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Enthalpy of Formation of p(BAMO)-b-GAP and Energetic Characteristics of Solid Propellants Based on the Copolymer

Ruoqian Xu,*[a] Zhongming Li,[a, b] Yanhui Chen,[a] Jiangfeng Pei,[c] and Junlin Zhang[c]

Abstract: The block copolymer of 3,3′-bis(azidomethy) oxetane and glycidyl azide polymer (p(BAMO)-b-GAP) is an ideal energetic binder for solid propellants. In this work, the enthalpy of formation of p(BAMO)-b-GAP was first investigated by the heat of combustion experimental method and group additivity method. Meanwhile, the energetic characteristics of solid propellants based on the copolymer were systematically calculated. The results proved that the $\Delta_f H$ of p(BAMO)-b-GAP could be estimated accurately by two methods and the positive $\Delta_f H$ values were obtained. Dual-oxidant formulas were designed in which AP was replaced gradually by some chlorine-free high-energy materials. The calculation results showed when AP was gradually replaced by RDX or HMX, the energy level of propellants based on p(BAMO)-b-GAP was improved first but then decreased with AP content further decreased, indicating there was an optimum ratio between AP and its alternative. However, when AP was replaced by CL-20 or ADN, the values of I_{sp} were improved steadily. When less than 40% AP was replaced, the contribution to the energy level of propellant by RDX or HMX was even more than that by CL-20.

Keywords: copolymer · enthalpy of formation · energetic characteristics · p(BAMO)-b-GAP · propellant

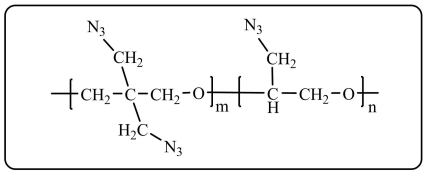
1 Introduction

As the power source of the rocket engines, the energetic performances of solid propellants directly affect the firing range and flight speed of missiles. From a practical perspective, the theoretical energetic characteristics studies of propellants are significant for formulation design. During the past decades, studies on azido polyether based propellants, such as GAP(glycidyl azide polymer), BAMO (3,3′-bis(azidomethy) oxetane), and AMMO(3-azidomethyl-3′-methyl oxetane), have attracted intensive attention due to their high energy levels, low mechanical sensitivities and low characteristic signals [1–2]. For instance, Xu group reported their investigations into the influence of RDX (1,3,5-trinitroperhydro-1,3,5-triazine), TTNZ(1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin), FOX-7(1,1-diamino-2,2-dinitroethylene) and some other insensitive energetic additives on the energetic characteristics of GAP based propellants [3]. Song group reported their studies on the mechanical properties of RDX/BAMO-AMMO based propellant [4].

More recently, the impact of high energetic materials and metal hydride on the specific impulse of propellants based on BAMO-THF (tetrahydrofuran) and BAMO-AMMO were calculated and discussed by the Zhai group [5] and Pei group [6,7], respectively. The energy and combustion characteristics of the propellants based on the copolymers p(BAMO-GAP) were also investigated [8]. The results showed that the energetic properties of propellants could be improved linearly when AP was replaced by ADN (ammonium dinitramide).

The block copolymer of 3,3′-bis(azidomethy) oxetane and glycidyl azide polymer(p(BAMO)-b-GAP), prepared by the functional groups polymerization from two segments of prepolymers, have higher molecular weight and nitrogen content than the random copolymer. It is a more promising energetic binder for solid propellants with excellent physical and chemical properties. Consisting of typical azide polymers, the main advantage of p(BAMO)-b-GAP is the low melt viscosity for blending with other fillers or further processing [9–12]. The copolymer also exhibits good compatibility with the most commonly applied components in propellants [13]. During the past decades, synthesis, characterization, thermal decomposition and combustion characteristics of p(BAMO)-b-GAP have been reported [14–19]. In this study, the enthalpy of formation of p(BAMO)-b-GAP was first investigated by two methods. The energetic characteristics of solid propellant based on the copolymer were also systematically calculated, providing a theoretical basis for the formulation design and practical application of p(BAMO)-b-GAP based solid propellant.

[a] *R. Xu, Z. Li, Y. Chen*
Northwestern Polytechnical University
710072 Xi'an, Shaanxi, China
**e-mail: nutar@163.com*
[b] *Z. Li*
Sichuan University, Chengdu
610065 Chengdu, Sichuan, China
[c] *J. Pei, J. Zhang*
Xi'an Modern Chemistry Research Institute
710065 Xi'an, Shaanxi, China



$(C_5H_8ON_6)_m(C_3H_5ON_3)_n$

Figure 1. Structural formula of p(BAMO)-b-GAP.

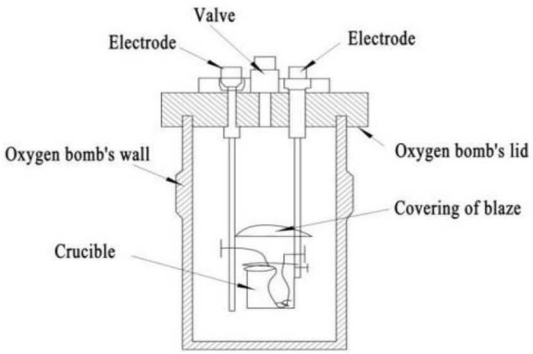


Figure 2. Oxygen bomb for the heat combustion.

2 Experimental Section

2.1 Samples

The p(BAMO)-b-GAP is prepared by Xi'an Modern Chemistry Research Institute according to the existing method [20]. A mass ratio of the two segments pBAMO and GAP is 1:1. The structural formula is shown in Figure 1.

2.2 Apparatus and Measurements

Relative molecular weight: both M_n and M_w of the copolymer were carried out by PL-GPC50 with PL gel 5 μm Mixed-E (7.5×300 mm) column and using tetrahydrofuran as eluent at 1 mL/min.

Elemental (CHN) analysis: the carbon (C), hydrogen (H), and nitrogen (N) contents were obtained by PE-2400 elemental analyzer. The percentage of oxygen was obtained by subtraction using the equation (1)

$$\%O = 100\,\% - \%C - \%H - \%N \quad (1)$$

Heat of combustion: a calorimetric oxygen bomb (model GR-3500, Figure 2) was employed to measure the heat of combustion. The pressure of oxygen was fixed at 3 MPa and the initial temperature was 293 K. The constant of the bomb was calibrated by the benzoic acid that the purity was about 99.999%. Five tests were performed for each sample and the average results were obtained. The amount of the sample for one test was 0.8 g–1.0 g.

Energy characteristics calculation: The theoretical energy characteristics of the propellants were investigated by "Energy Calculation Star (ECS)" [21] based on the principle of free-energy minimization. The assumptions of the calculation were: the pressure was 7.0 MPa in the combustion chamber and 0.1 MPa at the nozzle outlet. The initial temperature of the propellant was 298 K.

Table 1. Contents of the elements, empirical formulas, and molecular weights of the copolymer.

	Experimental results	*Theoretical results*
C%	36.19	36.04
H%	5.01	4.91
O%	12.93	12.84
N%	45.87	46.21
empirical formula for 1000 g	$C_{30.16}H_{50.10}O_{8.08}N_{32.76}$	$C_{30.03}H_{49.06}O_{8.03}N_{32.82}$
M_n (g/mol)[a]	7515	
M_w (g/mol)[b]	25212	

[a] M_n is number-average molecular weight; [b] M_w is weight-average molecular weight.

3 Results and Discussion

3.1 Elemental Analysis and Empirical Formula

Elemental analysis of p(BAMO)-b-GAP sample was first carried out with the results shown in Table 1, meanwhile, the experimental empirical formula was achieved by dividing the percentage of the element by its molar mass. The theoretical weight percentages of elements, which were calculated from the structural formula, the mass ratio between two blocks of the copolymer, and the relative molecular weight, were also listed in the table to validate the experimental values. The theoretical results and the obtained results from the experimental weight percentage of elements were compared. The two results were almost the same. The difference was from the experimental errors.

3.2 Estimation of Enthalpy of Formation

The enthalpy of formation of the copolymer was estimated by two widely used methods, heats of combustion experimental method [22] and group additivity method [23].

The heat of combustion experimental method:

The combustion reaction of the copolymer was shown in equation (1)

$$C_aH_bO_cN_d(s) + O_2(g) \rightarrow a\ CO_2(g) + H_2O(l) + N_2(g) + \Delta_cH^\theta \quad (1)$$

The mainly combustion products were CO_2, H_2O, and N_2. The enthalpy of combustion of the polymer could be obtained from the heat of combustion with the equation (2)

$$\Delta_c H^{\theta}(\text{polymer}) = \Delta_c U(\text{polymer}) + \Delta nRT \quad (2)$$

where Δn was the difference between the amount of gaseous products and reactants, $R = 8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $T = 298$ K.

Since the heat of the formation of nitrogen gas was zero, it did not contribute to the heat of the formation of the product. Therefore, the enthalpy of formation of the polymer was obtained with the following equation (3)

$$\Delta_f H^{\theta}(\text{polymer}) = a\Delta_f H^{\theta}(CO_2) + \Delta_f H^{\theta}(H_2O) - \Delta_c H^{\theta}(\text{polymer}) \quad (3)$$

where $\Delta_f H^{\theta}(CO_2) = -393.5\ \text{kJ}\cdot\text{mol}^{-1}$, $\Delta_f H^{\theta}(H_2O) = -285.8\ \text{kJ}\cdot\text{mol}^{-1}$.

Group additivity method:

Based on the structural formulation and the molecular weight of the copolymer, the $\Delta_f H^{\theta}$ was estimated with the group additivity method. The contributions of groups to the enthalpy of formation of polymers were shown in Table 2.

The enthalpy of combustion ($\Delta_c H$) and the enthalpy of formation ($\Delta_f H$) of the polymer was grouped and summarized in Table 3. The subscript of the $\Delta_f H$, exp, and gro indicated the values estimated by experimental and group additivity method respectively.

The combustion process was an exothermic reaction and, the $\Delta_c H$ was negative. The positive $\Delta_f H$ meant that a quantity of energy was absorbed during the formation of the molecule from basic elements and, consequently, the initial elements were more stable than the final product. The value of $\Delta_f H_{exp}$ was slightly lower than that of $\Delta_f H_{gro}$, which was caused by the element content test error and the inconsistent molecular structure of the polymer.

3.3 Energy Characteristics of the Propellants Based on the Copolymer

To obtain the effect of different high-energy materials (HEMs) on the energy characteristics of propellants based on the copolymer, the basic formulation was designed as: p(BAMO)-b-GAP 12%, Al 8%, AP 80%. And some commonly used chlorine-free high-energy materials, including RDX, HMX, ADN, and CL-20, were added to reduce the content of AP. The energetic properties (including ideal specific impulse, the relative molecular mass of gaseous products, oxygen coefficient, adiabatic flame temperature, and density) of corresponding propellants were further calculated. The chemical formulas, enthalpy of formation, and densities of the HEMs were listed in Table 4, and the calculation results were shown in Figure 3a–e.

Table 2. Contributions of groups to the enthalpy of the polymer [24].

Group	$\Delta_f H^{\theta}$/kJ·mol^{-1}
—CH_3	−46
—CH_2—	−22
—CH—	−2.7
—C—	+20
—O—	−120
—N_3	+356

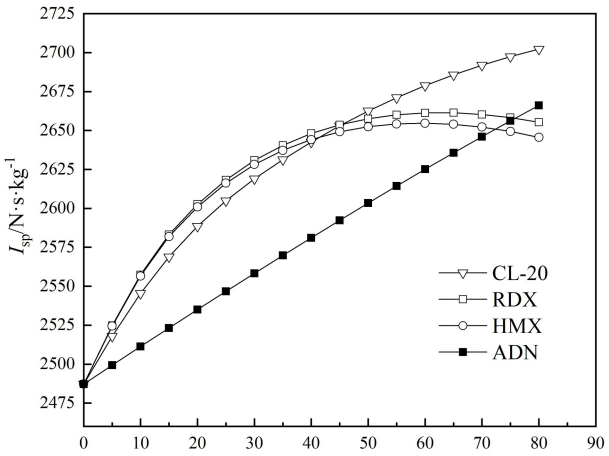
Table 3. $\Delta_c H$ and $\Delta_f H$ of the p(BAMO)-b-GAP.

$\Delta_c U$ (kJ/g)	$\Delta_c H$ (kJ/g)	$\Delta_f H_{exp}$ (kJ/g)	$\Delta_f H_{gro}$ (kJ/g)
−21.38	−21.27	2.24	2.51

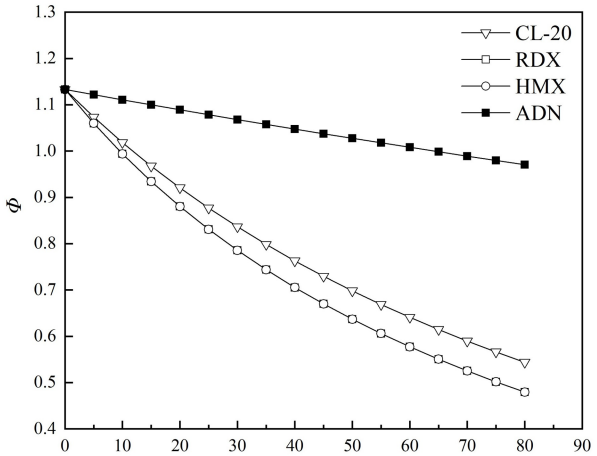
Table 4. Enthalpy and density of formation of the HEMs [25].

Components	formulas	$\Delta_f H$ (kJ/mol)	densities (g/cm^3)
AP	NH_4ClO_4	−294.1	1.95
RDX	$C_3H_6N_6O_6$	70.3	1.82
HMX	$C_4H_8N_8O_8$	75.0	1.90
CL-20	$C_6H_6N_{12}O_{12}$	415.5	1.98
ADN	$H_4N_4O_4$	−133.0	1.80

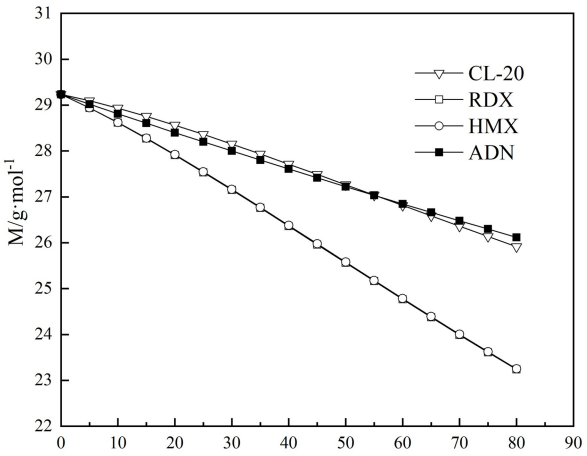
The results in Figure 3a showed that the energy level of propellant could be significantly improved in whole when AP was gradually replaced by four kinds of HEMs, however, the trends of variation were different for the different HEMs. For the propellant containing RDX or HMX, the values of I_{sp} were improved rapidly first but then decreased with AP content further decreased, indicating that there were optimum ratios between AP and its alternatives, and the values of I_{sp} reached the maximum at these ratios. The values of I_{sp} for RDX or HMX were very close when the contents of RDX and HMX were the same. This is because that the $\Delta_f H$ of RDX and HMX are close. When AP was replaced gradually by CL-20 or ADN, the values of I_{sp} were improved steadily, more interestingly, I_{sp} increased linearly with AP replaced gradually by ADN. It is noteworthy that there were crossing points between the I_{sp} curves based on RDX/AP or HMX/AP systems with the curves based on CL-20/AP or AND/AP systems. When the content of ADN or CL-20 was lower than that of the crossing point, propellants based on RDX/AP or HMX/AP systems showed higher values of I_{sp} than those



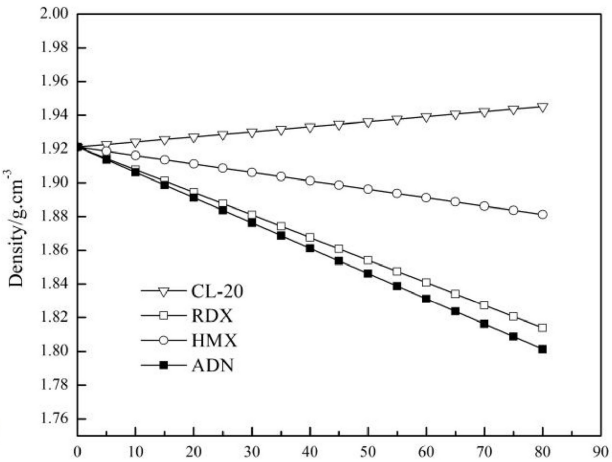
a) Effects of HEMs on I_{SP}



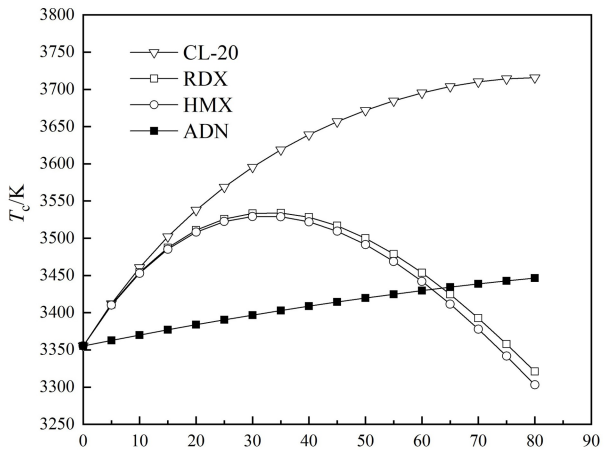
d) Effects of HEMs on Φ



b) Effects of HEMs on M



e) Effects of HEMs on densities of propellant



c) Effects of HEMs on T_C

Figure 3. Energy characteristics of propellants.

based on CL-20/AP or ADN/AP systems. In that case, the contribution of CL-20 or ADN for the improvement of the energy level of propellants was smaller than that of RDX or HMX. For instance, when less than 40% AP was replaced, the contribution to the energy level of propellant by RDX or HMX was more than that by CL-20. When more than 50% AP was replaced, CL-20 had the greatest contribution to the improvement of energy level of propellants. The mathematical expression $I_{sp} \propto (T_c/\bar{M})^{1/2}$ showed that the specific impulse was directly proportional to the square root of the combustion temperature and inversely proportional to the square root of the average molecular mass of the combustion product [26]. With AP replaced by other HEMs, the values of the molecular mass of gaseous products (M) decreased linearly. As shown in Figure 3b, the descending gradients of M for propellants based on RDX/AP or HMX/AP systems were higher than those based on CL-20/AP or ADN/AP systems, but the M values based on RDX/AP or HMX/AP systems were lower than those based on CL-20/AP or ADN/AP systems. The replacement of AP by RDX or HMX was more beneficial to reduce the molecular weight of combustion gas productions. Similar to the trend of the curve of I_{sp}, the values of T_c for propellants based on RDX/AP or HMX/AP systems increased first but then decreased with AP content further decreased (Figure 3c). The highest value of T_c was achieved from propellant based on CL-20/AP system, indicated that the combustion temperature of propellants was improved with the replacement of AP by CL-20, and it was good for enhancing the energy of propellants. However, the higher temperatures implied more aggressive thermal loads on the structure of the rocket motor.

The value of oxygen coefficient (Φ) of propellants measures the combustion reaction of propellants and further affects the energy level of propellants. Therefore, Φ of the propellants based on AP gradually replaced by HEMs of RDX, HMX, ADN, and CL-20 were also investigated. Figure 3d showed that the values of Φ were decreasing consecutively with AP was replaced gradually. The decreasing gradient of RDX/AP or HMX/AP systems was the highest in the four systems, and it was worth noting that the two curves were almost overlapped, which showed that RDX and HMX had the same effect on the oxygen coefficient of propellant. The decreasing gradient of ADN/AP system was much lower than the other four systems, and the value was decreasing a little but it still remained above 0.9 when AP was totally replaced by ADN. It indicated that as one of the most promising oxidants to replace AP [27–30], ADN was more effective to improve the oxygen content for low signature propellants.

Finally, density, one of the key parameters to measure the performance of propellant, was investigated with the results shown in Figure 3e. With AP gradually replaced by CL-20, the density of propellants increased because the density of CL-20 was higher than that of AP. This indicated that more weight of propellant can be obtained under the same volume, and the range of missile weapons would be improved. When AP was replaced by the other three HEMs, the densities of the propellant decreased, and the order of decreasing gradient was ADN/AP system > RDX/AP system > HMX/AP system. This was related to the density of the four HEMs themselves.

4 Conclusions

The enthalpy of formation of p(BAMO)-b-GAP was estimated accurately by experimental and calculation method, and both methods gave positive values of $\Delta_f H$ of p(BAMO)-b-GAP. Systematic calculation results showed when AP was gradually replaced by RDX or HMX, the energy level of propellants based on p(BAMO)-b-GAP was improved first but then decreased with AP content further decreased. The trend proved there were optimum ratios between AP and its alternatives, and the values of I_{sp} reached the maximum at these ratios. In contrast, when AP was replaced by CL-20 or ADN, the values of I_{sp} were improved steadily. When less than 40% AP was replaced, the contribution to the energy level of propellant by RDX or HMX was even more than that by CL-20. When more than 50% AP was replaced, CL-20 had the greatest contribution to the improvement of energy level of propellants, and it is beneficial to improve the density of propellants.

Data Availability Statement

Data available on request from the authors.

Acknowledgements

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