spectroscopy Analysis

Fig. 5 is the infrared spectrum of monomer product. In the figure, 3234cm-1 is the absorption peak of -NH stretching vibration, 1770cm-1-11710cm-1 is the absorption peak of bicarbonyl stretching vibration, 1647 cm-1 is the absorption peak of C = C stretching vibration, 999 cm-1-1927cm-1 is the absorption peak of = CH2 out of plane bending vibration.
Figure 5. Infrared spectroscopy of a monomer

Fig. 6 is the infrared spectrum of NPBA-1. In the figure, 3385 cm\(^{-1}\) is the expansion vibration absorption peak of \(-\text{oh}\). At 2935cm\(^{-1}\) and 1452cm\(^{-1}\), there are respectively \(-\text{C-H}\) stretching vibration absorption peak and bending vibration absorption peak in \(-\text{CH2}\). 1 070 cm\(^{-1}\) is the peak of \(-\text{C-O}\) stretching vibration absorption in \(-\text{CH2OH}\), which proves that hydroxyethyl acrylate is involved in the reaction. 2242 cm\(^{-1}\) is the characteristic absorption peak of cyano group, which proves that acrylonitrile is incorporated into polymer macromolecules. At 1772 cm\(^{-1}\) and 1702 cm\(^{-1}\), there are two shoulder peaks of carbonyl group. At 1169 cm\(^{-1}\), there was a \(-\text{C-N}\) stretching vibration absorption peak, which indicated that 3-allylhydantoin and diethylaminoethyl methacrylate were incorporated into the polymer molecule. It can be seen that all the monomers involved in the reaction and joined into the polymer molecular chain to synthesize a new bonding agent NPBA-1.

Figure 6. Infrared spectroscopy of NPBA-1

Fig. 7 is the NMR hydrogen spectrum of the monomer product. In the figure, 7.259ppm is the solvent peak. From high field to low field, near 3.973ppm is the methylene peak on the five membered ring; near 4.093ppm is the methylene peak connected with olefin. Near 5.185ppm is the end olefin methylene peak; near 5.789ppm is the olefin methylene peak. 6.928ppm is the proton peak of amide N atom. From high field to low field, the integral area ratio of the characteristic peak is 2:2:2:1:1, and the sum is 8, which is consistent with 8 hydrogen in 3-allyl hydantoin structure.

Fig. 8 is the NMR carbon spectrum of the monomer product. In the figure, the triple peak of solvent is near 77.093ppm. In addition to the solvent peak, there are six peaks, indicating that there are
six types of carbon atoms in the new monomer structure, which is consistent with that in the 3-allyl hydantoin structure. The resonance absorption range of saturated carbon atom is 0-100ppm. In addition to carbonyl carbon atom, the resonance absorption range of SP2 hybrid carbon atom is 100-160ppm. The absorption range of carboxylic acid, ester, anhydride and amide carbonyl carbon is 160-190ppm. From the high field to the low field, the methylene peak connected with olefin is at 40.645ppm. 46.581ppm is the methylene peak on the five membered ring. At 117.969 ppm, there was a peak of olefin terminated methylene group. At 131.024ppm, the end olefin methylene peak was observed. 158.575ppm is the carbonyl carbon peak connecting one N atom. 171.141ppm is the carbonyl carbon peak connecting two N atoms.

Figure 7. Nuclear magnetic resonance hydrogen spectra of a single body

Figure 8. Mr. Magnetic Resonance Carbon Spectroscopy

The results of IR and NMR analysis show that the monomer product is the confirmation of the synthesis of 3-allylhydantoin and NPBA-1.

3.2 Analysis and Test of Neutral Polymer Bonding Agent
Table 1 shows the molecular weight and hydroxyl value test results of three NPBA products. From the test results, it can be seen that the molecular weight and hydroxyl value of three NPBA products are close.
3.3 Prediction of Bond Performance between Polymer Bond Agent and Oxidant

The surface tension and polarity fraction of bonding agent were calculated by contact angle. The surface tension and polarity component data of AP, RDX and β - HMX tricrystals (β - HMX {110}, β - HMX {011}, β - HMX {010}) were found out from literature [7], and the results are listed in Table 2.

| Sample        | γ_s (mN·m⁻¹) | γ_p (mN·m⁻¹) | γ_d (mN·m⁻¹) | P   |
|---------------|--------------|--------------|--------------|-----|
| NPBA-1        | 23.90        | 31.02        | 54.92        | 0.564 |
| NPBA-2        | 28.02        | 18.11        | 46.13        | 0.393 |
| NPBA-3        | 24.90        | 16.24        | 41.14        | 0.395 |
| AP            | 22.39        | 22.08        | 44.37        | 0.498 |
| RDX           | 28.67        | 16.48        | 45.15        | 0.365 |
| β-HMX{110}    | 32.19        | 12.17        | 44.36        | 0.274 |
| β-HMX{011}    | 31.91        | 11.54        | 43.44        | 0.267 |
| β-HMX{010}    | 34.91        | 10.28        | 45.19        | 0.228 |

The adhesion work of the bonding agent and the oxidant is calculated from the surface tension. The results are listed in Table 3.

| Sample        | AP (mJ·m⁻²) | RDX (mJ·m⁻²) | β-HMX{110} (mJ·m⁻²) | β-HMX{011} (mJ·m⁻²) | β-HMX{010} (mJ·m⁻²) |
|---------------|-------------|--------------|---------------------|---------------------|---------------------|
| NPBA-1        | 98.61       | 97.57        | 94.33               | 93.07               | 93.48               |
| NPBA-2        | 90.09       | 91.24        | 89.76               | 88.72               | 89.84               |
| NPBA-3        | 85.10       | 86.16        | 84.74               | 83.76               | 84.81               |

It can be seen from Figure 7 that the new bonding agent NPBA-1 has greater adhesion work with the three crystal surfaces of oxidants AP, RDX and β - HMX compared with the traditional bonding agents NPBA-2 and NPBA-3, which indicates that the new bonding agent has better interface wettability and stronger interface adhesion with the oxidant. It is proved that the bonding agent and oxidant are strengthened by introducing bonding functional groups such as hydantoin ring group and amino group into the molecular chain of the bonding agent the bond action of.

4. Conclusions

(1) At first, the monomer 3-allylhydantoin was synthesized, which was confirmed by IR, NMR and elemental analysis. NPBA-1 was synthesized by acrylonitrile, 3-allylhydantoin, dimethylaminoethyl methacrylate and hydroxyethyl acrylate, and NPBA-2 and NPBA-3 were synthesized by acrylonitrile, methyl acrylate and hydroxyethyl acrylate. The molecular weight and hydroxyl value of the three kinds of NPBA were close to each other.

(2) By measuring the contact angle and calculating the adhesion work, the bonding properties of the three bonding agents and the oxidants AP, RDX and HMX are estimated. Compared with the two traditional bonding agents, the new bonding agent and the oxidant have greater adhesion work, which
shows that the new bonding agent and the oxidant have stronger interface bonding, and will have good bonding effect in NEPE propellant containing both ammonium nitrate and ammonium perchlorate.

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