

Thermal decomposition mechanism for azidopolyester based HTPB binder by using pyrolysis-GC/MS

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ABSTRACT

The energetic plasticizers like azidopolyester (APE) in Hydroxy Terminated Poly-Butadiene (HTPB) binder formulations are known to enhance the ballistic properties of explosive formulations. The pyrolysis gas chromatography-mass spectrometry (Py-GCMS) studies were carried out on HTPB with APE to get insight of the decomposition pathway of HTPB. Based on the results, decomposition mechanism is proposed for uncured and cured HTPB, with and without energetic plasticizer. It has been observed that the decomposition mechanism of cured HTPB is similar to the pure HTPB polymer. In case of energetic plasticizer based composition, it is seen that APE triggers the decomposition which results in the formation of monomers, dimer and oligomers. Overall, the study helps in understanding the role of energetic plasticizer on improving the performance of the binder composition. Copyright © 2016 VBRI Press.

Keywords: HTPB decomposition; azidopolyester; pyrolysis GCMS; energetic plasticizer.

Introduction

Hydroxy Terminated Poly-Butadiene (HTPB) is the most widely used polymeric binder /fuel in solid rocket propellants [1, 2]. It is also used as a coating material, adhesive and sealant in solid rocket propellants [3-5]. In the combustion chemistry description about the decomposition products, their rates of formation and the pyrolysis of HTPB, as well as the decomposed component of the diffusion flamelets in the composite solid propellant is one of the necessary tasks. There are several reports published on thermal decomposition of HTPB that approximate combustion [3-7]. Pyrolysis gas chromatography-mass spectrometry (Py-GCMS) is a general method of chemical analysis in which the samples are heated to decomposition which ultimately produces smaller molecules which are separated by gas chromatography (GC) and its molecular weight is detected using mass spectrometry (MS). Py-GCMS technique and thermal techniques were used to study thermal decomposition mechanism of various energetic materials [8-9].

The thorough study of high temperature thermal degradation of HTPB and its detailed analysis is an important task for the detection of its service temperature and measurements of the probable degradation products against toxicity and pollution. There are numerous methods reported for the thermal degradation of HTPB [7, 10-13]. Brill and his co-workers have successfully studied [14-16] the flash pyrolysis of HTPB and its implication for kinetics to combustion of organic polymers using T-jump/FTIR spectroscopy. A new energetic plasticizer, poly [(1, 2-propane diol 2, 3-bis(azido) succinate)] has been evaluated

in HTPB based binder system and explosive compositions, replacing dioctyl adipate (DOA) plasticizer. In our previous study the thermal and mechanical properties were extensively canvassed for newly developed plasticizer in the binder system. [17] The studies are useful to reveal better mechanical properties and high energy output. Further, the sheet explosives, pressed and cast plastic bonded explosives (PBX) were also attempted. The results also showed higher VOD and better mechanical properties.

In the present pyrolysis studies the decomposition products and the pathway of decomposition of HTPB pre-polymer as well as cured HTPB was carried out. The fragmentation species were separated and identified by pyrolyzer gas chromatography and mass spectrometry. This type of study is useful for extracting important information about the decomposition of HTPB.

Experimental

Materials/ chemicals details

1. Hydroxy Terminated PolyButadiene (HTPB) pre-polymer used during this study, was obtained from NOCIL, India having molecular weight in the range of 2500-2800 and OH value 42.0 ± 2.0 mg/g of KOH.
2. The energetic azidopolyester, poly [(1, 2-propane diol 2, 3-bis(azido) succinate)] having molecular weight in the range of 750-800 was synthesized in line with the reported procedure [18].
3. The controlled compositions were prepared from above HTPB for the current study. The cured HTPB composition was prepared by taking HTPB (60% w/w) in dioctyladipate (DOA: 40% w/w), pyrogallol (0.01%

w/w), hexamethyl diisocyanate (HMDI: 0.5% w/w) and dibutyl-tin-dilaurate (DBTDL: 0.001% w/w).

- The energetic binder composition was prepared by replacing DOA in 50%, 75% and 100% (w/w) with azidopolyester, without changing proportion and other ingredients.

Gas chromatography and mass spectrometry

Pyrolysis of the sample was carried out on CDS model 1000 pyroprobe (coil probe, sample taken in quartz capillary tube) under helium atmosphere. Pyrolyzer was connected to a gas chromatograph (PerkinElmer, Clarus500) with split / splitless injector (75/1). Helium was used as carrier gas at a flow rate of 1 ml/min with back up pressure of 10 psi. An Elite-5 capillary column (30 m × 0.25 mm × 250 mm) was employed for the study with cross bonded diphenyl-5% and dimethyl polysiloxane-95% as a stationary phase. Quadrupole mass spectrometer (PerkinElmer, Clarus500) hyphenated with GC was used to record the mass spectra of the corresponding pyrograms. Before its use, mass spectrometer detector (MSD) was calibrated using heptacosane calibration standard while GC was calibrated with test mix-1 and test mix 2, as supplied by PerkinElmer.

Sample (0.3 mg) was placed in a quartz capillary tube of pyroprobe and the assembly was kept in the pyrolyzer for thermal decomposition at 800 °C for 15 sec. Decomposed gaseous products from pyrolyzer were injected in GC with injector temperature at 225 °C. The GC oven temperature was programmed as described below: Initial temperature of the oven was kept at 40 °C for 2 min. Then it was gradually increased at the rate of 13 °C/min to reach target temperature of 250 °C which was held for 22 min. The separated pyrolyzates from the GC were transferred to mass spectrometer (MS) via a preheated interface which was kept at 200 °C temperature.

The mass spectrometer (MS) was equipped with an ion source of electron impact ionization (EI) with 70 eV energy. The ion source temperature was maintained at 200 °C. MS was capable to scan 2 to 1200 amu within 100 milliseconds. National Institute of Standard and Technology (NIST) library was referred for identifying the pyrolyzed products. The fragments with match factor more than 90% were considered for comparison purpose.

Results and discussion

In the present study, HTPB pre-polymer as well as cured HTPB was pyrolyzed at 800 °C. The pyrolyzed species separated by GC and identified with mass spectrometry are in good agreement with NIST library. In the total ion chromatogram, the species obtained below retention time 1.58 min were low molecular weight natural gases. The retention time (R.T) 1.79, 1.86, 1.92 and 1.99 min corresponded to 2-pentene, 1, 3-pentadiene, 1, 3-cyclopentadiene and 1, 3-pentyne, respectively. (Fig. 1).

The species like pentene and 1, 3-pentadiene were also observed which may be attributed to the free radical decomposition pathway of HTPB (Scheme 1). The results are in good agreement with previous studies [12-13]. The mechanism of degradation involves a radical process

forming cyclic compounds and CH transfer reactions to form linear oligomer. On the basis of heat of formation data, the formation of 1, 3-butadiene monomer is not favored during the primary chain scission process; however, it appears to emanate from the dissociation of high molecular weight cyclics and linear oligomers like cyclopentene.

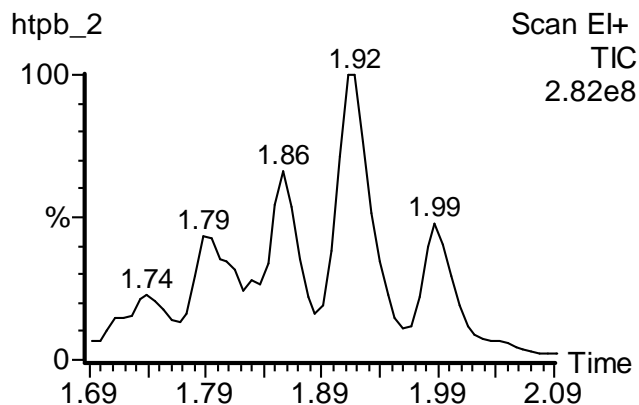
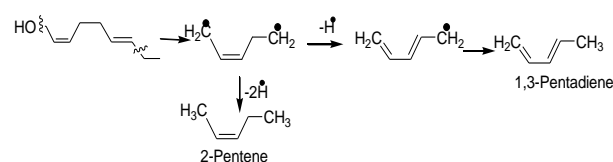
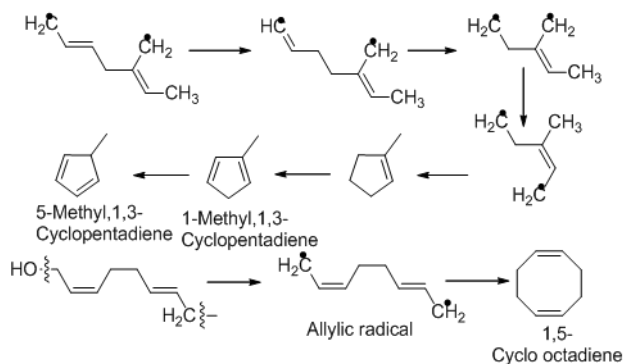


Fig. 1. Chromatogram of HTPB pyrolysis showing pentane (1.79 min), pentene (1.86 min), pentadiene (1.92 min) and pentyne (1.99 min).



Scheme 1. Decomposition Pathway of HTPB for the formation of monomers (such as 2-pentene or 1,3-pentadiene).

The major ingredients were identified such as butadiene, 1, 3-pentadiene, cyclopentene, 1, 5-hexadiene, 4-vinyl cyclohexane during pyrolysis. Some minor products were also detected such as benzene, 1, 3-cyclohexadiene, toluene, dimethyl ether, vinyl butadiene oligomer and cis-butadiene oligomer.



Scheme 2. Fragmentation of HTPB for the formation of cyclic oligomers.

The high molecular weight cyclic and linear oligomers formed from the oligomer decomposition and rearrangements lead to the formation of cyclopentene, cyclopentadiene, 1, 3-cyclopentadiene, 1-methyl-1, 3-cyclopentadiene and 5-methyl-1, 3-cyclopentadiene. The free radical defragmentation of vinyl part of HTPB gives allylic radicals. These allylic radicals combine and form cyclopentene ring which on further oxidation

(elimination of hydrogen radicals) gives 1-Methyl-1, 3-Cyclopentadiene and on further rearrangement it gives 5-Methyl-1, 3-Cyclopentadiene (**Scheme 2**). The R.T. 2.81, 2.90 and 3.01 min (**Table 1**) shows a triplet of benzene, cyclohexadiene and cyclohexene species respectively as shown in **Fig. 2**. The formations of these products are due to oxidative fragmentation of cyclic oligomers (**Scheme 3**).

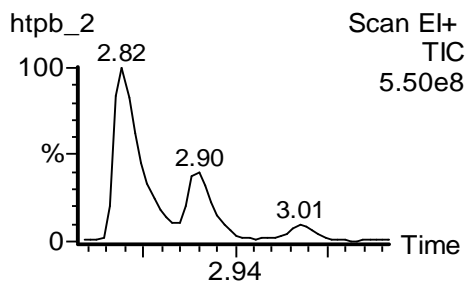
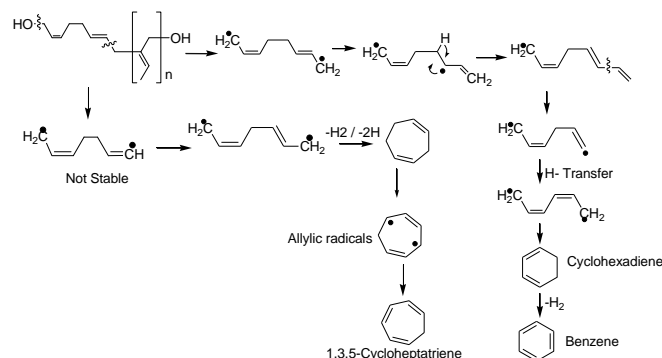


Fig. 2. Chromatogram of HTPB pyrolysis showing triplet of benzene (2.82 min), cyclohexadiene (2.90 min) and cyclohexene (3.01 min) species, respectively.

Table 1. Retention time and fragmentation species of HTPB.

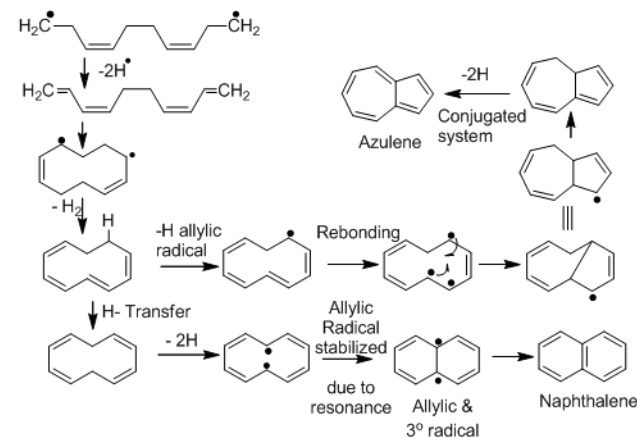
RT	m/z values	Species	Library Match (%)
1.5-1.6	41, 44, 50, 54, 56	Low mole wt gaseous product	
3.34	37, 52, 77, 78	2, 4-Hexadiene	92
3.88	41, 55, 70, 83, 96, 112	3-Methylene Heptane	98
4.79	39, 51, 65, 91, 92	Toluene	97
5.24	39, 54, 66, 79, 91, 93, 108	4-Ethynyl Cyclohexene	98
6.15	41, 55, 84, 91, 106	Cyclopentanone	95
6.72	51, 65, 91, 106	1, 3-Dimethyl Benzene	98
6.93	51, 63, 78, 104	Styrene	98
7.52	39, 65, 79, 91, 105, 120, 136	1, 2, 3-Trimethyl benzene	95
8.20	31, 41, 57, 70, 83, 98, 112	2-Propyl-1-pentanol	97
9.47	57, 76, 89, 116	Indene	95
11.56	51, 65, 78, 102, 128	Azulene	98
12.74	51, 63, 89, 115, 142, 176	1-Methyl-Naphthalene	96
13.07	57, 76, 89, 115, 142	2-Ethyl Indene	95



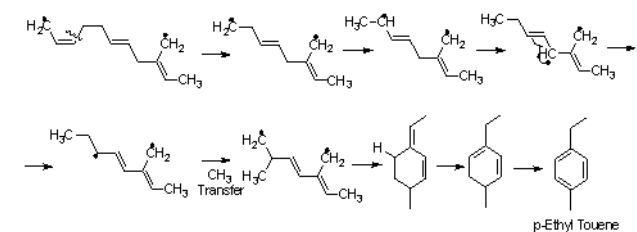
Scheme 3. Fragmentation of HTPB for the oxidative fragmentation of cyclic oligomers.

Formation of naphthalene was detected during the fragmentation and rearrangements of oligomers. The plausible mechanism could be secondary allylic radicals, obtained after intramolecular radical cyclization, may furnish the formation of naphthalene through tertiary allylic radical and dihydro-cyclodeca-tetraene which then leads to azulene via a different series of radical reactions

(**Scheme 4**). However, the vinyl part of the HTPB gives substituted benzene (**Scheme 5**). The major products during the pyrolysis were C-2, C-3 hydrocarbons and butadiene. The C-2 fragment in the pyrolyzate increases as compared to cross linked copolyurethanes of HTPB. The observed release of gaseous products might be due to redox chemistry.



Scheme 4. Fragmentation of HTPB for the oxidative fragmentation of polycyclic oligomers.



Scheme 5. Fragmentation of HTPB for the oxidative fragmentation of substituted cyclic oligomers.

Further study was extended for the HTPB. The curing was carried out cured as reported elsewhere [17]. The decomposition mechanism of cured HTPB is similar to HTPB pre-polymer, except that the peak height of the low molecular weight fragments is comparatively high eluted in the range of retention time 1.5 to 2.5 min. This may be attributed to the slow decomposition of cured HTPB because of its highly cross linked polyurethane skeleton.

During the pyrolysis it was observed that the pyrogram of the cured HTPB was similar to the uncured HTPB except R.T. 3.88, 11.74, 16.23 and 21.00 min. The peak corresponding to these were 3-methylene heptane, hexahydro-2(1H)-azocinone, 2-ethylhexyl ester cyclohexanecarboxylic acid and 5, 6-dipropyldodecane, respectively (**Table 2**).

It has been observed that 3-methylene heptane and 5, 6-dipropyldodecane are the dimer and tetramer of the HTPB molecule whereas hexahydro-2(1H)-azocinone (or cycloheptamide) was formed from the polyurethane linkage of the 1, 6-diisocyanato-hexane (HMDI) with HTPB. Dioctyladipate (DOA) entangled in between the cross chains of HTPB was decomposed with pyrolysis which gave 2-ethylhexyl ester cyclohexanecarboxylic acid or monoctyladipate. However, the azidopolyester gradually increases from 25% to 100%.

Table 2. Retention time and fragmentation species of controlled HTPB.

RT	m/z values	Species	Library Match (%)
1.5-1.6	41, 44, 50, 54, 56	Low mol. Wt. gaseous product	
3.33	37, 52, 77, 78	2, 4-Hexadiene	92
4.76	39, 51, 65, 91, 92	Toluene	97
5.23	39, 54, 66, 79, 91, 93, 108	4-Ethynyl Cyclohexene	98
6.71	51, 65, 91, 106	1, 3-Dimethyl Benzene	98
6.92	51, 63, 78, 104	Styrene	98
7.52	39, 65, 79, 91, 105, 120, 136	1, 2, 3-Trimethyl benzene	95
9.47	57, 76, 89, 116	Indene	95
11.57	51, 65, 78, 102, 128	Azulene	98
12.75	51, 63, 89, 115, 142, 176	1-Methyl-Naphthalene	96

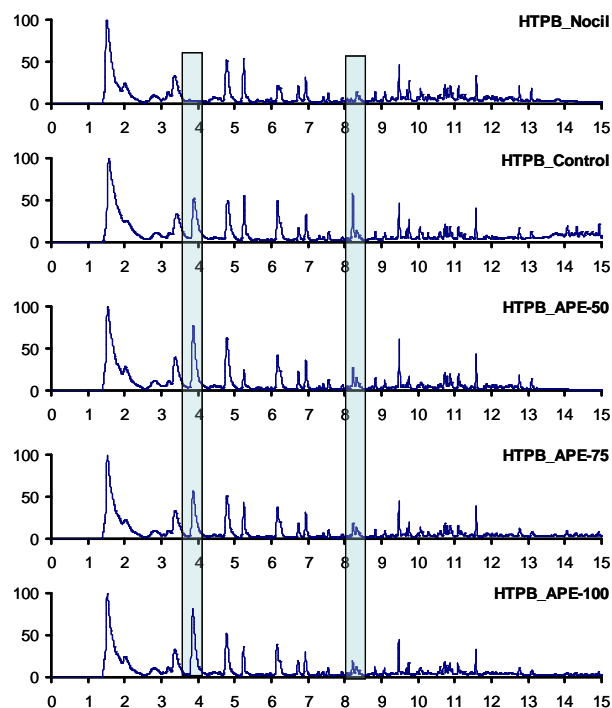


Fig. 3. Combined Pyrogram of HTPB and HTPB composition.
 *Highlighted area shows changes in peak intensity at the R.T. 3.8 min and R.T 8.2 min.
 *Total Ion chromatograms (TIC) in descending order are i. HTPB pure ii. HTPB control composition iii. Replacement of DOA with APE at 50%, 75% and 100%, respectively.

Fig. 3 shows the combined pyrogram of uncured and cured HTPB. The area under the curve of retention time 1.5-2.5 min corresponds to low molecular weight gaseous product and peak intensity increases with increase of azidopolyester concentration (**Table 3**). Cured HTPB upon fragmentation shows formation of more amounts of dimer, trimer and oligomer during pyrolysis. The quantitative estimation of pyrolyzates shows that increase in percentage of azidopolyester plasticizer increases low molecular weight entities as shown in **Fig. 4**. The additives also take part in the decomposition mechanism along with the HTPB, which results in the formation of monomer, dimer and oligomers. For HTPB, butadiene, 4-vinyl cyclohexene, and trans-butadiene oligomers are the major products. The gradual increase in the concentration of low molecular

weight fragments at retention time of 3.8 min as energetic plasticizer part increases in the composition. However, decrease in the concentration of high molecular weight fragments at retention time 8.2 min in the energetic plasticizer composition was observed which may be the probable cause of the overall performance of binder composition in the presence of energetic plasticizer.

Table 3. Retention time and fragmentation species of HTPB/Azidopolyester.

RT	m/z values	Species	Library Match (%)
1.52	41, 44, 50, 54, 56	Low mole wt gaseous product	
3.36	37, 52, 77, 78	2, 4-Hexadiene	92
3.85	41, 55, 70, 83, 96, 112	3-Methylene Heptane	98
4.77	39, 51, 65, 91, 92	Toluene	97
5.23	39, 54, 66, 79, 91, 93, 108	4-Ethynyl Cyclohexene	98
6.15	41, 55, 84, 91, 106	Cyclopentanone	95
6.71	51, 65, 91, 106	1, 3-Dimethyl Benzene	98
6.91	51, 63, 78, 104	Styrene	98
7.52	39, 65, 79, 91, 105, 120, 136	1, 2, 3-Trimethyl benzene	95
8.19	31, 41, 57, 70, 83, 98, 112	2-Propyl-1-pentanol	97
9.47	57, 76, 89, 116	Indene	95
11.57	51, 65, 78, 102, 128	Azulene	98
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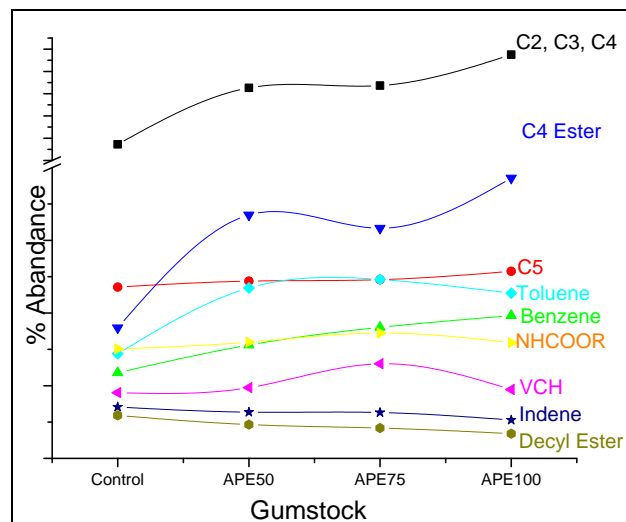


Fig. 4. Quantization of Peak Area of pyrolyzates with increasing percentage of Azidopolyester plasticizer.

Conclusion

The pyrolysis gas chromatography (GC) and mass spectrometry (MS) studies of Hydroxy Terminated Poly-Butadiene (HTPB) have been carried out to provide information about its decomposition mechanism. The major fragments were identified as butadiene, 1, 3-pentadiene, cyclopentene, 1, 5-hexadiene, 4-vinyl cyclohexane as major products during pyrolysis. There were some minor fragments such as benzene, 1, 3-cyclohexadiene, toluene, dimethyl ether, vinyl butadiene oligomer and cis-butadiene oligomer.

The decomposition mechanism of cured HTPB follows the mechanism of pure HTPB polymer. It has been observed that the additives also take part in the decomposition mechanism of cured HTPB simultaneously, which renders the decomposition of HTPB in the formation

of monomers, dimer and oligomers. Increase in the energetic plasticizer concentration results in the increase of low molecular weight fragment which clearly indicate the role of energetic plasticizer on the decomposition of HTPB. Further, the study will also be extended on HTPB based propellant system to understand the role of individual ingredient on decomposition pathway.

Acknowledgements

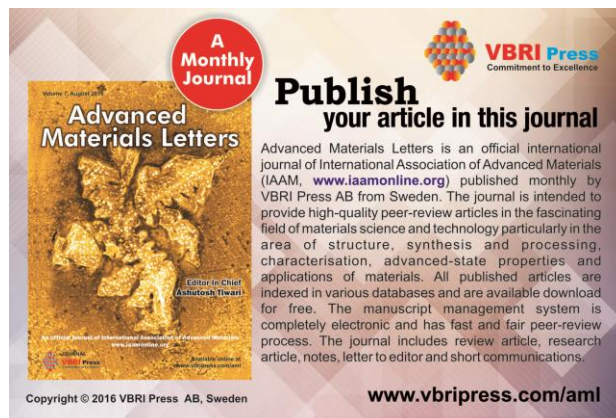
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Author's contributions

Conceived the plan, Performed the experiments, Data analysis and Wrote the paper: NN. Materials: JA; Guidance: NS, AS.

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