

# Thermal decomposition behavior of AN-based composite propellant with hydroxyl-terminated polybutadiene/polytetrahydrofuran blend as a binder

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## Abstract

Hydroxyl-terminated polybutadiene (HTPB) is widely used as a propellant binder and polytetrahydrofuran (PTHF) is a useful binder ingredient that improves the burning characteristics of composite propellant. The HTPB/PTHF blends have a preferable curing behavior and tensile property for a propellant binder. This study investigated the thermal decomposition behaviors of ammonium nitrate (AN)-based composite propellants with the HTPB/PTHF blends as a binder.

From the results of TG-DTA, the main decomposition temperature range of the HTPB/PTHF blends shifted lower as the proportion of PTHF in the binder ( $\xi$ ) increased. The AN/HTPB/PTHF propellant decomposed in two stages and the thermal decomposition of the AN/HTPB/PTHF propellants occurred at lower temperature, compared to that of the AN/HTPB propellant. In the visual observation of the decomposition phenomena, a small quantity of the HTPB/PTHF binders above  $\xi$  of 0.6 began to liquefy at 474 K, while the shape of the binder was preserved. The propellants decomposed heavily and the generation of smoke was more vigorous in the temperature range of 530–550 K. The size of the residue was smaller than that of the propellant sample before heating. The residue looked like a sponge, and the amount and the size of the voids in the residue increased with increasing  $\xi$ . It was found that the HTPB/PTHF binder around AN particles liquefied or decomposed, and the quantity of liquefied or decomposed binder increased with increasing  $\xi$ .

**Keywords**: polytetrahydrofuran, hydroxyl-terminated polybutadiene, thermal decomposition, ammonium nitrate, Propellant

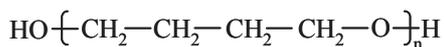
## 1. Introduction

The ammonium perchlorate (AP)-based propellants are widely used as solid propellant because they have excellent burning and mechanical characteristics. One of the few serious drawbacks of AP-based propellants is that the products of combustion, which include hydrogen chloride, chlorine, and chlorine oxides, cause atmospheric pollution.

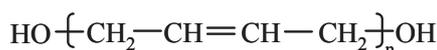
Recently, ammonium nitrate (AN)-based composite propellants have gained popularity, although there are some major problems associated with the use of AN-based propellants, namely: low burning rate, poor

ignitability, and low energy compared to AP-based propellants. Numerous approaches have been adopted to improve the burning characteristics of AN-based propellants, including the use of catalysts<sup>1-4)</sup>, the addition of metals<sup>5-9)</sup>, and the use of energetic binders based on azide polymers<sup>10-14)</sup>.

The application of an energetic binder is an effective approach that can be applied to AN-based propellants. However, the synthetic processes for the preparation of energetic binders are complicated, therefore the manufacturing of these binders industrially is difficult. To date, these energetic binders have not been used for



(a) PTHF



(b) HTPB

**Fig. 1** Chemical structures of PTHF and HTPB

practical applications because they are too expensive.

Polytetrahydrofuran (PTHF) is a raw material for rubber products that has been produced on a commercial basis. Figure 1 shows the chemical structures of PTHF and hydroxyl-terminated polybutadiene (HTPB), a widely used binder. The repeat unit of PTHF consists of oxygen, carbon and hydrogen, and both sides of the molecular chain have a hydroxide group. The structure of PTHF is similar to that of HTPB. PTHF is not an energetic binder. However, it is expected that the performance of a solid propellant could be improved by using PTHF as a binder, relative to HTPB, because the number of oxygen atoms per mole of PTHF is greater than that of HTPB.

The effect of PTHF as a propellant plasticizer or binder on processability, mechanical properties, thermal decomposition behavior, and burning rate characteristics has been reported<sup>15–18</sup>. The burning rate characteristics of the propellant did not improve when PTHF was used as a plasticizer, because the added amount of PTHF was too low<sup>18</sup>. However, the burning characteristics of the propellant improved when PTHF was used as a binder<sup>15,16</sup>.

In a previous study<sup>19</sup>, blends of HTPB and PTHF were used as a binder. The curing behavior and tensile properties of the HTPB/PTHF blends were investigated. Both of these properties were found to depend on the molecular weight of PTHF and the HTPB/PTHF mass ratio. In this study, the influence of the HTPB/PTHF blend on the thermal decomposition behavior of AN-based composite propellants was investigated. This paper is one in a series of studies investigating the influence of PTHF on thermal decomposition behavior and burning characteristics of propellants.

## 2. Experiment

### 2.1 Sample preparation

AN (Kanto Chemical Co., Inc.) was used as an oxidizer and was ground with a vibration ball mill for 5 minutes to generate a powder. The weight mean diameter of AN was 125  $\mu\text{m}$ . PTHF (DuPont) and HTPB were used as binder materials. PTHF is produced in several different molecular weights. Three PTHF samples with molecular weights of 650, 1400, and 2900, designated as PTHF1, PTHF2, and PTHF3, respectively, were used in this study. The proportion of PTHF in the binder ( $\xi$ ) is 0, 0.2, 0.4, 0.6, and 0.8.

Isophorone diisocyanate (IPDI, Tokyo Chemical Industry Co., Ltd.) was used as the curing agent. The ratio of the NCO group of IPDI to the OH group of HTPB and PTHF was 1.2. Table 1 describes the binder formulations.

We prepared the blend binder in the following manner.

**Table 1** Binder formulations.

Binder	$\xi$ [–]	Mass fraction [%]		
		HTPB	PTHF	IPDI
PTHF1	0	92.5	0.0	7.5
	0.2	69.7	17.4	12.8
	0.4	49.5	32.9	17.6
	0.6	31.3	46.9	21.8
	0.8	14.9	59.5	25.6
PTHF2	0	92.5	0.0	7.5
	0.2	72.5	18.1	9.4
	0.4	53.3	35.6	11.1
	0.6	34.9	52.3	12.8
	0.8	17.1	68.5	14.4
PTHF3	0	92.5	0.0	7.5
	0.2	73.8	18.5	7.7
	0.4	55.3	36.8	7.9
	0.6	36.8	55.2	8.1
	0.8	18.4	73.4	8.2

First, PTHF and HTPB were blended sufficiently until a homogeneous material was achieved. Second, we added IPDI to the mixture and blended. The blend remained in a thermostat at 353 K for a week to cure. In the case of propellant preparation, AN was well-mixed with the blend binder and IPDI, and then the mixture was left in a thermostat at 353 K for a week.

### 2.2 Measurement of thermal decomposition

The thermal decompositions of the binders and propellants were measured by differential thermal analysis (DTA) and thermogravimetry (TG) using Rigaku Thermo plus 2 TG-DTA 8120. The equipment was operated under flowing nitrogen at atmospheric pressure. DTA and TG were carried out with a heating rate of 20 K  $\text{min}^{-1}$ , and the TG-DTA measurements were conducted more than four times for each sample. The averages of the TG-DTA curves from the data were used in this experiment.

Decomposition phenomena of AN, binders, and propellants were observed using a hot plate heated from room temperature to 636 K at a heating rate of approximately 12 K  $\text{min}^{-1}$  under atmospheric pressure. The temperature at the surface of the hot plate was measured with a K-type thermocouple. AN was in powder form, and the size of the binder and propellant was 6  $\times$  6  $\times$  3 mm. The sample was placed on a glass dish (20  $\times$  20  $\times$  0.2 mm), which was then placed on the hot plate.

## 3. Results and discussion

### 3.1 Thermal decomposition behavior of binders

#### 3.1.1 TG-DTA

The TG-DTA curves of HTPB/PTHF binders are provided in reference 19. The influence of  $\xi$  on TG-DTA curves of the binders was not significantly dependent on the molecular weight of PTHF. Figure 2 shows the TG-DTA curves of HTPB/PTHF2 binders. In the DTA curve

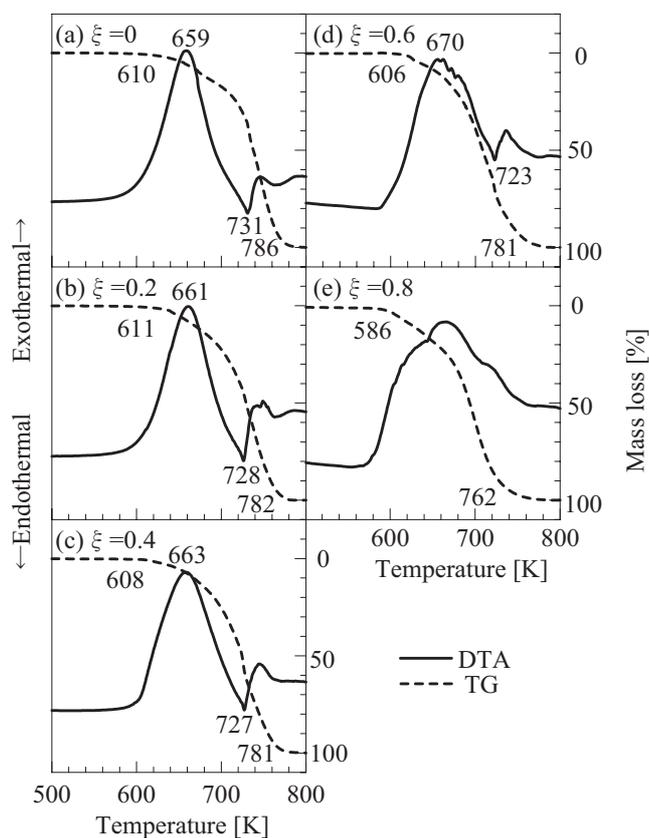


Fig. 2 TG-DTA curves of the HTPB/PTHF2 binders

of HTPB binder, there is an exothermic peak at 659 K. In the DTA curves of HTPB/PTHF2 binders at  $\xi$  of 0.2–0.6, the exothermic peak is observed in the temperature range of 661–670 K. The peak becomes broader as the value of  $\xi$  increases, and a definitive peak is not observed in the DTA curve of the binder at  $\xi$  of 0.8. There is an endothermic peak around 727 K in the DTA curves of the binders at  $\xi$  of 0–0.6, while the endothermic peak is not observed in the DTA curve of the binder at  $\xi$  of 0.8.

According to the TG curves, the consumption of the binders at  $\xi$  of 0–0.6 is observed beginning at approximately 610 K, and the sample is completely consumed at around 783 K. The consumption of the binder at  $\xi$  of 0.8 starts at 586 K and ends at 762 K. The decomposition temperature range of the binder at  $\xi$  of 0.8 is approximately 20 K lower than that of the binders at  $\xi$  of 0–0.6. Furthermore, the mass loss of the blended binders is greater than that of the HTPB binder, which is

below approximately 700 K.

The peak consumption rate of the binder was determined from the first derivative mass loss. Table 2 reports the temperature of the peak consumption rate for different binder formulations. This temperature decreases with increasing  $\xi$ , suggesting that the main thermal decomposition temperature range shifts to lower temperatures as the value of  $\xi$  is increased.

### 3.1.2 Decomposition phenomena

The binders were heated on a hot plate from room temperature to 636 K, and the decomposition phenomena of the HTPB/PTHF binders were observed by visual inspection. Figure 3 shows the decomposition phenomena of the HTPB/PTHF2 binders at  $\xi$  of 0, 0.4, and 0.8. The portion of the HTPB binder that was in contact with the hot plate changes to yellow, and varies from yellow to brown at temperatures above 460 K. The colored portion spreads through the whole sample, and the depth of the brown color increases as the temperature increases. At 636 K, the entire sample becomes black. The liquefaction of the HTPB binder is not observed up to 636 K; that is, there is no deformation.

The decomposition phenomena of the binder at  $\xi$  of 0.4 were almost the same as those at  $\xi$  of 0.2. For the HTPB/PTHF2 binder at  $\xi$  of 0.4, the portion of the sample that came in contact with the heater changes to a brown color at 546 K. The colored portion spreads through the whole sample, and the depth of the brown color increases as the temperature increases. At 636 K, the entire sample becomes dark brown. The liquefaction of the sample is not observed at temperatures up to 636 K; the shape of the binders at  $\xi$  of 0.4 does not deform in a manner similar to the HTPB binder.

The decomposition phenomena of the binder at  $\xi$  of 0.8 were almost the same as those at  $\xi$  of 0.6. For the HTPB/PTHF2 binder at  $\xi$  of 0.8, the portion of the sample in contact with the heater liquefies at approximately 474 K, and the liquefied binder is transparent and yellow. The quantity of the liquefied sample increases with increasing temperature. The solid sample changes to a yellow color, and the liquefied component varies from yellow to brown as the temperature increases. The entire sample is a light brown color at approximately 636 K. The shape of the sample remains nearly unchanged. The quantity of the liquefied sample at  $\xi$  of 0.8 is greater than that at  $\xi$  of 0.6. The depth of the brown color at 636 K decreases as the value of  $\xi$  increases.

The PTHF/glycerin binder started to liquefy at approximately 460 K and was completely liquefied at 582 K. Furthermore, the sample decomposed with a white smoke at above 510 K<sup>16)</sup>. On the other hand, for the HTPB/PTHF2 binder, no smoke was observed up to 636 K, and the shape remained nearly unchanged.

The decomposition phenomena of the HTPB/PTHF1 and HTPB/PTHF3 binders were almost identical to those of the HTPB/PTHF2 binder. It was observed that the shape of the binder remained unchanged at temperatures up to 636 K, whereas a small quantity of the HTPB/PTHF

Table 2 Temperature of the peak consumption rate that determined the first derivative mass loss for HTPB/PTHF binder.

Binder	HTPB/PTHF1	HTPB/PTHF2	HTPB/PTHF3
$\xi$ [–]	Temperature of the peak consumption rate [K]		
0	749	749	749
0.2	730	740	749
0.4	725	728	723
0.6	698	706	715
0.8	698	700	705

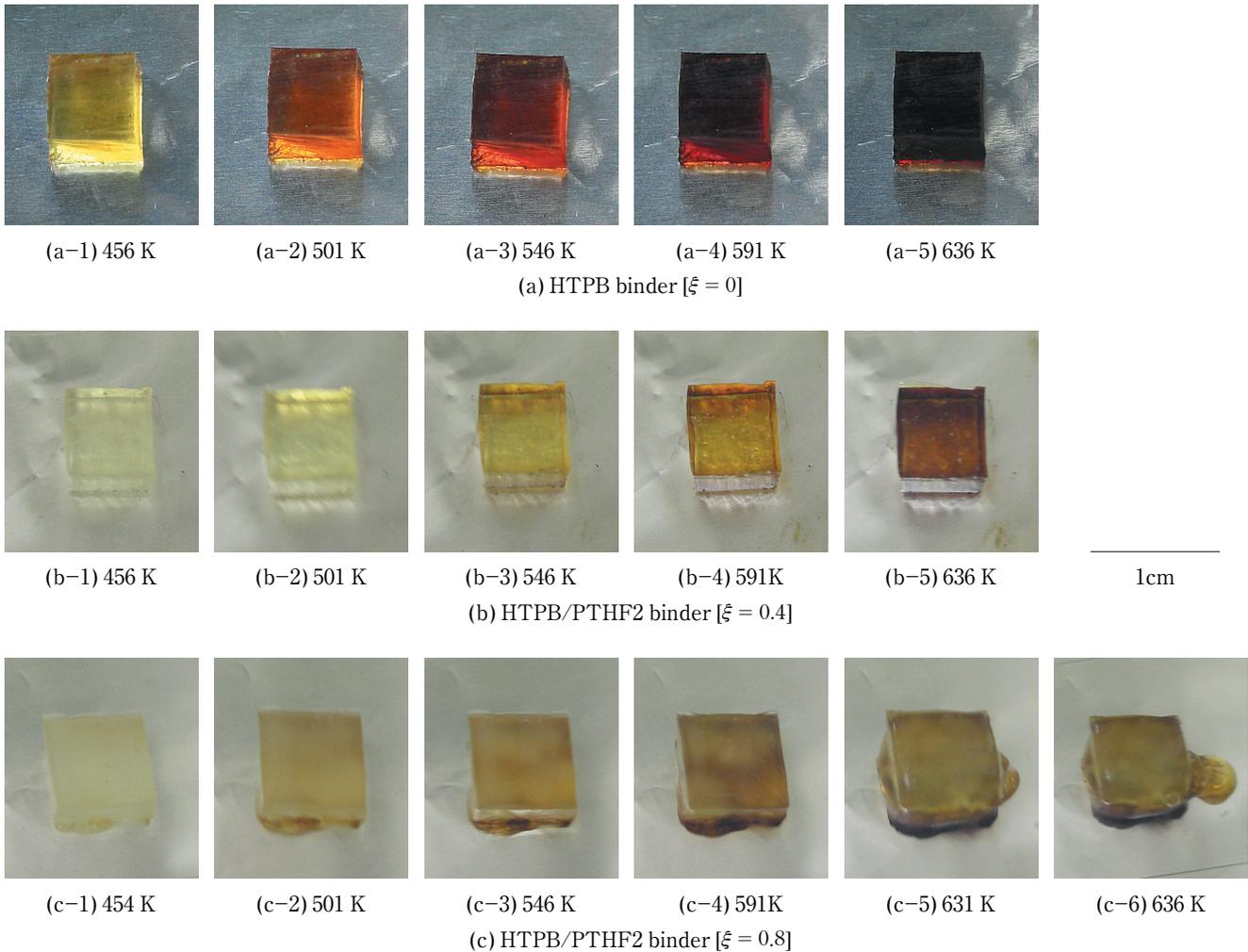


Fig. 3 Decomposition phenomena of the HTPB/PTHF2 binders at  $\xi$  of 0, 0.4, and 0.8

binders at  $\xi$  of 0.6 and 0.8 began to liquefy at approximately 474 K.

### 3.2 Thermal decomposition behavior of propellants

#### 3.2.1 TG-DTA

The influence of  $\xi$  on the TG-DTA curves of the propellants was not significantly dependent on the molecular weight of PTHF. Figure 4 shows the TG-DTA curves of AN/HTPB/PTHF2 propellants. These propellants display an endothermic peak at 442 K due to the melting of AN; after this peak, an exothermic decomposition occurs.

For the AN/HTPB propellant, a peak temperature of the exothermic decomposition is observed at 537 K. According to the TG curve, the consumption of the propellant begins at approximately 480 K, and the sample is completely consumed at approximately 550 K.

In the DTA curves of AN/HTPB/PTHF2 propellants, two exothermic peaks are observed in the temperature range of 502–521 K and 532–540 K. According to the TG curve, the consumption of the propellants at  $\xi = 0.2$ –0.6 is observed beginning at 475–480 K, and the sample is completely consumed at approximately 560 K. The consumption of the propellant at  $\xi$  of 0.8 begins at around 463 K, and the sample is completely consumed at 540 K. The consumption temperature range of the propellant at  $\xi$

Table 3 Temperature of the peak consumption rate that determined the first derivative mass loss of AN/HTPB/PTHF propellant.

Propellant	AN/HTPB/ PTHF1	AN/HTPB/ PTHF2	AN/HTPB/ PTHF3
$\xi$ [-]	Temperature of the peak consumption rate [K]		
0	530	530	530
0.2	512,526	518,540	508,539
0.4	503,537	524,530	508,537
0.6	508,533	502,531	505,539
0.8	507,523	509,528	502,548

= 0.8 is lower than that of the propellants at  $\xi=0$ –0.6.

The consumption rate of the propellant was determined from the first derivative mass loss. Figure 5 shows the first derivative mass loss curve of the AN/HTPB/PTHF2 propellants. In the temperature range of 475–520 K, the consumption rate of the AN/HTPB/PTHF2 propellants is larger than that of the AN/HTPB propellant. The first derivative curve of the AN/HTPB propellant has one peak, whereas those of the AN/HTPB/PTHF2 propellants have two. Table 3 provides the peak temperature of the first derivative mass loss of the AN/HTPB/PTHF propellants. The peak temperature of the AN/HTPB

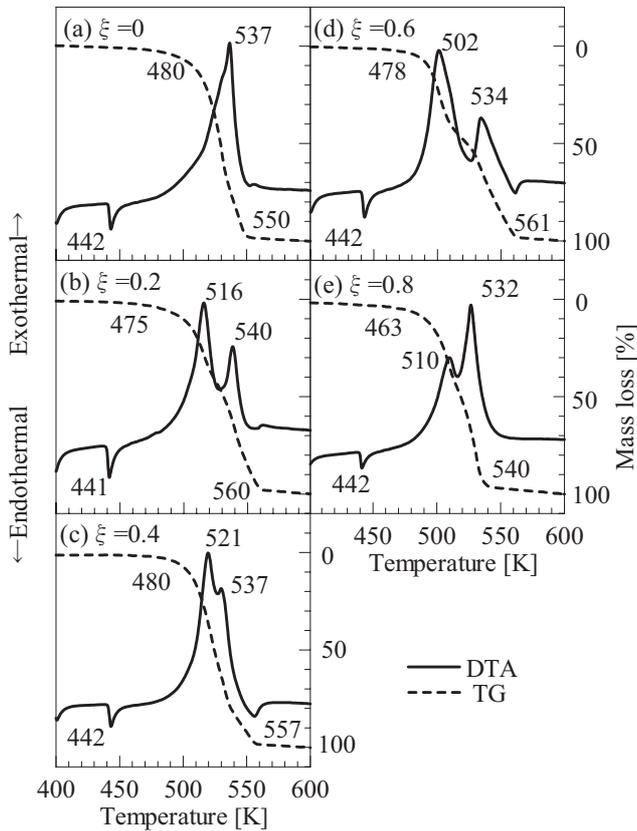


Fig. 4 TG-DTA curves of AN/HTPB/PTHF2 propellants

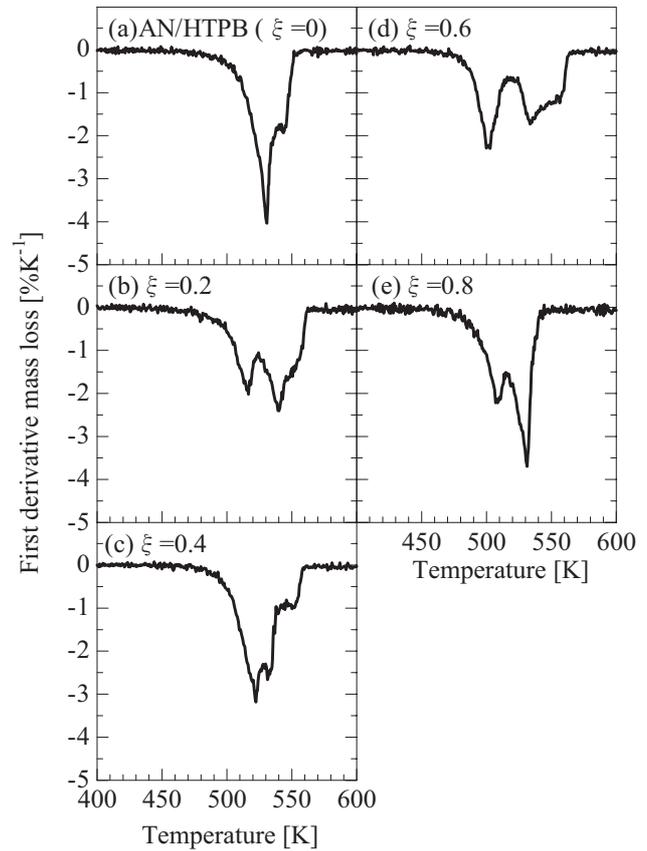


Fig. 5 First derivative mass loss of AN/HTPB/PTHF2 propellants

propellant is 530 K, and those of the AN/HTPB/PTHF propellants are observed in the range of 502–524 K and 523–548 K. The low temperature peak of the AN/HTPB/PTHF propellants is lower than that of the AN/HTPB propellant.

The thermal decomposition of the AN/HTPB/PTHF propellants was found to occur at a lower temperature, compared to that of the AN/HTPB propellant, and the AN/HTPB/PTHF propellant decomposed in two stages. The thermal decomposition mechanism of the AN/HTPB/PTHF propellant is not proposed in this study.

### 3.2.2 Decomposition phenomena

The decomposition phenomena of AN were observed by visual inspection. AN started to melt at around 428 K, but the melting point of AN (443 K) was higher in our experiment, because the heating condition was different from that of the standard method for determining the melting point. The decomposition of AN began at approximately 438 K, and produced heavy white smoke at approximately 456 K. At 560 K, AN was completely decomposed, and no residue was observed on the plate.

The decomposition phenomena of the propellants were observed by visual inspection in a similar manner as was done for the binders. Figure 6 shows the decomposition phenomena of the AN/HTPB propellant and AN/HTPB/PTHF2 propellants. For the AN/HTPB propellant, a transparent and colorless liquid is produced in the portion of sample in contact with the heater at approximately 470 K. This liquefied material is determined to be AN because AN melts at approximately 428 K, the melted AN is a

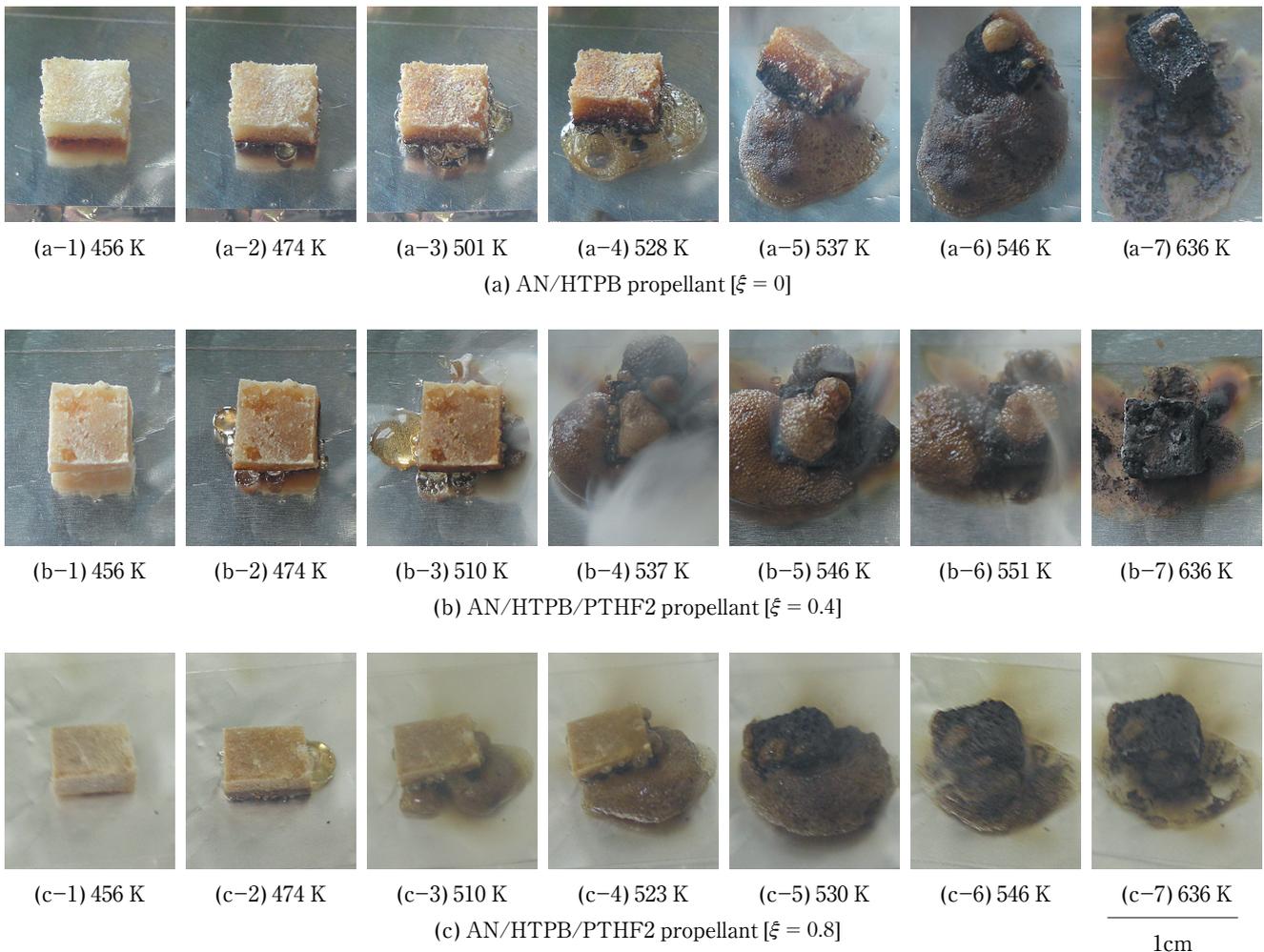
transparent and colorless liquid, and because the HTPB binder did not liquefy even up to 636 K as described in Section 3.1.2.

The liquefied material begins to form some bubbles and generates white smoke at approximately 501 K. The principal constituent of the smoke is determined to be the decomposition gases of AN because the AN decomposed with white smoke at above 456 K, and the HTPB binder did not generate smoke up to 636 K.

In the temperature range of 528–543 K, the AN inside the propellant decomposes rapidly, and some bubbles are observed on the surface of the sample. The color of the liquefied material becomes yellow. The melted AN was shown to be transparent and colorless. Therefore, the liquefied material contained the HTPB binder, although a liquefaction of the HTPB binder alone was not observed in Section 3.1.2. In addition, a small amount of the decomposition gas was produced by the reaction between AN and HTPB in the liquefied material.

No smoke is generated at 609 K according to the visual observation. At 636 K, there is a black residue produced because of carbonization of the HTPB binder; the size of the residue is smaller than that of the propellant sample before heating. A black film remains on the hot plate, which is determined to be the residue of the liquefied HTPB binder.

For the AN/HTPB/PTHF2 propellant at  $\xi$  of 0.4, a yellow liquefied material is produced at the portion in contact with the heater at approximately 470 K. The main ingredient of this liquefied material is AN because AN



**Fig. 6** Decomposition phenomena of AN/HTPB and AN/HTPB/PTHF2 propellants [ $\xi=0, 0.4,$  and  $0.8$ ]

melts at approximately 428K, and the HTPB/PTHF2 binder at  $\xi$  of 0.4 did not liquefy even up to 636 K as described in section 3.1.2. However, the liquefied material of the propellant at 474K is yellow, indicating that the small amount of HTPB/PTHF2 binder contained in the propellant liquefied, and then reacted with AN. Smoke is generated at approximately 510K, and the generation of smoke is more vigorous in the temperature range of 530–546 K. The smoke is observed up to approximately 617 K. At 636 K, there is a black residue produced because of carbonization of the HTPB/PTHF2 binder; the size of the residue is smaller than that of the propellant sample before heating. A black film remains on the hot plate, which is determined to be the residue of the liquefied HTPB/PTHF2 binder.

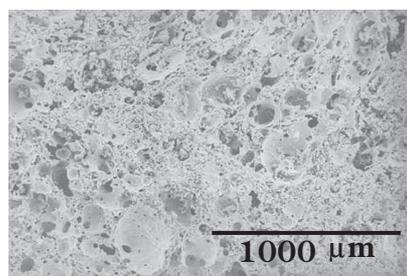
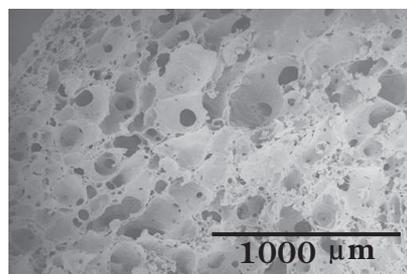
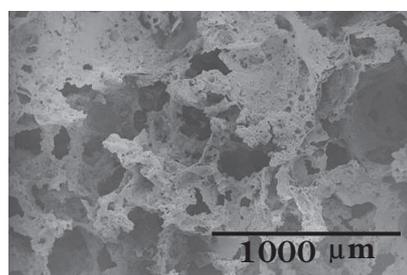
For the AN/HTPB/PTHF2 propellant at  $\xi$  of 0.8, a transparent and yellow liquefied material is observed for the portion in contact with the heater at approximately 470 K and becomes an opaque and yellow liquid at approximately 500 K. As described in Section 3.1.2, the HTPB/PTHF2 binder at  $\xi$  of 0.8 liquefied at approximately 474 K and was a yellow color. Therefore, the liquefied material produced at approximately 500 K must be a mixture of AN and the binder, wherein AN has reacted with the binder. The liquefied material must change from a transparent yellow to an opaque yellow

because the quantity of the liquefied binder increases with increasing temperature.

Smoke is generated at approximately 492 K, and the generation of smoke is more vigorous in the temperature range of 537–546 K. The smoke is observed up to approximately 591 K. At 636 K, there is a black residue produced because of carbonization of the HTPB/PTHF2 binder; the size of the residue is smaller than that of the propellant sample before heating, and the residue has no edge. A black film remains on the hot plate, which is determined to be the residue of the liquefied HTPB/PTHF2 binder.

From the observation of the decomposition phenomenon of the AN/PTHF/glycerin propellant, the propellant liquefied completely, and only a black film remained on the hot plate at 636 K; that is, the shape of the residue did not match that of the sample before heating<sup>16</sup>). The AN/HTPB/PTHF propellants did not liquefy completely, and the charred black residue of the propellant was formed because of the HTPB contained in the propellant.

The weight of the residue was in the range of 14–17% of the propellant sample before heating; most of the binder became charred residue because the content of binder was 20%. This indicates during the thermal decomposition process, the amount of the binder that had decomposed

(a) AN/HTPB propellant [ $\xi=0$ ](b) AN/HTPB/PTHF2 propellant [ $\xi=0.4$ ](c) AN/HTPB/PTHF2 propellant [ $\xi=0.8$ ]

**Fig. 7** SEM photograph of the cross section of the propellant residue [ $\xi=0, 0.4, \text{ and } 0.8$ ]

was fairly low.

The residue that was formed after the propellant was heated at up to 636 K was examined with the SEM. Figure 7 shows the SEM photograph of the cross section of the residue at  $\xi$  of 0, 0.4, and 0.8. The residue looks like a sponge. What appear to be voids in sponge are the traces of AN particles. The amount and size of the voids increase with increasing  $\xi$ .

The propellants were prepared with the same AN sample and the same amount of AN. The amount and size of the void in the residue should be constant if the binder did not liquefy at temperatures up to 636 K. As previously mentioned, the amount and size of the void increased with increasing  $\xi$ ; this indicates that the HTPB/PTHF binder around the AN particles liquefied or decomposed, and the quantity of the liquefied or decomposed binder increased with increasing  $\xi$ .

#### 4. Conclusions

The influence of the HTPB/PTHF blend on the thermal decomposition behavior of AN-based composite propellants was investigated. For the HTPB/PTHF blends, the main thermal decomposition temperature range shifted to lower values as the proportion of PTHF in the binder ( $\xi$ ) increased. Visual inspection of the binders' decomposition phenomena showed that the shape of the binder was maintained up to 636 K, whereas a small

quantity of the HTPB/PTHF binders at  $\xi$  of 0.6 and 0.8 began to liquefy at 474 K.

From the results of TG-DTA, the thermal decomposition of the AN/HTPB/PTHF propellants occurred at a lower temperature, compared to that of the AN/HTPB propellant, and the AN/HTPB/PTHF propellant decomposed in two stages. By visual observation, the propellants were found to decompose rapidly, and the generation of smoke was more vigorous in the temperature range of 530–550 K. The size of the black residue was smaller than that of the propellant sample before heating. The residue looked like a sponge, and the amount and the size of the voids in the residue increased with increasing  $\xi$ . It was found that the HTPB/PTHF binder around the AN particles liquefied or decomposed, and the quantity of liquefied or decomposed binder increased with increasing  $\xi$ .

The burning characteristics of the AN/HTPB/PTHF propellant will be reported in the next paper.

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# 末端水酸基ポリブタジエン／ポリテトラヒドロフラン ブレンドをバインダとして用いたAN系コンポジット 推進薬の熱分解性

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末端水酸基ポリブタジエン (HTPB) はバインダとして広く用いられている。またポリテトラヒドロフラン (PTHF) は推進薬の燃焼特性向上に有用なバインダである。HTPB/PTHFブレンドは良好な硬化特性・機械的特性を有するバインダであった。本実験では、HTPB/PTHFブレンドをバインダとして用いたAN系推進薬の熱分解性について調べた。

TG-DTAの結果によれば、PTHF含有率 ( $\xi$ ) の増加にしたがって、HTPB/PTHFブレンドの主分解となる温度範囲は低温側に移動した。AN/HTPB/PTHF系推進薬の熱分解は2段階で起こり、その分解はAN/HTPB系推進薬と比較して低温で起こることがわかった。熱分解を目視観察で観察したところ、 $\xi$ が0.6以上のHTPB/PTHFバインダは、474 Kからわずかな量のバインダが液化し始めることがわかった。しかし、その形状はほぼ維持していた。推進薬は530~550 Kの温度範囲で、激しく白煙を出しながら分解した。推進薬の残渣の大きさは、加熱前の推進薬のそれより小さくなった。推進薬残渣はスポンジ状をしており、残渣内の空隙の大きさと量は、 $\xi$ の増加にしたがって大きくなった。AN粒子を囲んでいるHTPB/PTHFバインダは液化又は分解し、そのバインダ量は $\xi$ の増加にしたがって多くなることがわかった。

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