Research paper

Characterization of the new energetic hydrazone binder for solid rocket propellant

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Abstract

The new prepolymer for solid composite propellant was designed and synthesized. The results of the theoretical calculations and the burning rate measurements indicated that the prepolymer greatly improves the burning rate and the specific impulse of the composite propellant. Especially, in the AN-based propellant, the stable combustion was observed even at the pressure range which the HTPB propellant didn't. And it was also confirmed that no difference exists in impact and friction sensitivities between the propellants of both binders.

Keywords: Energetic binder, Hydrazone, Combustion performance, Solid propellant

1. Introduction

Typical composite solid propellant used in solid rocket motors for missiles consists of 80 % of oxidizer and 20 % of polymer binder as fuel and binding agent. Besides, plasticizer, curing agent, and catalyst etc. is added to it. To improve the specific impulse of solid rocket motors, it is the most effective to increase the energy of the solid oxidizer or the polymer binder. Ammonium perchlorate (AP) is now mostly used as the solid oxidizer. But it is known that it generates plenty of gaseous hydrogen chloride during the combustion. The hydrogen chloride absorbs atmospheric water and changes to hydrochloric acid. So it is said not to be harmless. For that reason, the studies about eco-friendly propellant have been conducted, which is called Green Propellant, and the ways to replace AP by ammonium nitrate (AN), which doesn't emit hydrogen chloride during combustion, have been proposed recently. Because hydrochloric acid mist is one of the reasons that rocket motors emit white smoke, this replacement of AP by AN also contributes to smokeless of rocket motor. However, because of the low energy density of AN, the simple replacement of AP by AN lowers the burning rate of the propellant. For this reason, when AP is replaced by AN, the energy should be supplied by another component. In order to supply the energy by another component, the use of the energetic binder is a major means. As the energetic binder, BAMO (3,3-bis(azidomethyl) oxetane), NMMO (3-nitratometyl-3-methyl oxetane) and GAP

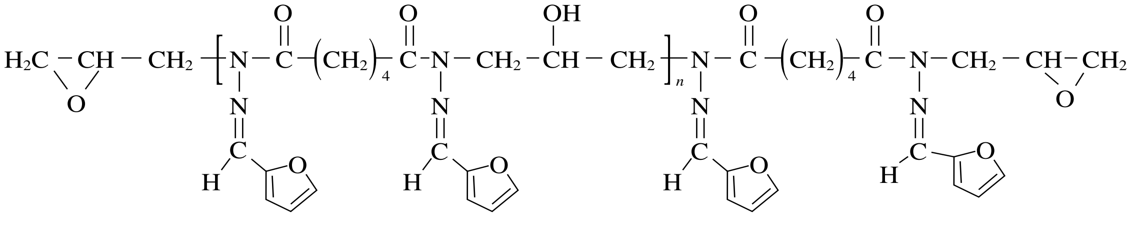

Fig. 1 Chemical structure of DEFAH.

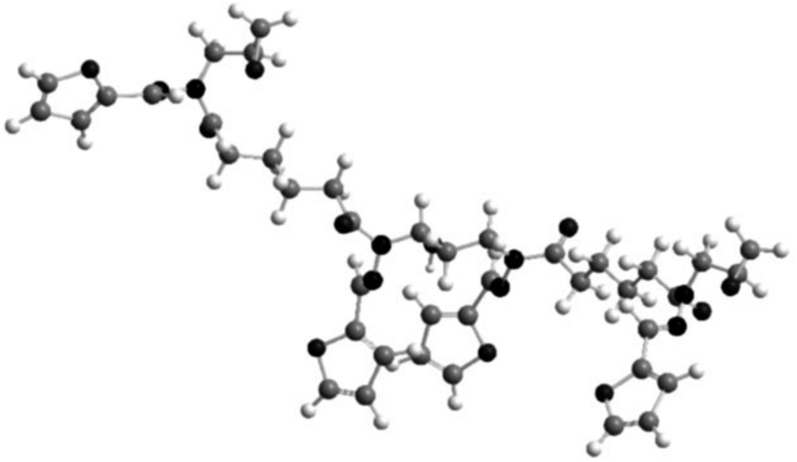

Fig. 2 Calculated conformation of DEFAH molecule by MOPAC.

(glycidyl azide polymer) have been investigated in the past[1), 2)]. However, while these are the effective binders for increasing the specific impulse, these are inferior to HTPB (hydroxyl terminated polybutadiene), the binder mostly used in conventional munitions, in the cost and the physical properties. In general, binder is required to have a function to form three-dimensional network and to incorporate the solid oxidizer into its matrix. Thus the design of the energetic binder by considering its molecular structure and its curing mechanism is desired.

From another point of view about propellant, due to the requirement of IM (Insensitive munitions) characteristics, it is preferred that the solid oxidizer content in the propellant is minimized to reduce the sensitivity against the outer stimulation, e.g., an impact. Taking the oxygen balance as the whole propellant into consideration, oxygen was supplied in another ingredient in order to decrease the quantity of oxidizer.

In this study the energetic binder including the more oxygen content was investigated. First, hydrazon-based energetic prepolymer having N-N bonds, which are the energetic functional groups, was designed and synthesized, and then solid propellant was manufactured. Combustion characteristics of the new energetic propellant were also evaluated here.

2. Molecular design

One of the typical requirements for the energetic polymer is to emit more energy during the thermal decomposition and / or the combustion. For the purpose of it, high energy functional groups are added in the molecule. For example, azide groups (-N=N=N) emit a large quantity of heat during the bond cleavage process. In this study, N-N bonds, which originate from hydrazine, was focused as energetic

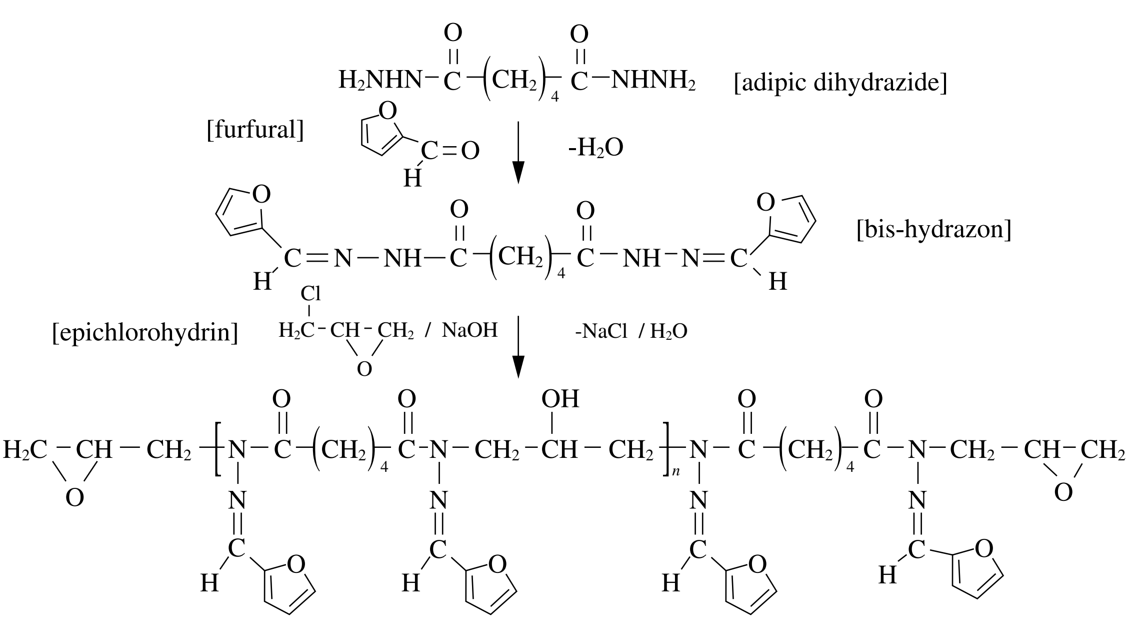

Fig. 3 Synthesis steps of DEFAH.

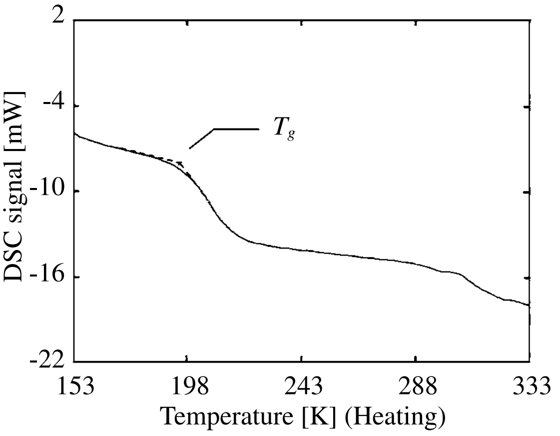

Fig. 4 DSC curve of DEFAH prepolymer at low temperature.

bonds. Hydrazine derivatives are such reactive having aldehyde groups and epoxide groups that it appropriates to polymerization. Moreover it is required that prepolymer forms three-dimensional network with curing agent first, in order to use polymer as the binder. In this purpose, it is the general procedure that terminal hydroxyl groups are made to form urethane bonds by isocyanate curing agent. But in view of reactivity to hydrazine derivatives, in this study, it is considered that epoxy bonds by epoxide group were used to cure. Considering among epoxy resins of hydrazine derivatives with N-N bonds, it was already reported that material with furfural in side chain had the high combustion performance3), 4). And it is anticipated that the reaction of furfural and hydrazine derivative makes hydrazone having -N-N=C- bonds, double bonds produce the elasticity, which contributes to mechanical properties. So hydrazone-based polymer having double bonds and furfural in side chain were considered. If the length of hydrocarbon in the center of the polymer framework is longer, the oxygen balance turns to be worse. And if too short, there is less elastic for polymer. Since to balance the both requirements, four repeat units were established. The designed polymer structure was shown in Fig.1. While this polymer molecule is called DEFAH (Diepoxide of furfural (adipic) hydrazone) molecule for distinction, the polymer synthesized in this study is called DEFAH prepolymer here after.

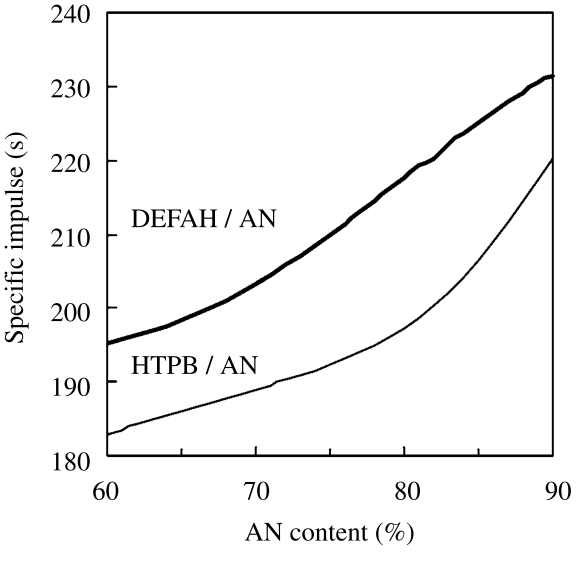

Fig. 5 Specific impulse of the AN-based propellant.

In order to determine the heat of formation of DEFAH molecule, molecular orbital calculation with MOPAC (semi-empirical molecular orbital package) optimized the molecular structure (configuration) as shown in Fig. 2. Assuming that the degree of polymerization is n=1, the heat of formation becomes +1.83 MJ mol^{-1}. Since molecular weight is 829, the heat of formation corresponds to +1.82 MJ kg^{-1}. In comparison with the heat of formation of HTPB prepolymer, that is -0.31 MJ kg^{-1} and that of GAP prepolymer, which is known as the energetic binder, +0.96 MJ kg^{-1}5), the DEFAH molecule is found to be relatively high. ξ(O), weight percentage of oxygen, in the molecule concerned is 19.3 %. This is extremely high in comparison to 3.96 % of ξ(O) for HTPB prepolymer and nearly equal to that for GAP prepolymer, 17.9 %. Considering the system of propellant, the high ξ(O) suggests that the solid oxidizer content can be decreased with the constant balance of oxygen level.

Adipic dihydrazide was used as the starting material. This is the material used for polymer's plasticizer or epoxy curing agent in general. Furfural was added to this adipic dihydrazide and the mixture was heated under reflux. Then, excess furfural was removed with methanol and bishydrazon produced was purified. Excess epichlorohydrin and sodium hydroxide in methanol was added to this bishydrazon and the mixture was heated under reflux to synthesize the copolymer. Methyl ethyl ketone and methyl formamide were used remove excess organic materials (excess epichlorohydrin etc.) from the mixture. The process of synthesis is described in Fig. 3.

The DSC curve in low temperature (under ordinary temperature) is shown in Fig. 4. Glass transition temperature, T_g was found to be 195.7 K, which is nearly equal to that of HTPB prepolymer (193.2 K). New binder designed here expected to show good mechanical properties in low temperature.

3. Theoretical performance calculations

Specific impulse, I_{sp} is a parameter to define the energy efficiency of propellant combustion, which is represented by the following equation5). F is the thrust, m_g is the mass flow rate in the nozzle, and g is the gravitational acceleration.

$$I_{sp} = \frac{F}{\dot{m}_g g}$$

For each of the case that the oxidizer was AP and the oxidizer was AN, the relation between the propellant composition and I_{sp} was predicted by calculations6). The results were shown in Fig. 5 and Fig. 6. The calculated condition

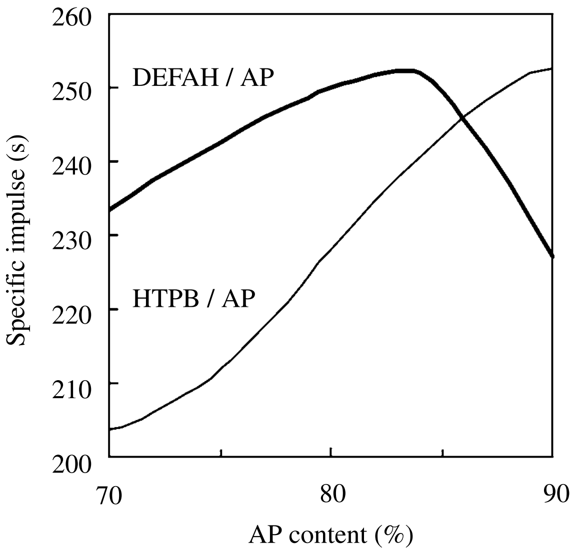

Fig. 6 Specific impulse of the AP-based propellant.

was assumed that the pressure in the combustion chamber was 6.9 MPa, atmospheric pressure was 0.1 MPa, burned gas was in thermal equilibrium during expansion process in the nozzle, and it was appropriate expansion.

From Fig. 5 for the specific impulse of the AN-based propellant, when AN contents of the propellants were equal, DEFAH / AN showed the higher specific impulse than HTPB / AN. Because the specific impulse increase gradually with increase of the AN contents, it is better to simply increase AN content to make the propellant with a high specific impulse. The compositions of the samples were shown in Table 1. AN-based propellant used in this study is 70 % of AN content because of the manufacturing constraints. Meanwhile, Fig. 6 indicates that the specific impulse of DEFAH / AP shows the maximum, 252 s at about 83.5 % of AP content. The specific impulse of HTPB / AP increase gradually according to the rise of the AP contents and it can exceed this 252 s when AP content is over 88 %. 80 % of AP content was selected to maximize the specific impulse of DEFAH / AP in AP-based propellants

Table 1 Compositions of propellant samples (wt %).

Sample	Binder		Oxidizer	
	DEFAH	HTPB	AN	AP
DEFAH / AN	30		70	—
HTPB / AN	—	30	70	—
DEFAH / AP	20	—	—	80
HTPB / AP	—	20	—	80

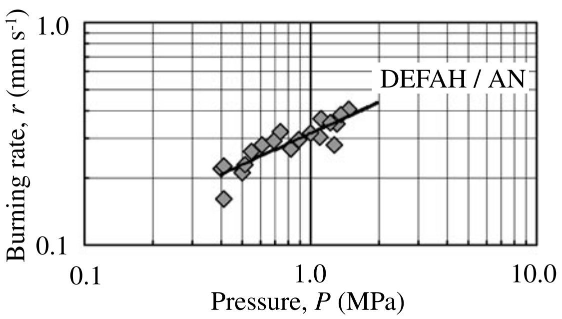

Fig. 7 Burning rate of AN-based propellant.

4. Burning rates

In order to evaluate the burning rate, the measurements were conducted by using of chimney-type strand burner at atmospheric temperature. The combustion chamber was pressurized with nitrogen gas. The burning rate was determined by using of a high speed video camera image through the observation window of the chamber.

The pressure dependence of the burning rate of the samples with AN as solid oxidizer was shown in Fig. 7. The burning rate of HTPB / AN tested as the reference wasn't obtained because the sample couldn't burn itself without the contact of electro-thermo wire. Meanwhile, for DEFAH / AN, the burning rate could be measured in spite of very low speed. The samples couldn't sustain the combustion in the pressure range from 0.1 MPa to 0.3 MPa. It was found there was the lower limit of combustion at 0.3 MPa. During the combustion, the samples burned emitting white smoke with soot formation and its flame was invisible. After combustion, a relatively hard char structure was obtained. It was supposed that the binder couldn't burn completely with the decomposition products from AN, its carbon chain of its main structure wouldn't cut and its carbon atom was used for the soot formation.

From Vieille's law, $r = aP^n$, the pressure exponent n is represented by following equation[7].

$$n \equiv \left(\frac{\partial \ln r}{\partial \ln P} \right)_{T_0} \qquad (1)$$

r is the burning rate, a is the constant which is dependent on the chemical composition and the initial propellant temperature, T_0. The burning rate curve of DEFAH / AN was fitted on a straight line and then the pressure exponent calculated by the equation (1) was about 0.47. Since the pressure exponent of AN and HTPB-based propellant is about 0.85 nevertheless it is obtained over 2 MPa of the pressure and the pressure exponent of this DEFAH / AN sample is lower than that, it is supposed that the stability against the pressure fluctuation was improved by using of DEFAH binder.

The pressure dependence of the burning rate of the samples with AP as solid oxidizer was shown in Fig. 8. The burning rate of DEFAH / AP at the pressure of 1.0 MPa is about 7.8 mm s^{-1} and this is more than double of that of HTPB / AP, 3.2 mm s^{-1} at the same pressure. The

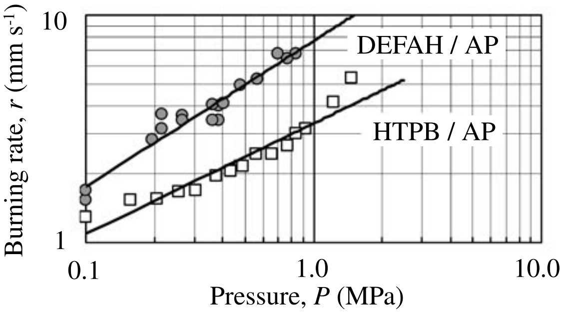

Fig. 8 Burning rate of AP-based propellant.

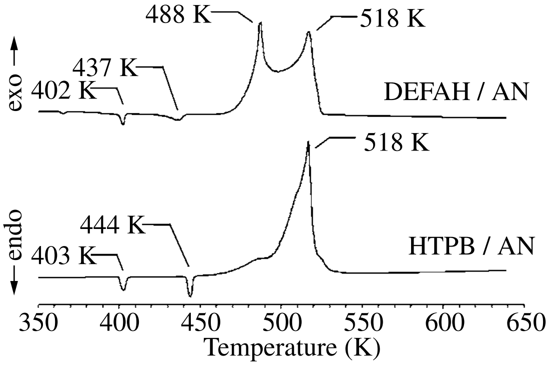

Fig. 9 DSC curves of DEFAH / AN and HTPB / AN.

pressure exponent of DEFAH / AP and HTPB / AP calculated by the equation (1) was about 0.64 and 0.48 respectively. Both pressure exponents were relatively higher than the existed propellants because the ballistic modifiers weren't used in this study, in order to clarify the difference of the binder. On the other hand, for the conditions after burning, DEFAH / AP didn't produce the combustion residue, differing from DEFAH / AN. It is considered that the AP's higher combustion temperature affects this difference. Meanwhile, for HTPB / AP, the sample burned completely from an end through the combustion. Furthermore, when DEFAH / AP data are extrapolated to the pressure range at operational rocket motors, the burning rate is expected over 30 mm s^{-1}. Therefore, DEFAH can be a candidate of high burning rate propellant binder with an improvement of the presence exponent.

5. Thermal decomposition

In order to clarify the effect of binder, the thermal decomposition characteristics were measured for the AN-based sample. Each DSC curve was shown in Fig. 9. For each sample, the DSC curve shows endotherms for the phase transition of AN of about 403 K, and at 443 K, and an exothermic peak for the decomposition of AN occurs at about 518 K. The most remarkable difference was an exothermic peak at about 488 K in the DEFAH / AN. This derives from DEFAH binder[9]. The heats of decomposition of DEFAH / AN and HTPB / AN were 2.16 MJ kg^{-1} and 1.89 MJ kg^{-1} respectively. This increase of exotherm generated the increase in the burning rate and the expected reaction process is the improvement of heat balance in gas phase owing to exothermic decomposition of DEFAH prior to the thermal decomposition of AN.

6. Sensitivity

Impact and friction test results were shown in Table. 2. No difference is found between the two different propellant samples in the Japanese standard[10), 11)] for the sensitivity against impact and friction. This indicates that these DEFAH binder-based samples were very excellent in IM performance.

7. Conclusions

The results of the theoretical calculations and the burning rate measurements indicated that DEFAH prepolymer greatly improves the burning rate and the specific impulse of the composite propellant. Especially, in the AN-based propellant, the stable combustion was observed even at the pressure range which the HTPB propellant didn't. And it was also confirmed that no difference exists in impact and friction sensitivities between the both DEFAH-based propellant and HTPB-based propellant.

Table 1 Compositions of propellant samples (wt %).

Sample	Binder		Oxidizer	
	DEFAH	HTPB	AN	AP
DEFAH / AN	30		70	—
HTPB / AN	—	30	70	—
DEFAH / AP	20	—	—	80
HTPB / AP	—	20	—	80

Table 2 Impact and friction sensitivities of propellant samples.

Sample	Impact sensitivity	Friction sensitivity
DEFAH / AP	Class 5 (10 - 15 J)	Class 5 (78.5 - 156.9 N)
HTPB / AP	Class 5 (10 - 15 J)	Class 5 (78.5 - 156.9 N)
DEFAH / AN	Class 8 (> 25 J)	Class 7 (> 353.0 N)
HTPB / AN	Class 8 (> 25 J)	Class 7 (> 353.0 N)

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固体ロケット推進薬用新規高エネルギーヒドラゾン系バインダーのキャラクタリゼーション

藤村郁子

新規に固体コンポジット推進薬用のプレポリマーの設計と合成を行った。理論数値計算及び燃焼速度測定の結果から，このプレポリマーはコンポジット推進薬の比推力及び燃焼速度を大きく向上できることが分かった。特にAN系推進薬については，従来型のHTPBバインダー推進薬では着火できない圧力範囲でも安定した燃焼が得られた。また，両方のバインダーの推進薬で，衝撃感度及び摩擦感度には違いがないことが分かった。

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