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Technical Notes

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Burning Characteristics of Polytetrahydrofuran-Based Composite Propellant

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Introduction

DEVELOPMENT of a wide variety of rockets has required development of propellants having a wide range of performance corresponding to the purposes for which they are used. Especially, a high burning rate propellant is needed when developing a high performance rocket motor. The use of burning rate modifiers, metal fuels, and high energetic materials is a typical method to obtain a high burning rate propellant. Recently, nanosized metal fuels [1–4] and high energetic materials [5,6] have been developed, and researchers have been investigating the burning characteristics of solid propellants using them [1–13]. Glycidyl azide polymer is a typical energetic binder characterized by the $-N_3$ chemical bond [5,6,9–11]. The burning characteristics of the glycidyl azide polymer-based propellant are superior to those of common propellants, such as the hydroxyl-terminated polybutadiene (HTPB)-based propellant. However, it is presently difficult to make a practical solid propellant using high energetic binders and nanosized metal fuels because these materials are expensive and cannot be mass-produced. It is necessary to find an inexpensive material to obtain a high performance propellant.

Another approach is the application of new nonenergetic materials as the propellant fuel-binder. For example, hydrogenated hydroxyl-terminated polyisoprene [14], polymethylmethacrylate [15], polyethylene [16,17], polyvinyl chloride [18,19], polycaprolactone [20], etc., are now being evaluated. The burning performances of propellants using these polymers are not inferior to those of the HTPB-based propellant.

Polytetrahydrofuran (PTHF) is used as an ingredient for rubber products and is produced in several different molecular weights. This polymer is mass-produced commercially and inexpensive. The chemical properties of PTHF are shown in Table 1. The repeating unit of PTHF consists of a single bond and has one oxygen atom, four carbon atoms, and eight hydrogen atoms. PTHF has a hydroxide group on one side of the molecular chain of PTHF and a hydrogen atom on the other side. The molecular structure of PTHF is similar to that of HTPB. PTHF is not an energetic binder. However, it could be expected that the burning performance of a solid propellant could be improved by using PTHF as a binder, compared with HTPB, because the amount of oxygen atom per mole of PTHF is greater than that of HTPB.

In this study, the burning rate characteristics of the PTHF-based composite propellant were investigated and compared with the characteristics of the HTPB-based composite propellant. According to the results, it was found that the performance of the PTHF-based composite propellant is superior to that of the HTPB-based propellant.

Experimental

PTHF and HTPB were used as binder materials. HTPB was used to compare with the burning characteristics of the PTHF-based propellant. PTHF is produced in several different molecular weights. Three kinds of PTHF were used in this study. The molecular weights of the PTHF samples were 650, 1400, and 2900. These PTHF samples were designated as PTHF1, PTHF2, and PTHF3. The number of the symbol increased with the increasing molecular weight. Two blended polymers were prepared with these PTHF samples. Table 2 shows the composition and average molecular weight of the blend polymer. The highest molecular weight is 2900, for PTHF3. The melting point of PTHF increases with the increasing molecular weight [21]. The PTHF blends were obtained by stirring the mixture at 333 K, i.e., above the melting point of PTHF3, for one day. Isophorone diisocyanate (IPDI) was used as the curing agent. Ammonium perchlorate (AP) was used as the oxidizer.

The propellant was prepared at 80% AP. Each strand was 10×10 mm in cross section and 40 mm in length. The burning rate was measured in a chimney-type strand burner that was pressurized with nitrogen at 288 ± 1.5 K. The pressure ranged from 0.6 to 7 MPa. The strand sample was ignited by an electrically heated nichrome wire attached to the top of each strand sample. Two fuse wires were threaded through the strand sample 25 mm apart. The fuse wire was cut as soon as the burning surface passed through the fuse wire. The burning rate was calculated using the cutoff period of the two fuses.

Results and Discussion

Preparation of Binder

The curing reaction of PTHF and IPDI is the urethane reaction. That is to say, the OH group of the PTHF molecule reacts with the NCO group of IPDI and the network is composed. The system has a rubbery consistency by making a dense network. PTHF has two OH groups in the molecule and IPDI has two NCO groups. It is expected that the cross-linking reaction is most efficient when the number of OH groups is the same as that of NCO; the curing test of the PTHF/IPDI system was carried out under this condition of equal group numbers. The curing temperature was 353 K. This mixture was viscous liquid and did not harden even if the mixture was heated for nine days. This result suggested that a dense network could not be formed by the curing reaction because PTHF has a linear molecular structure. It was considered that it was necessary to use a cross-linking modifier to make a rubbery PTHF. Glycerin was used as a cross-linking modifier in this study because glycerin has three OH groups in its molecular structure and is inexpensive.

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Table 1 Chemical properties of binder

Property	1 PTHF (polytetrahydrofuran)	2 HTPB (hydroxyl-terminated polybutadiene)
Molecular structure	HO–[–CH_2–CH_2–CH_2–CH_2–O–]$_n$–OH	HO–[–CH_2–CH = CH–CH_2–]$_n$–OH
Density	0.978 g/cm^3 (PTHF1), 0.981 g/cm^3 (PTHF2), 0.970 g/cm^3 (PTHF3)	0.902 g/cm^3
Melting point	284–292 K (PTHF1), 306–309 K (PTHF2), 303–316 K (PTHF3)	——
Heat of formulation	−219.2 kJ/mol	−21.1 kJ/mol

Table 2 Composition and average molecular weight of PTHF blends

Symbol	Average molecular weight	Mole ratio of blend (-)		
		PTHF1	PTHF2	PTHF3
PTHF4	1400	2	——	1
PTHF5	2150	——	1	1

Table 3 Determination of the optimum propellant preparation for PTHF/IPDI/Glycerin systems

Entry	PTHF sample	PTHF/IPDI/Glycerin mole ratio	Time, day	State at 353 K
1	PTHF1	1.00/2.50/1.00	7	Viscous liquid
2	PTHF1	1.00/2.00/0.67	3	Effervescent rubber
3	PTHF1	1.00/1.50/0.33	7	Rubber
4	PTHF2	1.00/2.50/1.00	7	Viscous liquid
5	PTHF2	1.00/2.00/0.67	3	Effervescent rubber
6	PTHF2	1.00/1.50/0.33	6	Rubber
7	PTHF3	1.00/2.50/1.00	7	Viscous liquid
8	PTHF3	1.00/2.00/0.67	5	Effervescent rubber
9	PTHF3	1.00/1.50/0.33	6	Rubber
10	PTHF4	1.00/2.50/1.00	7	Viscous liquid
11	PTHF4	1.00/2.00/0.67	3	Effervescent rubber
12	PTHF4	1.00/1.50/0.33	5	Rubber
13	PTHF5	1.00/2.50/1.00	7	Viscous liquid
14	PTHF5	1.00/2.00/0.67	5	Effervescent rubber
15	PTHF5	1.00/1.50/0.33	6	Rubber

The curing test of the PTHF/IPDI/glycerin system was carried out with a 3 mol ratio of each unit in the PTHF/IPDI/glycerin, i.e., 1.00/2.00/0.67, 1.00/1.50/0.33, and 1.00/2.50/1.00. Table 3 shows the results of the curing test. When the mole ratio of each unit in the PTHF/IPDI/glycerin is 1.00/1.50/0.33, the mixtures became rubbery within seven days. When the mole ratio in the PTHF/IPDI/glycerin is 1.00/2.50/1.00, the mixtures are viscous liquids and are not hard enough to prepare a solid propellant. On the other hand, the mixtures have a sufficiently hard solid state for a short period when the mole ratio in the PTHF/IPDI/glycerin is 1.00/2.00/0.67. These systems are effervescent rubbers, that is, there are some bubbles in the rubbery composition. The bubble contamination in the propellant influences the burning rate characteristics and, consequently, the reliability of the burning rate is poor [22,23]. This mixture, which has some bubbles, could not be used as a binder of the propellant. The mixture, of which the PTHF/IPDI/glycerin mole ratio of these systems is 1.00/1.50/0.33, could be used as a binder.

The curing test was conducted at both 333 and 393 K in the same way already described. At 333 K, all mixtures are liquid. The result of the curing test at 393 K is the same as that at 353 K. The curing temperature was 353 K in this experiment. Ethylene glycol has two OH groups in its molecule. Ethylene glycol was used as a cross-linking modifier instead of glycerin and the curing test of the PTHF/IPDI/ethylene glycol system was carried out. This system did not become rubbery enough to prepare a solid propellant.

Three kinds of PTHFs and two blends were used in this study. The results of the curing test did not show a definitive dependence of the molecular weight and PTHF blend on the curing characteristics. The mixture, of which the PTHF/IPDI/glycerin mole ratio was 1.00/1.50/0.33, was used as a binder of the propellant in this experiment. Table 4 shows the propellant formulations and the propellant density. The AP content of the propellant was 80%. The density was calculated from the propellant volume and weight. The densities of the AP/PTHF propellants are in the range of 1.62–1.65 g/cm^3, and are higher when compared with that of the AP/HTPB propellant.

Theoretical Propellant Performance

The number of oxygen atoms per unit mass of the binder was calculated and the result is also shown in Table 5. The number for the PTHF binder is almost constant at about 13.7, and that for HTPB binder is 1.2. The number of oxygen atoms per unit mass for the PTHF binder is approximately 11.4 times greater than that for the HTPB binder.

The adiabatic flame temperature and specific impulse were calculated using the NASA SP-273 program [24] with the combustion pressure of 7 MPa and the exit pressure of 0.1 MPa. The results are summarized in Table 5. The performance of the AP/PTHF propellants is almost constant with PTHF type. The adiabatic flame temperature of the AP/PTHF propellant is 260–298 K higher than that of the AP/HTPB propellant. The specific impulse of the AP/PTHF propellant is 9–10 s greater than that of the AP/HTPB propellant. These results indicate that the performance of the AP/PTHF propellants would be superior to that of the AP/HTPB propellant at this composition.

Table 6 shows the estimated principal gas products theoretically evolved from the propellants. The mole fractions of H_2 and H_2O of the AP/PTHF propellant are distinct from those of the AP/HTPB propellant. The mole fraction of H_2 for the AP/PTHF propellant is smaller than that for the AP/HTPB propellant and the fraction of H_2O for the AP/PTHF propellant is greater than that for the AP/HTPB propellant. Furthermore, the mole fraction of CO of the AP/PTHF propellant is lower and that of CO_2 is slightly higher when compared with those of the AP/HTPB propellant. These results suggest that the amounts of the carbon and hydrogen that react with oxygen increase and, therefore, the heat of combustion increases. The oxygen included in the PTHF binder would influence the compositions of the reaction products and cause the changes in the flame temperature and specific impulse of the AP/PTHF propellants.

Figure 1 illustrates the theoretical specific impulse of the AP/PTHF1 propellant and the AP/HTPB propellant. The specific impulse of the AP/PTHF propellant is almost constant, that is, it is

Table 4 Formulation and density of propellant

Propellant	AP, %	PTHF1, %	PTHF2, %	PTHF3, %	PTHF4, %	PTHF5, %	HTPB, %	Glycerin, %	IPDI, %	Density, g/cm^3
AP/PTHF1	80	12.82	——	——	——	——	——	0.59	6.59	1.65
AP/PTHF2		——	15.87	——	——	——	——	0.35	3.78	1.65
AP/PTHF3		——	——	17.76	——	——	——	0.18	2.06	1.63
AP/PTHF4		——	——	——	15.87	——	——	0.35	3.78	1.63
AP/PTHF5		——	——	——	——	17.10	——	0.24	2.66	1.62
AP/HTPB		——	——	——	——	——	18.52	——	1.48	1.58

Table 5 Theoretical performance of propellant

Propellant	Number of oxygen atom per unit mass of binder (-)	Adiabatic flame temperature, K	Specific impulse, s
AP/PTHF1	13.6	2687	240
AP/PTHF2	13.7	2653	239
AP/PTHF3	13.8	2631	239
AP/PTHF4	13.7	2653	239
AP/PTHF5	13.8	2639	239
AP/HTPB	1.2	2358	230

Table 6 Principal reaction products of propellant

Propellant	Mole fraction of reaction products (-)						
	CH_4	CO	CO_2	HCl	H_2	H_2O	N_2
AP/PTHF1	——	0.117	0.144	0.164	0.175	0.312	0.089
AP/PTHF2	——	0.118	0.143	0.162	0.185	0.308	0.085
AP/PTHF3	——	0.118	0.142	0.161	0.189	0.306	0.083
AP/PTHF4	——	0.118	0.143	0.162	0.185	0.308	0.085
AP/PTHF5	——	0.118	0.142	0.161	0.191	0.305	0.083
AP/HTPB	0.001	0.177	0.134	0.150	0.299	0.162	0.077

independent of the molecular weight and PTHF blend. The specific impulse of the AP/HTPB propellant is a strong function of AP loading, reaching a maximum (253 s) at 89% AP. Similarly AP/PTHF propellant reaches a peak (251 s) at 87% AP. The maximum specific impulse of the AP/PTHF propellant is 2 s lower than that of the AP/HTPB propellant. However, the AP content at the maximum specific impulse of the AP/PTHF propellant is 2% smaller than that of the AP/HTPB propellant. The propellant was prepared at 80% AP in this experiment. 80% AP is closer to ideal AP loading for PTHF and farther from ideal AP loading for HTPB and the specific impulse of the AP/PTHF propellant is 9 s higher than that of the AP/HTPB propellant.

Burning Rate Characteristics

Figure 2 shows the experimental data and corresponding fitting lines of the burning rate characteristics of the AP/PTHF propellants and the AP/HTPB propellant. The experimental error is within ±5%. Their burning rates linearly increase on the logarithmic scale in the pressure range of 0.6–7 MPa. The burning rate characteristics of the AP/PTHF propellants are almost constant. This indicates that the burning rates of the propellants prepared with the PTHF binder were independent of the molecular weight and PTHF blend. The burning rates of the AP/PTHF propellants were approximately twice as high as that of the AP/HTPB propellant. The pressure exponent of the AP/PTHF propellant is approximately 0.43 and is slightly higher than that of the AP/HTPB propellant of 0.37. This value does not matter in practical applications [25,26]. It is found that the PTHF/IPDI/

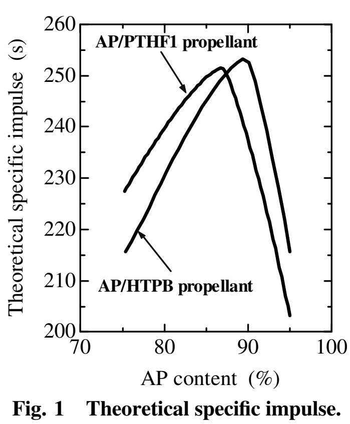

Fig. 1 Theoretical specific impulse.

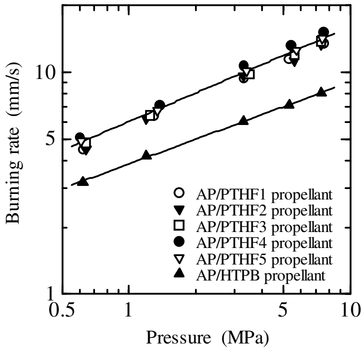

Fig. 2 Burning rate characteristics.

glycerin system is an effective binder for obtaining a high burning rate composite propellant.

Conclusions

The burning characteristics of ammonium perchlorate (AP)/polytetrahydrofuran (PTHF) composite propellants were investigated and compared with those of the AP/hydroxyl-terminated polybutadiene (HTPB) propellant. PTHF could not become a solid with only isophorone diisocyanate as the curing agent. PTHF becomes sufficiently rubbery for use as a binder by the addition of glycerin as a cross-linking modifier. The burning characteristics of the AP/PTHF propellants are superior to that of the AP/HTPB propellant at 80% AP. The burning characteristics of the AP/PTHF propellants are independent of the molecular weight and PTHF blend.

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