Research paper

Application of polytetrahydrofuran as a plasticizer of HTPB binder

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Abstract

Hydroxyl-terminated polybutadiene (HTPB) has been generally used as a binder for composite propellant. The liquid plasticizer is added to the propellant in order to improve its processing and mechanical properties. It was reported that polytetrahydrofuran (PTHF) would be an attractive propellant binder. The chemical structure of PTHF is similar to that of HTPB, and therefore, PTHF should mix easily and uniformly with HTPB. And there is oxygen in the repeating unit of PTHF. It was expected that PTHF would be useful not only as the binder ingredient but also as the plasticizer of a HTPB binder. The effects of PTHF as a plasticizer of a HTPB binder were evaluated in this study. With an increasing quantity of PTHF, the blend softened enough to be of use as a binder for a composite propellant when the mole ratio of PTHF to HTPB was below 0.16. The processability, mechanical properties, and thermal decomposition behavior of HTPB binder was improved by a small amount addition of PTHF to HTPB. The molecular weight of PTHF influenced the curing behavior of binders though it did not affect the mechanical properties and thermal decomposition behavior.

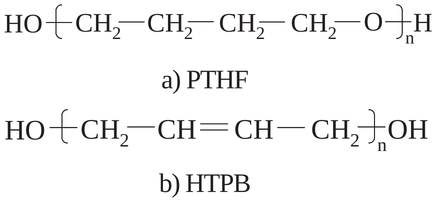
Keywords : plasticizer, polytetrahydrofuran, hydroxy-terminated polybutadiene, propellant binder

1. Introduction

Solid propellants should have the burning characteristics required to move a rocket forward. Furthermore, the mechanical properties of solid propellants are based on the structural loads that they are likely to be subjected to during processing, handling, curing, transportation, flight, and other environmental extremes1). The major solid propellants of rocket motors are double base propellants and composite propellants. Double base propellants form a homogeneous propellant grain composed of nitrocellulose, nitroglycerin, and minor percentages of additives. Composite propellants form a heterogeneous propellant grain with powdered oxidizers and a fuel held together in a matrix of synthetic rubber binder. Composite propellant has flexible burning characteristics and mechanical properties, compared with double base propellant.

Composite propellant is produced by the following method. The first step is the mixing of the oxidizer, binder, burning rate modifier, plasticizer, metal fuel, etc. The next involves the removal of air from the mixture. The final step is casting the propellant to a rocket motor. Hydroxyl-terminated polybutadiene (HTPB) has been generally used as a binder for composite propellants. The liquid plasticizer is added to propellant in order to improve mechanical properties, such as its strength, elongation, and modulus and to improve processing properties, such as mixing viscosity, casting, and pot life. Polyurethanes are one of the desirable binder systems mainly due to the ease with which the propellant properties can be tailored. Dioctyl phthalate, dioctyl adipate, isodecyl pelargonete, and others are used as plasticizer for composite propellants2−5). Recently, researchers developed several energetic plasticizers and investigated the effects, finding improvements in the mechanical properties of cured HTPB after addition of these plasticizers6−14). However, the synthetic processes of the energetic plasticizers are complicated, and therefore, it is difficult to manufacture these plasticizers industrially. Currently, these energetic plasticizers have not been used for practical applications because they are expensive.

Polytetrahydrofuran (PTHF) is a raw material for rub-



$$HO\{CH_2-CH_2-CH_2-CH_2-O\}_nH$$

a) PTHF

$$HO\{CH_2-CH=CH-CH_2\}_nOH$$

b) HTPB

Fig. 1 Chemical structures of PTHF and HTPB.

ber products. This prepolymer has been produced on a commercial basis. Figure 1 shows the chemical structures of PTHF and HTPB. The structure of PTHF is similar to that of HTPB. Because there is oxygen in the repeating unit of PTHF, the specific impulse and burning rate characteristics of the AP-based composite propellant could be improved by the use of PTHF as a binder, compared with the propellant used with HTPB [15]. However, PTHF is not an energetic binder.

The thermal behavior and tensile property of PTHF/HTPB mixtures at various values of mass ratio were measured to investigate the effectiveness of PTHF as a binder[16]. The mixtures prepared at a PTHF/HTPB mass ratio of 0.6 had favorable curing behavior, thermal decomposition behavior, and tensile properties for the propellant binder. It was proved that PTHF would be an attractive binder ingredient.

As described above, the plasticizer is added to the propellant binder to improve processing and mechanical properties. The amount of plasticizer added to a binder is small-less than 10% of binder. PTHF could uniformly mix into HTPB because the chemical structure of PTHF is similar to that of HTPB. The processing and mechanical properties of HTPB binder would improve, even if the quantity of PTHF added to HTPB is small. We expected that PTHF would be useful not only as the binder ingredient for a composite propellant but also as the plasticizer of a HTPB binder. In order to evaluate the effects of PTHF as a plasticizer of a HTPB binder, we investigated the curing behavior, mechanical properties, and thermochemical behavior of HTPB containing PTHF as the plasticizer in this study.

2. Experimental methods

2.1 Materials and preparation

We used HTPB R-45M as a binder material and PTHF as a plasticizer. Commercial PTHFs of three different average molecular weights were utilized in this study. Table 1 shows the physical properties of HTPB and PTHF. The densities of the PTHF samples were almost constant and were slightly larger than those of the HTPB samples. The melting point of PTHF increases with increasing average molecular weight.

Table 1 Physicalproperties of HTPB and PTHF.

Symbol	M_n	Density at 298 K (gcm^{-3})	Melting point (K)	Apparent viscosity at 333 K (Pa s)
HTPB	3270	0.902	–	1.24
PTHF1	650	0.978	284–292	0.09
PTHF2	1400	1.000	306–309	0.25
PTHF3	2900	0.970	303–316	1.52

Isophrone diisocyanate (IPDI) was used as a curing agent. The ratio of NCO groups of IPDI to OH groups of HTPB was 1.22. In previous study on the PTHF/HTPB mixtures at various values of mass ratio, the ratio of NCO groups of IPDI to OH groups of HTPB and PTHF was 1.22[16].

We prepared the blend as follows. First, PTHF was added to HTPB and blended sufficiently. Second, we added IPDI as a curing agent to the mixture. The blend remained in a thermostat for a week to cure. The mixing and curing temperature was 333 K in this study since this was the temperature to mix and cure HTPB-based composite propellants[17]. The melting point of PTHF is less than 316 K and thus, PTHF samples are liquid at 333 K, the mixing and curing temperature.

The HTPB added with PTHFshould possess adequate hardness to use as a binder for composite propellants. According to the results of a curing test, the HTPB became softer with an increasing quantity of PTHF and was a high viscous liquid when the mole ratio of PTHF to HTPB (ξ) was greater than 0.16. Therefore, the blend having a $\xi > 0.16$ was not used as a binder for a composite propellant. We investigated the curing behavior, mechanical properties, and thermochemical behavior of the HTPB binders at ξ of 0, 0.02, 0.04, 0.08, and 0.16 in this study. Table 2 lists the formulations of the blends prepared below a ξ of 0.16 prepared in this study. The HTPB binders added with PTHF1, PTHF2, and PTHF3 were designated as HTPB1, HTPB2, and HTPB3.

As described above, HTPB and IPDI were in the mole ratio 1 : 1.22. At $\xi = 0.22$, the sum of the OH groups of HTPB and PTHF theoretically equaled the number of NCO groups of IPDI. Therefore, the HTPB binder at $\xi = 0.16$ is stoichiometrically in excess of the NCO groups.

2.2 Measurement of viscosity

We measured the apparent viscosity of the blend with a

Table 2 Formulations of HTPB binders prepared in this study.

ξ	HTPB1			HTPB2			HTPB3		
(–)	HTPB (%)	PTHF1 (%)	IPDI (%)	HTPB (%)	PTHF2 (%)	IPDI (%)	HTPB (%)	PTHF3 (%)	IPDI (%)
0	92.59	0	7.41	92.59	0	7.41	92.59	0	7.41
0.02	92.02	0.37	7.61	91.64	0.79	7.58	90.87	1.61	7.52
0.04	91.69	0.73	7.58	90.92	1.55	7.52	89.43	3.17	7.40
0.08	91.02	1.45	7.53	89.53	3.06	7.41	86.68	6.15	7.17
0.16	89.73	2.85	7.42	86.87	5.94	7.19	81.67	11.57	6.76

capillary type flow tester. The measurement of apparent viscosities of the materials alone and the HTPB binders added with IPDI were conducted using a die with ϕ 0.5 × 15 mm and that with ϕ 0.5×1 mm, respectively. The load was 0.98 MPa and the temperature was 333 K.

2.3 Swelling test

The sample size was approximately 20×20×3 mm, and the temperature was 298 K. We used toluene as a swelling solvent. The cured HTPB binders completely swelled to equilibrium after 2 days. We measured the mass of the sample before and after immersion in toluene and calculated the volumes. The densities of the cured binders were in the range of 0.89−0.94 g cm^{-3}. The volume fraction of the sample in the swollen HTPB (v_s) was determined from dividing the volume before swelling by that of the swollen HTPB volume.

2.4 Measurement of mechanical properties

We investigated the mechanical properties of the cured binder by a tension test and a hardness test. The mechanical properties were averaged from five measurements. The tensile test was carried out using dumb−bells conforming to JIS K 6251 at a cross-head speed of 500 mm min^{-1} at 293 K with an autograph. Dumb-bell shaped samples were punched out of the cured sample in approximately 3 mm thicknesses.

The hardness test measurements were done on the basis of ASTM D2240. We measured the hardness at 253, 279, 298, and 333 K using a Durometer Type OO rubber hardness tester. This durometer can be used to measure the hardness of soft rubber, thermoplastic elastomers, and very soft plastics. We converted the indicated value of the durometer into a force in Newtons according to the standard mentioned above.

2.5 Measurement of thermal decomposition behavior

We investigated the thermal decomposition behavior of the cured binder by differential thermal analysis (DTA) and thermogravimetry (TG). The equipment was operated with a nitrogen flow condition at atmospheric pressure. The sample containers for the equipment were made of aluminum. The sample mass was approximately 4 mg. The heating rate was 20 K min^{-1}.

3. Results and discussion

3.1 Curing behavior

During the manufacture of composite propellants, the uncured propellant is sufficiently mixed and then cast into the motor case. A low viscosity uncured propellant is desirable for easier mixing and casting. The pot life should also be extended by decreasing the curing rate of the binder. Extending the pot life should provide sufficient time for mixing and casting. If there were no other bonding forces between the particles and binder ingredients, the viscosity of the uncured propellant would be dependent on that of the liquid propellant ingredients, and the viscosity of the uncured propellant would decrease with decreasing viscosity of the binder and/or the plasticizer.

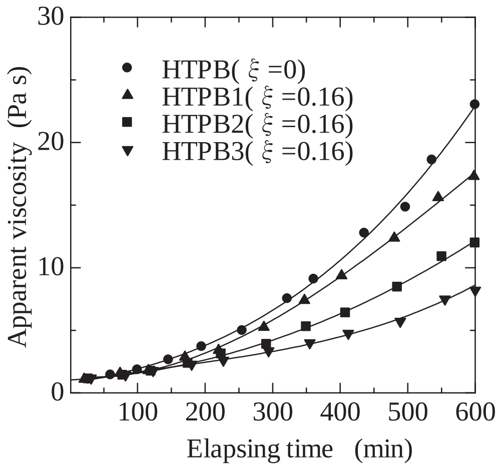


Fig. 2 Relationships between viscosity and elapsing time of HTPB ($\xi = 0$) and HTPBs1−3 ($\xi = 0.16$).

Table 1 shows the apparent viscosities of HTPB and PTHF from the use of a die with ϕ 0.5 × 15 mm at 333 K. These samples did not contain IPDI. The apparent viscosities of PTHF1 and PTHF2 were lower than that of HTPB. The viscosity of PTHF3 was close to that of HTPB because the molecular weight of PTHF3 is almost the same as that of HTPB. The viscosity of the HTPB1 and HTPB2 would be smaller that that of HTPB alone because the viscosity of the PTHFs1 and 2 was lower than that of HTPB. The viscosity of the HTPB3 was almost the same as that of HTPB because the viscosity of the PTHF3 was close to that of HTPB.

Figure 2 shows the apparent viscosities of the HTPB ($\xi = 0$) and the HTPBs1−3 ($\xi = 0.16$) versus elapsing time. These viscosities increased with increasing time because we added IPDI as a curing agent to the samples. The initial viscosity of the HTPB binders was in the range of 1.01 −1.19 Pa s. These values were barely decreased by the addition of PTHF to the HTPB because the added amount of PTHF was small. The apparent viscosities of HTPBs1−3 were almost the same as that of HTPB until 100 minutes. Thereafter, the apparent viscosities of the blends were lower than that of the HTPB, and the increase in viscosity versus time decreased with the increasing molecular weight of PTHF. Table 3 shows the apparent viscosities at 600 minutes after heating. The viscosity of HTPB3 was approximately one−third of that of HTPB.

The increasing rate of viscosity versus time decreased with the addition of PTHF even for a slight quantity of PTHF, and the increase in the viscosities of the binders depended on the molecular weight of PTHF. PTHF is linear, and the length of the main chain increases as the molecular weight of PTHF increases. We believed that PTHF with a larger molecular weight could not easily react with

Table 3 Apparent viscosity of HTPB binders at 600 minutes.

Symbol	Apparent viscosity (Pa s)
HTPB ($\xi = 0$)	23.0
HTPB1 ($\xi = 0.16$)	17.4
HTPB2 ($\xi = 0.16$)	12.0
HTPB3 ($\xi = 0.16$)	8.2

Table 4 Values of v_s and N.

ξ (−)	HTPB1		HTPB2		HTPB3	
	v_s (−)	N (mol cm^{-3})	v_s (−)	N (mol cm^{-3})	v_s (−)	N (mol cm^{-3})
0	0.186	15.1×10^{-5}	0.186	15.1×10^{-5}	0.186	15.1×10^{-5}
0.02	0.134	7.5×10^{-5}	0.136	7.7×10^{-5}	0.130	7.1×10^{-5}
0.04	0124	6.4×10^{-5}	0.121	6.1×10^{-5}	0.121	6.1×10^{-5}
0.08	0.104	4.6×10^{-5}	0.096	3.9×10^{-5}	0.102	4.4×10^{-5}
0.16	0.068	2.0×10^{-5}	0.059	1.5×10^{-5}	0.055	1.4×10^{-5}

IPDI and, furthermore, would interfere with the reaction between HTPB and IPDI.

Based on the experimental results described above, we expected that the addition of PTHF would be effective not only in decreasing the processing viscosity of HTPB–based composite propellants but also in extending their pot life. These effects depended on the molecular weight of PTHF. These results should facilitate the manufacture of new HTPB–based propellants using PTHF as a modifier for processing.

3.2 Swelling behavior

Uncrosslinked polymers dissolve in a solvent. On the other hand, crosslinked polymers do not dissolve but swell. The swelling of a sample implies that the polymer is crosslinked. The crosslinked polymer swells with solvent to equilibrium and the amount of swelling is dependent on the interaction between the polymer and the solvent, the length between crosslinking points, the temperature, and several other factors. We estimated the crosslink density (N) of HTPB by the amount of swelling to equilibrium[18].

All of the cured samples swelled with toluene, and thereby, we found that they were all crosslinked. From the swelling experiment, v_s was calculated and is listed in Table 4. The relationship between N and v_s is represented by the following equation[18]:

$$\ln(1-v_s)+v_s+\chi v_s^2 = -NV_1\left(v_s^{\frac{1}{3}}-\frac{v_s}{2}\right) \tag{1}$$

where χ is the Flory–Huggins polymer-solvent dimensionless interaction term and V_1 is the molar volume of the solvent. The V_1 of toluene was 106 cm^3 mol^{-1}, and χ of a polybutadiene–toluene system is 0.35[18]. Because the structure of PTHF is similar to that of HTPB and the amount of PTHF in HTPB was small, χ of the blend–toluene systems would almost equal that of the HTPB–toluene system, so the value of χ used in this study was 0.35, the χ of polybutadiene–toluene. We calculated N with Equation (1) and listed the results in Table 4. The N at $\xi=0$ is 15.1×10^{-5} mol cm^{-3}. The Ns of the blends were not dependent on the average molecular weight of PTHF and decreased with increasing ξ. The N at $\xi = 0.16$ was 1.4–2.0×10^{-5} mol cm^{-3},approximately one–tenth as large as that at ξ of 0.

The network structure of crosslinked polymer cannot be entirely evaluated merely by the value N. However, a decreasing N generally suggests that the network would loosen. As seen in Table 4, the value of N decreased with increasing ξ. This fact indicated that the network structure of HTPB would loosen with the presence of a small amount of PTHF in HTPB.

3.3 Mechanical properties

Figure 3 shows the stress-strain curves of HTPB2. The stress increased with increasing strain, and samples broke at certain strains. The ultimate tensile strain was almost the same as the elongation at breaking. We determined the ultimate tensile strength (σ_m) and ultimate tensile strain (ε_m) of the samples from these curves.

Figure 4 shows the effects of ξ on σ_m and ε_m. The σ_m increased with increasing ξ below a ξ of approximately 0.07, and above that value, σ_m decreased. That is to say, σ_m reached a maximum value at a ξ value of approximately 0.07 for all samples. The maximum values of σ_m were almost constant in a range of 0.81–0.86 MPa. On the other hand, ε_m increased with increasing ξ. The σ_m and ε_m at ξ = 0.16 were 0.42–0.58 MPa and 1433–1828%, respectively. The tensile properties of HTPBs1–3 were scarcely influenced by the average molecular weight of PTHF.

The value of σ_m increased with decreasing ε_m because σ_m increased and ε_m decreased as the degree of crosslinking increased[19]. Therefore, σ_m generally increased when ε_m decreased. As shown in Figure 4, both σ_m and ε_m of HTPBs1–3 increased with increasing ξ below a ξ of 0.07. It was found that the cured blends had a unique tension behavior below a ξ of 0.07.

As mentioned above, the value of N decreased because the network structure would loosen as ξ increased. This result suggested that σ_m decreased and ε_m increased as ξ increased. From the standpoint of network density, below a ξ of 0.07, the increase in ε_m could be rationalized; however, the increase in σ_m could not. We expected that this

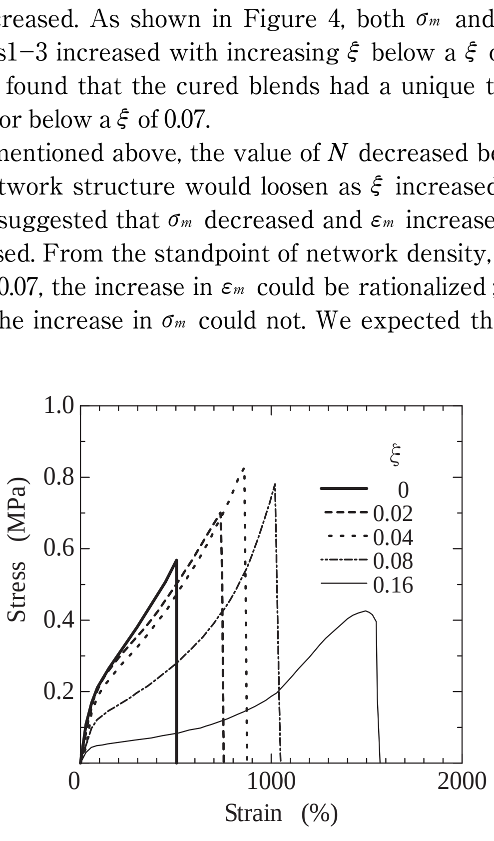


Fig. 3 Stress–strain curves of the cured HTPB2.

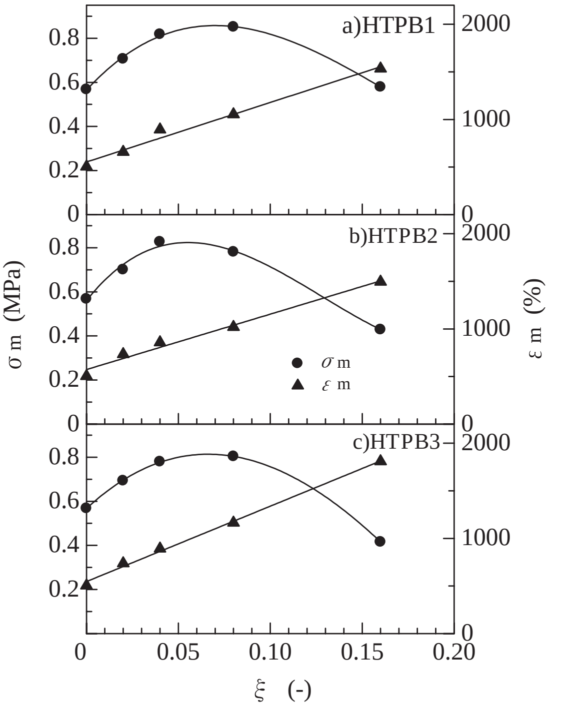


Fig. 4 Effects of ξ on σ_m and ε_m.

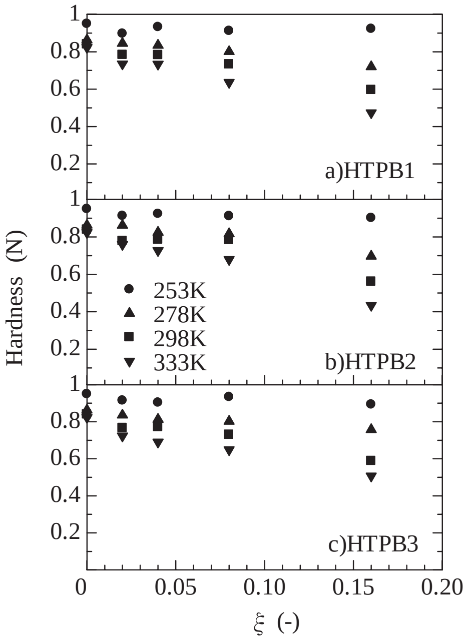


Fig. 5 Effects of temperature and ξ on hardness.

contradiction would be attributable to the presence of PTHF in the HTPB network that forms the continuous matrix. A detailed reason could not be resolved in this study.

Figure 5 shows the effects of temperature and ξ on the hardness. The hardness of HTPBs1−3 was lower than that of HTPB alone in this temperature range. At 253 K, the hardness of HTPBs1−3 scarcely depended on ξ. Above 278 K, the hardness decreased with increasing ξ,and the influence of ξ on the hardness increased as the temperature increased. The hardness of the blend was barely dependent on the molecular weight of the PTHF.

We expected that the hardness of the propellant would decrease by a decrease in the hardness of the binder ingredient. The reduction in hardness indicated that the material softened. A softer solid propellant is convenient for resisting an explosion of the rocket motor due to impact and friction. Thus, the vulnerability of the propellant would be reduced. The addition of PTHF to the HTPB may be an effective way to obtain a less sensitive HTPB-based propellant.

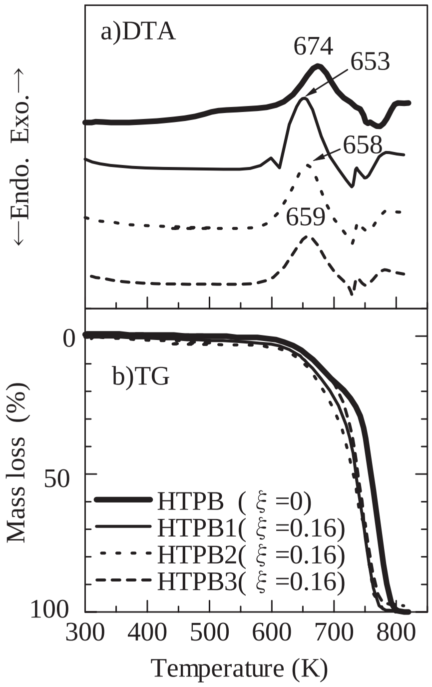


Fig. 6 TG−DTA thermograms of HTPB (ξ = 0) and HTPBs1−3 (ξ = 0.16).

3.4 Thermal decomposition behavior

We investigated the thermal decomposition behavior of the HTPB (ξ=0) and HTPBs1−3 (ξ=0.16) by TG−DTA. Figure 6 shows the TG−DTA thermograms of these samples. According to the DTA thermograms, the peak of the exothermic decomposition of the HTPB was 674 K, and those of HTPBs1−3 were almost constant over a range of 653−659 K. The exothermic decomposition peak shifted approximately 20 K lower by the addition of PTHF to the HTPB.

According to the TG thermograms, the consumption of the HTPB and the blends began around 600 K. The end temperature decomposition of HTPB was at 790 K while that of HTPBs1−3 was around 778 K. First derivative mass loss of HTPB was 769 K and those of the blends were constant around 748 K. The temperature ranges of the remarkable consumptions of the cured blends were also approximately 20 K lower than that of the cured HTPB. These results indicated that PTHF shifted the main decomposition region of HTPB to lower temperatures.

We found that the thermal decomposition behavior of the blends was superior to that of HTPB. These results suggested that the addition of PTHF to HTPB would improve the thermal decompositions of HTPB-based composite propellants and would give HTPB-based propellants enhanced burning rates.

4. Conclusions

The chemical structure of polytetrahydrofuran (PTHF) is similar to that of hydroxyl-terminated polybutadiene (HTPB) commonly used as a composite propellant binder. It was expected that PTHF would be useful as a plasticizer of a HTPB binder. We investigated the mechanical properties and thermochemical behavior of the cured HTPB added with PTHF and the viscosities of the uncured samples in order to evaluate the application of PTHF as a plasticizer for a HTPB binder. The results were as follows. (1) The increases in viscosity versus elapsing time of HTPB added with PTHF were smaller than that of HTPB alone. (2) The hardness decreased with both an increasing PTHF/HTPB mole ratio and an increasing temperature above 278 K. (3) The ultimate tensile strength increased with an increasing PTHF/HTPB mole ratio below approximately 0.07 ; above that value, the strength decreased. The ultimate tensile strain increased as the PTHF/HTPB mole ratio increased. (4) The presence of PTHF in HTPB shifted the main decomposition region of HTPB to lower temperatures. It was found that PTHF was an effective plasticizer to prepare high performance composite propellants.

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HTPBバインダの可塑剤としてのポリテトラヒドロフラン

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末端水酸基ポリブタジエン（HTPB）はコンポジット推進薬のバインダとして最も広く使用されている。可塑剤は，推進薬の製造性，機械的特性や燃焼性などの改善のために少量添加されている。ポリテトラヒドロフラン（PTHF）は推進薬バインダとして有効であることは報告された。PTHFの構造はHTPBと似ているため，PTHFは容易かつ均一にHTPBと混合できる。また，PTHFはその繰り返し単位中に酸素を含んでいる。PTHFはバインダとしてだけでなく，HTPBバインダの可塑剤としても使用できると考えた。本実験では，PTHFのHTPBバインダの可塑剤としての有効性について調べた。PTHFの添加量の増加にしたがって，HTPBバインダは軟らかくなった。PTHF/HTPBのモル比が0.16以下では，推進薬バインダとして使用可能であることがわかった。HTPBバインダの製造性，機械的特性，熱分解性は，少量のPTHFを添加することによって改善できた。PTHFの平均分子量は，硬化特性には影響したが，機械的特性と熱分解性には影響しなかった。

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