

THERMAL DECOMPOSITION STUDIES OF SOLID PROPELLANT BINDER HTPB

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ABSTRACT

The thermal decomposition of a sample of a commercial composite solid propellant binder, hydroxy-terminated polybutadiene (HTPB), was studied by thermogravimetry–derivative thermogravimetry–differential scanning calorimetry simultaneous techniques (TG–DTG–DSC) applied simultaneously at heating rates varying from 8 to 60 °C min⁻¹. Decomposition of HTPB under this dynamic heating program is indicated by two major stages of weight loss of different natures and indistinct separation. The first stage is primarily depolymerization, cyclization and crosslinking of material not undergoing depolymerization. The second stage is decomposition of a residue yielded in the first stage. Kinetic parameters of the decomposition process at different heating rates were evaluated by means of the maximum rate method for a TG trace by Fouss et al., the simplified method for the DSC thermogram by Maycock, and the multiple-heating rate method for TG traces by Freidman. The DSC data indicate that in the temperature range of the first stage of decomposition, the overall process is also exothermic even at the lower temperature, and that the exothermicity is reduced with increasing heating rate. The apparent activation energy for the decomposition, calculated by the simplified DSC method, increases with increasing heating rate. Increasing the heating rate results in increased depolymerization in the first stage, and increased temperatures of the exothermic DSC peak and completion of the second stage. Increasing the sample size leads to reduced depolymerization in the first stage and increased residue in the second stage. The relevance of the generated kinetic data to solid propellant combustion is compared.

INTRODUCTION

The combustion of modern rocket propellant occurs via a series of complex physicochemical processes. No mathematically tractable model can so far take all burning reactions into consideration. The burning process may take place, to varying degrees, in the gas phase, on the solid surface, or in the condensed phase; the composition, microstructure and environmental condition of the propellant have relative importance. Even though it is unlikely that the degree of importance of these various processes can be known exactly for most practical combustion situations, and predictions for

burning effect are based largely on experience rather than theory, establishment of an analytical and predictive model would be possible if detailed information on the energetics, kinetics and mechanism of the thermal decomposition of the propellant material were known.

In order to understand such detailed information, a detailed knowledge of the thermal decomposition characteristic of polybutadiene binders (functionally carboxy and hydroxy terminated polybutadiene polymers of different molecular weights), which play an important role in modern rocket propellant manufacture, is necessary. Although there have been many studies [1–6] in recent times on the thermal decomposition of polybutadiene, as well as of carboxy terminated polybutadiene (CTPB), the thermal decomposition of HTPB binder has not been investigated on a systematic basis. The present work is an attempt to research into the thermal decomposition processes of HTPB binder, the energy changes, kinetic parameters and their regularity by means of thermal analysis and combined gas chromatography–mass spectrometry techniques (GC–MS) etc., so as to provide some fundamental information necessary for establishing a mathematically tractable model to explain the phenomena on a rational basis.

EXPERIMENTAL

A commercially available HTPB resin (Chemical plant, Fushun, People's Republic of China) was used in the present study. The molecular weight of this resin is 4600, the hydroxy content 0.48 meq. g^{-1} ; the *cis*-1,4 structure constitutes 14%, the *trans*-1,4 structure 62% and the 1,2-vinyl structure 21% of the total isomers.

A Thermoflex thermal analyzer (TG–DTG–DSC simultaneous system, Rigaku Corp.) was interfaced with a SP-2305E gas chromatograph (Analytic Instrument Factory, Beijing, People's Republic of China). The interface, i.e. a multiplex automatic gas sampler constructed from 12-position micro-volume valves placed in the thermostat, allowed up to 11 samples of the volatile products to be collected from each thermal analytical experiment. The interface was maintained at a temperature of 200°C to prevent condensation in the loops used for collecting samples for GC analysis. 10% Apiezon-L grease on 60–80 mesh 102 white support was packed in the upper part of the protected tube in the thermal analyzer to prevent high boiling > 10 C products from entering the GC column.

The GC analysis was performed in a 2 m × 3 mm stainless steel column packed with 15% di-isooctyl tetrachlorophthalate on 60–80 mesh 102 white silanized support. The conditions of chromatographic analysis were as follows: the temperatures of column, injector and FID were 130, 150 and 150°C respectively; the flow rate of the carrier gas (high-purity nitrogen) was 30 ml min^{-1} , that of air 320 ml min^{-1} and that of hydrogen 35 ml min^{-1} .

The MS analysis of the decomposition products was carried out in an JMS-D300 GC-MS (JEOL Ltd.) mass spectrometer. The volatile products passed through the multiplex automatic gas sampler were collected in a stainless steel sampling ring by means of a liquid-nitrogen cold trap. The sampling ring was then placed in boiling water and the vaporized sample was drawn up and injected into the sample access port of the GC-MS instrument. The temperature of the GC-MS separator was 150 °C, the MS resolution 500, the electron energy of electron-bombarded ionization 70 eV and the scanning range 100–200/10–250 mass units.

RESULTS AND DISCUSSION

Figure 1 illustrates typical TG-DTG-DSC [7–9] thermograms of HTPB obtained at a 15 °C min⁻¹ heating rate with a static helium atmosphere.

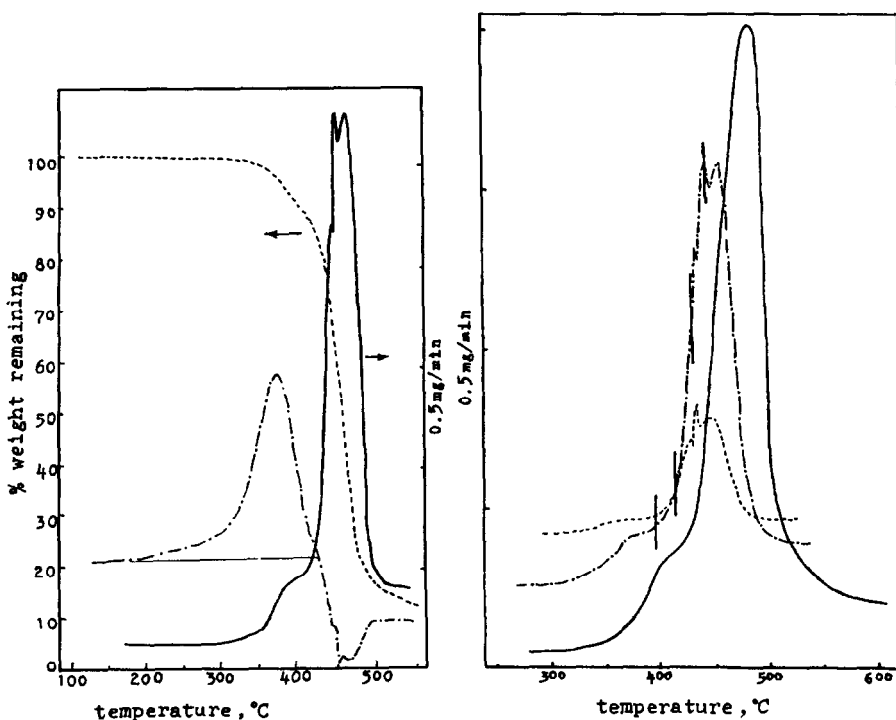


Fig. 1. TG (-----), DTG (——) and DSC (— · — ·) traces of HTPB at heating rate of 15 °C min⁻¹. Sample size, 5 mg; atmosphere, static helium; DSC sensitivity, 0.64 mcal s⁻¹ cm⁻¹.

Fig. 2. DTG traces of HTPB at heating rates of 8 °C min⁻¹ (-----), 15 °C min⁻¹ (— · — ·), and 60 °C min⁻¹ (——). Sample size, 5.2 mg.

TABLE 1

Effect of sample size on thermal decomposition of HTPB (heating rate $30^{\circ}\text{C min}^{-1}$)

Sample size (mg)	First stage			Second stage		DSC exothermic peak temp. ($^{\circ}\text{C}$)
	Weight loss (%)	Maximum decomposition rate (mg min^{-1})	Temp. of max. decomposition rate ($^{\circ}\text{C}$)	Weight remaining (%)	Temp. of completion ($^{\circ}\text{C}$)	
2.45	8.6	0.185	414	13.1	514	391
5.16	5.5	0.293	402	15.4	513	391
8.25	4.8	0.380	409	18.1	515	390
11.62	4.1	0.500	405	20.2	513	390
14.40	2.8	0.517	402	21.0	514	392
19.40	2.3	0.528	398	22.2	514	391

HTPB leaves about 14% carbonaceous residue at 503°C . This residue is lost at a constant rate through volatilization with a continued rise in temperature. The DTG trace indicates two major weight loss stages with indistinct separation. For the first stage, the maximum rate of weight loss occurs around 394°C . The second stage is then separated into three small stages in which maximum rates of weight loss occur at around 451 , 457 and 470°C , respectively. Figure 2 shows DTG thermograms obtained at heating rates of 8 , 15 and $60^{\circ}\text{C min}^{-1}$. The vertical markers on the trace indicate points at which samples of the volatile products were collected for analysis. All traces show that the separation between the first and second stages is indistinct, the first stage showing only a shoulder rather than a peak. At the slow heating rate three distinct peaks are observed in the second stage corresponding to three small weight loss stages. The above mentioned cases are different from those of CTPB [6] and polybutadiene [4].

Table 1 summarizes the observed weight loss, the maximum decomposition rate, the temperature at which it occurs for the first stage of weight loss, and the DSC exothermic peak temperature as a function of sample size for a constant heating rate of $30^{\circ}\text{C min}^{-1}$. The remanent weight and the temperature of completion of the second stage are also detailed in Table 1. Increasing the sample size can result in a marked decrease in the first stage weight loss, a large increase in the maximum decomposition rate in the first stage and the remanent weight at the completion of the second stage, but it does not lead to a significant change in the the temperature at the completion of the second stage or the DSC exothermic peak temperature.

Table 2 presents the effect of heating rate on the thermal decomposition of HTPB at a constant sample size of 5.2 mg . The data show that for the first stage the weight loss and the maximum decomposition rate are both increased, and that the temperature of maximum decomposition rate and

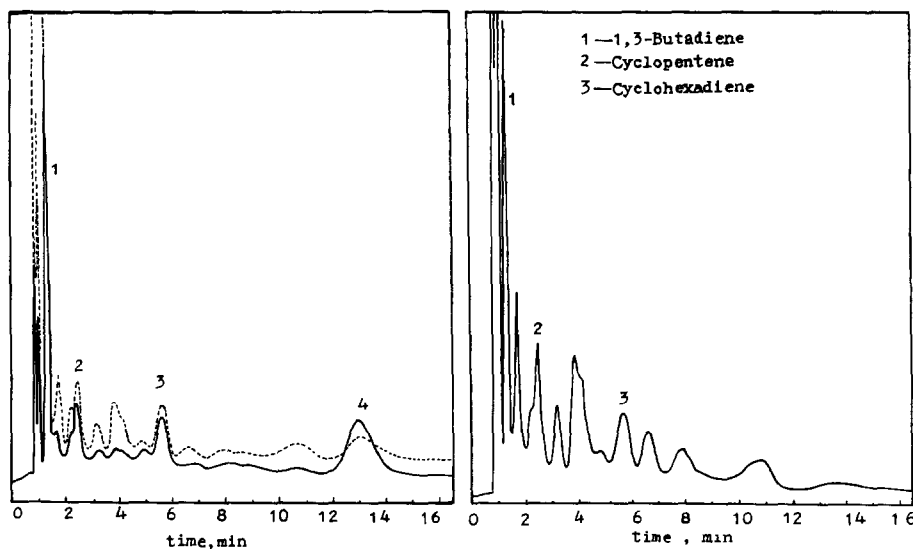


Fig. 3. Chromatograms of volatile products collected around maximum decomposition rate (400°C , —) of the first stage and at the start of the second stage (420°C , - - - - -). Heating rate $15^{\circ}\text{C min}^{-1}$; GC sensitivity $1/16$.

Fig. 4. Chromatograms of volatile products collected during the second stage at 440°C . Same conditions as in Fig. 3.

DSC exothermic peak temperature have risen. For the second stage, the weight remaining is essentially non-variant (within $\pm 3\%$ experimental error) and the temperature of completion is increased.

Figures 3, 4 and 5 show typical chromatograms of volatile fractions collected around the maximum decomposition rate of the first stage after the start of the second stage, and around the maximum decomposition rate of the second stage. MS analysis shows that the major volatile products from the first stage are 1,3-butadiene, cyclopentene, cyclohexadiene and 4-vinylcyclohexene. At the start of the second stage (420°C , the dotted line in Fig. 1) 4-vinylcyclohexene decreases strongly, whereas 1,3-butadiene is approximately constant. As temperature increases to 440°C , 4-vinylcyclohexene is not observed, however 1,3-butadiene increases strongly up to a maximum at the maximum decomposition rate of the second stage (460°C , Fig. 5). The results show clearly that the first stage is primarily depolymerization, cyclization and crosslinking, accompanied by partial decomposition of the cyclized product. Unlike the first stage, the second stage primarily involves decomposition of the cyclized product with increasing temperature, while depolymerization and cyclization reactions gradually disappear. In the first stage competition between depolymerization and cyclization is evident. Increasing the heating rate favors depolymerization and results in increased depolymerization at the expense of cyclization, thereby increasing weight

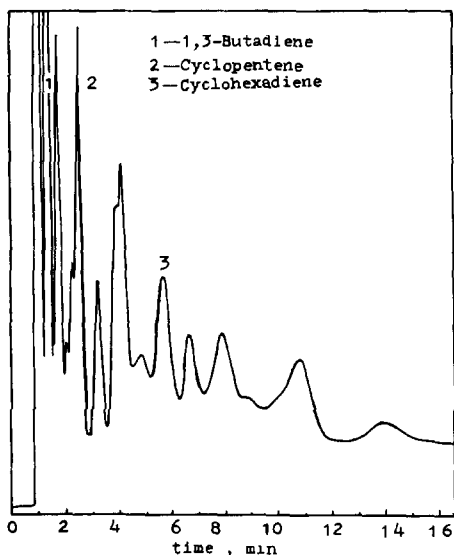


Fig. 5. Chromatograms of volatile products collected around maximum decomposition rate (460°C). Same conditions as in Fig. 3.

loss and maximum decomposition rate; however, increasing the sample size and retaining a constant heating rate results in increased cyclization and crosslinking at the expense of depolymerization, and so results in decreased weight loss and temperature of maximum rate (in contrast to the results of CTPB thermal decomposition [6]). The DSC and DTG traces in Fig. 1 show that the crosslinking and cyclization of HTPB proceed before the onset of measured weight loss ($\sim 270^{\circ}\text{C}$) indicating the exotherm. The exothermicity data in Table 2 were calculated on the basis of the DSC peak area. The baselines of the area calculation are drawn as shown by simply extending the

TABLE 2

Effect of heating rate on thermal decomposition of HTPB (sample size 5.2 mg)

Heating rate ($^{\circ}\text{C min}^{-1}$)	First stage			Second stage		DSC exothermic peak temp. ($^{\circ}\text{C}$)	Exothermicity, (kcal g^{-1})
	Weight loss (%)	Max. decomposition rate, (mg min^{-1})	Temp. of max. decomposition rate ($^{\circ}\text{C}$)	Weight remaining (%)	Temp. of completion ($^{\circ}\text{C}$)		
8	5.4	0.070	380	13.7	493	367	0.446
15	5.5	0.124	394	14.1	503	378	0.460
30	5.8	0.248	402	14.3	513	391	0.316
45	6.2	0.450	414	13.6	522	399	0.271
60	6.8	0.670	424	14.4	526	407	0.269

TABLE 3

Calculated kinetic parameters of HTPB ^a by three processing methods

Heating rate (°C min ⁻¹)	Activation energy (kcal mol ⁻¹)			Pre-exponential factor (s ⁻¹)		
	TG max. rate method	DSC sim- plified method	TG multi- ple-heat- ing rate method	TG max. rate method	DSC sim- plified method	TG multi- ple-heat- ing rate method
8	26.5	18.2		3.09 × 10 ⁶		
15	26.3	21.2		3.09 × 10 ⁶		
30	28.6	22.5		2.88 × 10 ⁷		
45	29.2	24.3		4.57 × 10 ⁷		
60	28.5	28.7		1.32 × 10 ⁷		
mean value	27.6 ± 1.6		60.1	1.10 × 10 ⁷		2.69 × 10 ⁷

^a 5.2 mg samples.

baseline before crosslinking and cyclization commenced through the exotherm (Fig. 1). DSC analysis has indicated that in the temperature range of the first stage of decomposition, and even at lower temperatures before this stage, the overall process is exothermic. This exothermicity is apparently due to the fact that the energy released for the formation of new bonds during crosslinking and cyclization of HTPB is greater than the absorbed energy for bond scission during depolymerization. With increasing heating rate, depolymerization increases while crosslinking and cyclization decrease, relatively and exothermicity therefore also decreases (Table 2).

In Table 3 kinetic parameters obtained by three processing methods at different heating rates are listed. The apparent activation energy determined at a higher heating rate by the simplified DSC method is comparable with that calculated using the maximum rate TG method and is almost the same as that obtained by Varney and Strahle [10] and Thomas et al. [6]), although the former shows a linear increase with heating rate (this is contrary to CTPB [6]) and the latter is not greatly affected by the heating rate. Using the multiple heating rate method for TG, the kinetic parameters calculated from the TG data differ very much from those obtained by the preceding two methods. Considerable work including the present experiment all shows that butadiene and vinylcyclohexene are the major volatile products formed in the first stage; the DTG activation energy of 60.1 kcal mol⁻¹ obtained by the multiple heating rate method corresponds to the depolymerization process [4]. The 60.1 kcal mol⁻¹ value is closer to that found experimentally [12] for main-chain scission of saturated polymers (e.g. polyethylene) and is in good agreement with literature values [4,11].

Golub and Gargiulo [13] suggested the mechanism to form the major decomposition products for 1,4-polybutadiene. The mechanism of the forma-

TABLE 4

Kinetic parameters of HTPB and CTPB and temperatures of burning surface of corresponding propellant

Binder	Activation energy (kcal mol ⁻¹)	Pre-exponential factor (s ⁻¹) ^b	Calculated temp. (K)
CTPB ^a	28	3.4×10^5	3070
HTPB	60.1	2.69×10^7	3370

^a From ref. 10.

^b Using the formula from ref. 10.

tion of more volatile products was discussed in detail by Tamura and Gillham [14]. All mechanisms reported by these authors involve the generally accepted free-radical cleavage mechanism. From the experimental results obtained in the present study, the mechanism of the thermal decomposition of HTPB is similar to that of 1,4-polybutadiene, in agreement with the free-radical cleavage mechanism of a single bond on the main-chain of saturated polymers. Since activation energies [4] for the formation of butadiene and vinylcyclohexene are 56 and 42.1 kcal mol⁻¹, respectively, the butadiene content of the depolymerization fraction increases with increasing temperature; however vinylcyclohexene decreases in the second stage (Figs. 3, 4 and 5).

The HTPB resins are mainly used in the manufacture of composite solid propellants. These are composed mainly of ammonium perchlorate (AP), powdered metal and different functionally terminated polybutadiene polymers, in which the propellants using HTPB binder have the highest specific impulse [15]. This is in accord with data related to the calculated kinetic parameters of HTPB and CTPB using the Varney and Strahle formula [10] and the surface temperature of combustion of the corresponding composite solid propellant, so that for the same burning rate, the surface temperature of HTPB is 300 K higher than that of CTPB (Table 4).

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