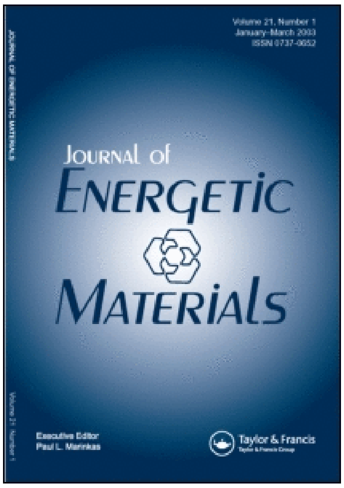

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Studies on Nonaluminized High Burning Rate AP-Composite Propellants

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This paper discusses the effect of replacement of hydroxyl terminated poly butadiene (HTPB) by butacene on the burning rates of a nonaluminized ammonium perchlorate (AP)–based composite propellant. A remarkable burning rate enhancement (60–100%) was observed on replacement of HTPB by butacene to the extent of 25%. Replacement of 50–75% HTPB by butacene led to further increase in burning rate by merely 10–20%, and no incremental effect was observed on complete replacement of HTPB. Butacene-based propellants also exhibited a lower pressure exponent (n) of the burning rate. The results obtained are in line with the findings of other researchers on aluminized AP composite propellants. Addition of transition metal oxides, ferric oxide (FO), and copper chromite (CC) to butacene-based formulations led to further enhancement of the burning rates, albeit to a less extent than in the case of HTPB-based systems. However, the burning rates of the former were higher than those of the latter in the case of

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ballistically modified compositions as well. DSC results for butacene-based formulations revealed lower activation energy (Ea) for decomposition than that for HTPB-based propellants. TGA studies brought out that butacene-based compositions decompose following a pattern similar to that of HTPB-based formulations. However, lower decomposition temperatures (1st and 2nd stages) were observed for butacene-based propellants.

Keywords: ammonium perchlorate, propellant rocket

Introduction

Reduction of the operational time for quick-action missiles has motivated technologists to develop composite propellants with superior burning rates. A combination of ultrafine ammonium perchlorate (AP) and burning rate catalysts are effective means of realizing high to ultra-high (>40 mm/s) burning rates. Transition metal compounds, particularly ferric oxide (FO) and copper chromite (CC), are the preferred choice as catalysts popularly referred as ballistic modifiers (BMs). However, introduction of solid catalysts in large amounts generates unfavorable changes in the rheological properties of the propellant, limiting their proportion to 2–3%. Thereby, an increase in solid catalyst content beyond 2–3% is possible only at the cost of energy-producing solid (oxidizer/metal fuel) components. Alkyl ferrocenes, being liquid, offer an attractive alternative. In contrast to solid catalysts, ferrocenes can be added in quantities larger than 3% at times as replacement of the plasticizer without an adverse effect on processability and offer a 2–3 times burning rate enhancement [1]. Substituted ferrocene compoundspossessing specific functional groups also act as bonding agents and impart improved processability apart from being BMs [2, 3]. However, the increase in ferrocenes' content poses a migration problem due to their volatile nature [4, 5]. The direct implication of this phenomenon is undesirable changes in designed burning rate regime during storage, thereby leading to alterations of programmed ballistics of rocket propellants. Ferrocenes accumulated on the propellant surface are also known to produce hazardous products on oxidation. Moreover, ferrocenes also pose fire hazards during processing, if their vapors come in contact with AP aerosols eventually present in the atmosphere of the process facility [6].

High molecular weight ferrocenes like catocene and 1,3 diferrocenyl 1-butene mitigate these problems to some extent [4, 7]. Ferrocene compounds with a reactive functional group can be rendered immobile. SNPE, France, achieved a technological breakthrough in this direction by adopting an approach of grafting ferrocenyl groups to pendant C=C double bonds on the vinyl component of hydroxyl terminated polybutadiene (HTPB) to preclude the migration of the ferrocene compounds [8]. This new class of prepolymer, popularly known as ''butacene,'' is obtained by reaction of organosilicon ferrocene derivatives like Fe-R-SiH $(CH_3)_2$ (where R = alkyl or phenyl group) with HTPB. Doriath et al. [8] as well as Fonblance and Herran [9] have reported that butacene-based aluminized AP-composite propellant formulations demonstrate good processability, aging, and safety properties. Bohnlein–Mauss et al. [7] (ICT, Germany) have reported the superiority of butacene over other ferrocene derivatives in regard to migration and oxidation problems. The burning rates achievable with butacene-based aluminized composite propellants are comparable to those obtained with catocene-based composite propellants. At constant iron content, marginally higher efficiency is observed due to the presence of Si atoms in butacene [6]. Gotzmer et al. [5] have found that all chemically bonded ferrocenes demonstrate favorable burning behavior with high burning rates at low pressure range, resulting in low-pressure index values.

The present work was undertaken to assess the effect of the incremental replacement of HTPB by butacene on burning rates of nonmetallized AP-HTPB propellants. Results obtained are discussed in light of the findings of other researchers. FO and CC were also evaluated as co-catalysts in butacene-based formulations, and results obtained are compared with those of corresponding HTPB-based propellants. Thermal studies (differential scanning calorimetry [DSC] and thermogravimetry [TG]) of propellants were carried out to gain insight into the decomposition pattern, and results are discussed in light of the combustion behavior of butacene-based propellants.

Experimental

Processing of Propellant

Propellant compositions containing 78% AP and 22% binder were prepared by a slurry-cast technique [10] using a vertical mixer of 1 lit capacity. Binder-comprised HTPB and butacene prepolymer alone as well as in 3:1, 1:1, and 1:3 proportions were mixed with plasticizer [(dioctyl adipate (DOA)] in a 45:55 proportion. It was added to the planetary mixer and heated to 55 ± 3°C. The contents were mixed for 20 min and evacuated (2–5 torr) for half an hour. AP [monomodal- 4 µm] was added in installments to the binder and mixed for half an hour. Mixing was continued for an additional 1 hr under vacuum (2–5 torr). The contents were allowed to cool down to room temperature, and toluene diisocyanate (TDI) was added in 1:1 stoichiometry. Final mixing was carried out for half an hour under vacuum. The propellant was cured at 70°C for 8 days. Butacene (molecular weight $\overline{\mathrm{Mn}}$ 13,500, hydroxyl value 16 mg KOH/g, iron 8 ± 0.5 weight %, functionality 2.3, viscosity <1000 Poises at 25°) supplied by SNPE, France, and HTPB (molecular weight $\overline{\mathrm{Mn}}$ 2200, hydroxyl value 42 mg KOH/g, functionality 2, viscosity <70 Poises at 30°C) manufactured by NOCIL, India, were used for the present work.

Strand Burning Rate

Strand burning rates of propellants were determined in the pressure range 2–9 MPa by employing the acoustic emission technique [11]. The methodology involved combustion of the strand of dimensions $100 \times 6 \times 6$ mm in the nitrogen-pressurized steel bomb. The progress of the flame front was monitored by acoustic signals generated due to perturbations caused by the deflagrating sample. The signals were unidirectionally transmitted through a water medium and recorded by a piezo-electric transducer (200 GHz) in conjunction with an X-Y chart recorder. The burning rates were computed from the recorded time.

Thermal Methods

Thermal analysis was carried out on a Perkin Elmer Pyris differential scanning calorimeter at heating rates of 5–25°C/min (at an increment of 5°C/min) under a nitrogen atmosphere. Activation energy of the decomposition (*Ea*) was calculated from DSC results using the ASTM standard method based on the Kissinger correlation; $\ln[\beta/Tm^2] = \ln[ZR/E] - E/RTm$, where β-heating rate in deg/min, *Tm*-peak temperature (K), and *Z*-preexponential factor. The slope of $[d\text{-}\ln\ (\beta/Tm^2)]$ against $d[1/Tm]$ gave *Ea* in kJ/mol. Thermogravimetric analysis in conjunction with FTIR was carried out on a Mettler Toledo-Bruker analyzer for monitoring gaseous products and weight loss during decomposition.

Results and Discussion

Initially compositions were engineered by varying the butacene: HTPB ratio [see Table 1 and Figure 1]. HTPB-based AP-composite propellant was taken as a reference. It gave burning rates of 8.2–17.9 mm/s in the pressure range 2–9 MPa.

Table 1

Burning rates of propellant compositions with different HTPB-butacene combinations

HTPB: butacene	Burning rate (mm/s) at pressures (MPa)					
	2	3	5	7	9	*n*
1:0	8.2	11.6	14.7	16.9	17.9	0.53
3:1	18.1	20.9	23.1	26.5	28.2	0.29
1:1	19.7	23.4	26.5	29.6	31.2	0.30
1:3	23.7	27.1	30.8	32.6	33.7	0.22
0:1	24.0	27.3	30.8	32.9	34.0	0.23

Basic composition: Binder 22%, AP(4 µm) 78%.

Binder composition: HTPB or butacene: DOA (45:55), TDI(NCO:OH, 1:1).

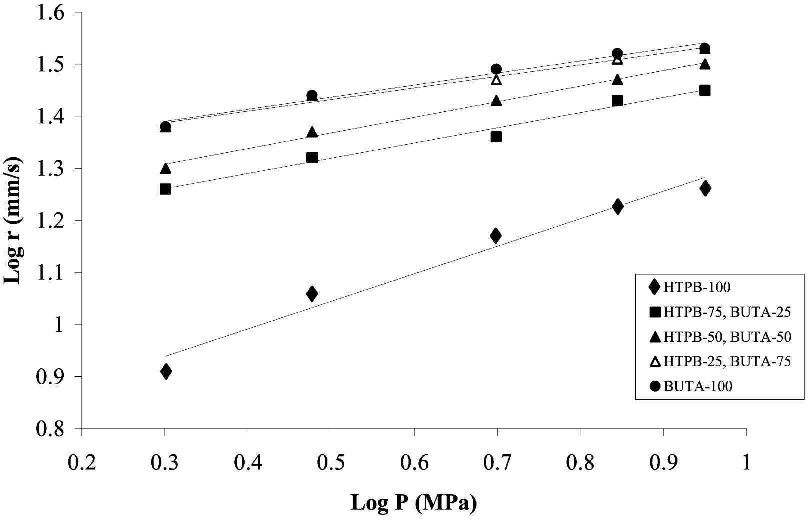


Figure 1. Burning rates of propellant compositions with different HTPB-butacene combinations.

Replacement of 25% HTPB by butacene resulted in 100% enhancement in burning rates in the lower-pressure region (2,3 MPa) and 57% increase in burning rates in the higher-pressure range (5–9 MPa). An outcome of this phenomenon was a lower pressure exponent (*n*) value compared to the HTPB-based reference composition. These results are in line with those reported by Jutta Bohnlein-Maub [9] for aluminized AP-butacene propellants. Replacement of 50% and 75% HTPB by butacene led to an additional increase in burning rates by 9–15% and 5–20%, respectively, while complete replacement of HTPB by butacene did not result in a further catalytic effect on burning rates. However, Doriath [6] has reported consistent enhancement in burning rates on replacement of HTPB by butacene in the case of aluminized AP-composite propellants.

The compositions based on 1:1 butacene-HTPB combination and butacene alone, incorporating FO and CC, were also evaluated in a strand burner (Table 2 and Figures 2–4). Incorporation of Fe_2O_3 and CC as cocatalyst (3 parts over 100 parts of composition) in 1:1 butacene-HTPB–based and buta-

Table 2
Effect of ballistic modiers on HTPB-butacene–based propellant compositions

HTPB: butacene	BMs (p)	Burning rate (mm/s) at pressure (MPa)					*n*
		2	3	5	7	9	
1:0	–	8.2	11.6	14.7	16.9	17.9	0.53
1:0	CC (3)	17.1	21.1	26.1	29.5	31.3	0.41
1:0	FO (3)	17.2	22.2	28.3	31.8	32.6	0.43
1:1	–	19.7	23.4	26.5	29.6	31.2	0.30
1:1	CC (3)	24.5	28.9	30.7	31.8	38.4	0.22
1:1	FO (3)	26.8	29.1	31.3	32.8	38.9	0.22
0:1	–	27.2	31.9	36.3	38.5	39.6	0.23
0:1	CC (3)	28.8	39.4	40.5	41.2	42.9	0.22
0:1	FO (3)	32.3	39.7	41.1	43.1	46.2	0.21

Basic composition: Binder 22%, AP(4 µm) 78%.

Binder composition: HTPB/butacene: DOA (45:55), TDI(NCO:OH, 1:1).

cene formulations led to 8–25% and 11–36% burning rate enhancements, respectively. Although the burning rates of the cocatalyst-containing formulations were much higher than corresponding ballistically modified HTPB compositions the burning rate enhancement effect of Fe_2O_3 and CC was less pronounced in the former.

Inami et al. [12] reported that catalysts play a dual role and accelerate the decomposition of AP as well as promote the oxidation of the fuel by heterogeneous reactions. It is speculated that in metal oxide–catalyzed oxidation, the metal ions in the lattice undergo a redox cycle involving interaction of hydrocarbons with their high-valence state followed by reoxidation by molecular oxygen.

Pearson [13] and Boggs et al. [14] established that heat release occurs on sequential exposure of CC to fuel vapor and

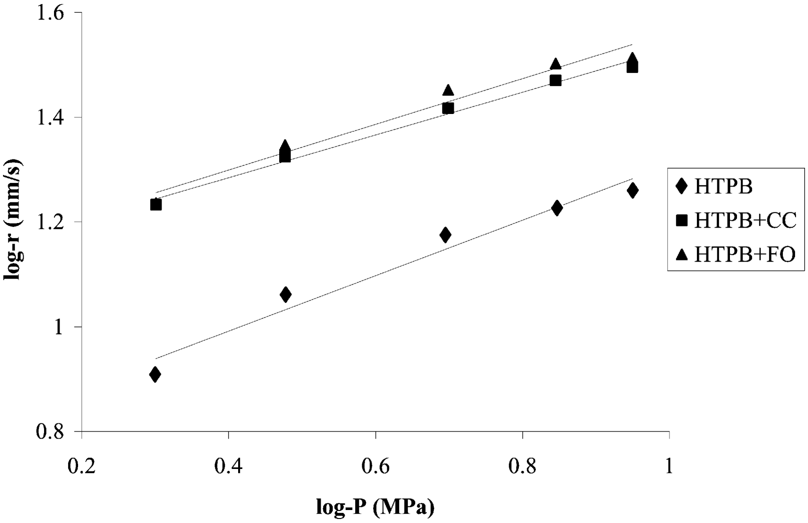


Figure 2. Effect of ballistic modifiers on HTPB-based propellant composition.

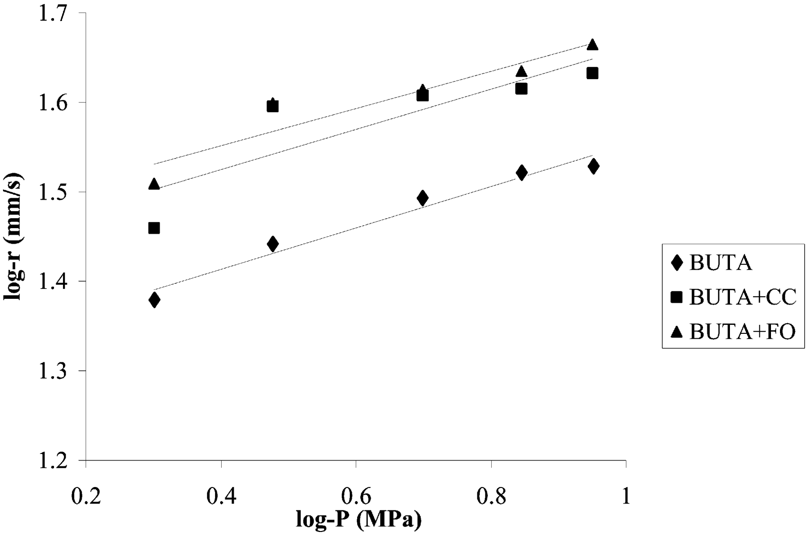


Figure 3. Effect of ballistic modifiers on butacene-based propellant composition.

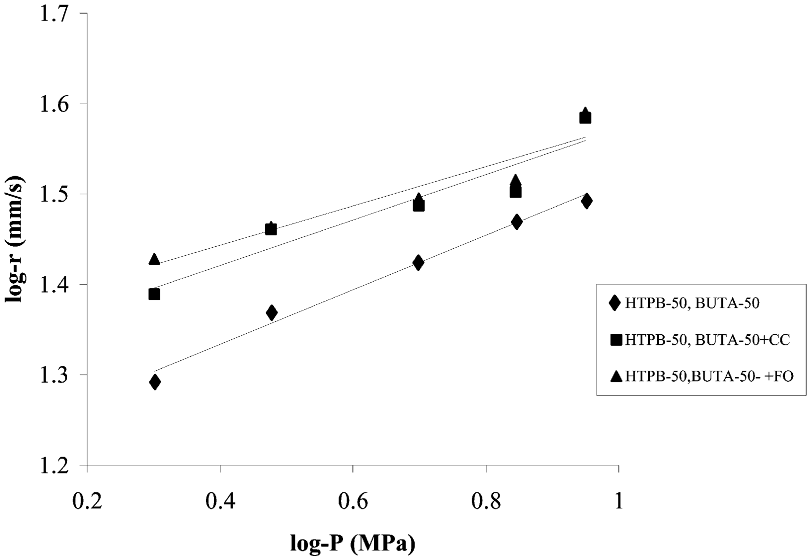


Figure 4. Effect of ballistic modifiers on HTPB-butacene–based propellant composition.

oxidizing species. Pearson [13] proposed three modes of reactions in the case of CC (1) involving activation of fuel molecules by absorption on the surface of the catalyst followed by the subsequent reaction with oxygen, (2) reaction of fuel molecules with an oxygen catalyst in the surface layer, and (3) reaction of fuel molecules with an oxygen catalyst throughout the bulk of catalyst. It has been established that CC is effective at temperatures close to those prevailing on the propellant surface in promoting reactions associated with olefins. It is proposed that the heat release on the CC particles involves a redox cycle between cupric oxide/cuprous oxide/copper on the propellant surface, resulting in the increased heat transfer and, as a consequence, enhancement of the propellant burning rate.

A large number of findings suggest that Fe_2O_3 does not act in the subsurface region, and the condensed phase is not the location of its prominent action [15, 16]. Beckstead [17] speculated that the final flame is too far to influence the burning rate, and thereby the primary flame region is the logical site for the catalytic reactions by Fe_2O_3. Wang et al. [18] have reported that iron catalysts serve as an in situ source of α-Fe_2O_3 particles that eject in the flame and provide the effective site for catalysis of the primary reaction by a heterogeneous mechanism. Pittman [15], Flanagan [16], and Pearson [19] have demonstrated that Fe_2O_3 catalyzes the decomposition of AP in the vapor phase.

Ferrocenes tend to decompose exothermically to produce hydrocarbons and Fe. The latter is presumed to get oxidized, producing ultra-fine particles of αFe_2O_3 in situ. Ferrocene compounds are known to reduce the activation energy of decomposition of composite propellants [20, 21]. Ferrocenes like butyl ferrocene are presumed to accelerate thermal decomposition of AP as well as the binder [22]. Pittman [15] found that it is difficult to locate the site of the catalyst action in propellants containing *n*-butyl ferrocene because the rate-controlling combustion zone at the surface is very thin, involving both condensed and gas phase regimes with a large thermal gradient across them.

The chemical structure of ferrocene-grafted HTPB appears to promote the catalytic effect to a greater extent because of the presence of Si, which acts as a good energy supplier [3]. Further, the proximity of ferrocene to AP because of its being a part of polymeric chain may be a decisive factor for its pronounced effect in the near-surface region [6].

Thermal Studies

A large number of researchers [23–25] have reported that Ea's for catalyzed AP are higher than those of pure AP. However, Dubey et al. [26] observed that catalysts lower Ea in the temperature range 220–260°C and increase it in the temperature range 220–380°C. The frequency factor is presumed to play an important role in this respect. However, many researchers have observed lowering of the decomposition temperature of propellants by ballistic modifiers. Ferrocenes are reported to undergo exothermic oxidation, resulting in a positive effect on ΔH of AP/HTPB propellants.

In DSC undertaken during this work, butacene and HTPB-based composite propellants exhibited two prominent exothermic peaks at all the scanning rates. However, replacement of HTPB by butacene resulted in lowering of the decomposition temperature ($T_{\max}$) of first (from 323 to 249°C) and second (from 371 to 323°C) stage, suggesting catalytic activation by butacene. A representative thermogram of decomposition of propellants using DSC is shown in Figures 5a, 5b, and 5c.

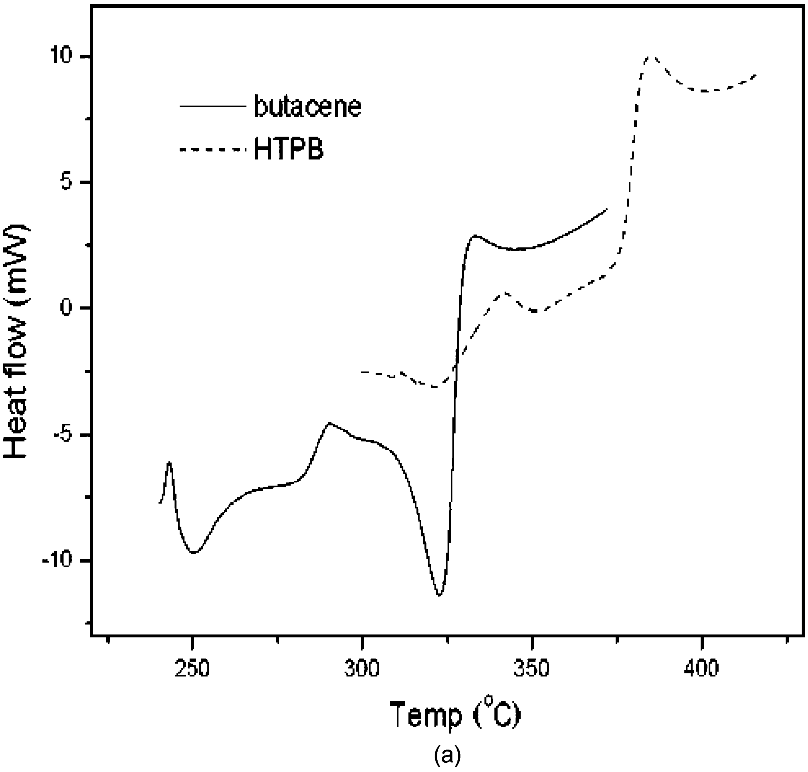
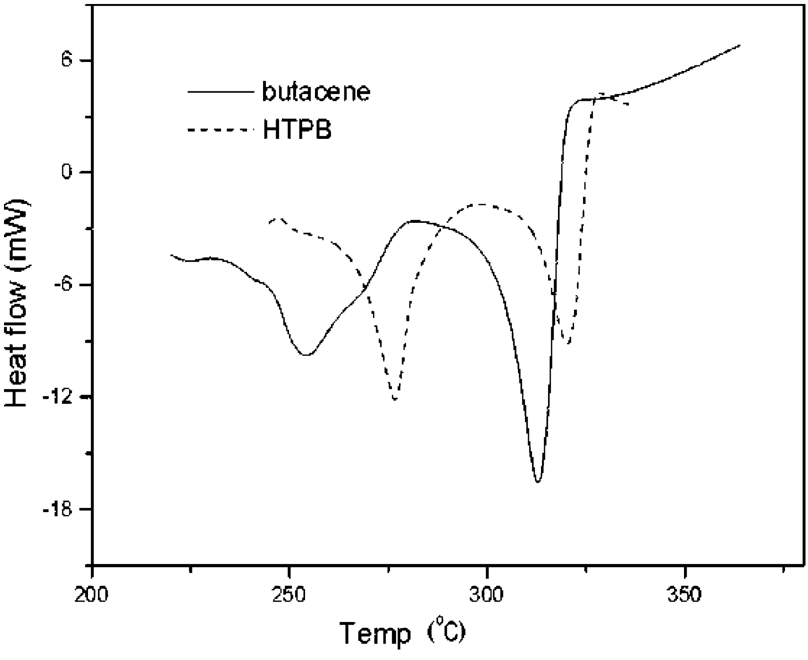


Figure 5. (a) DSC thermogram of butacene- and HTPB-based propellants. (b) DSC thermogram of butacene- and HTPB-based propellants ballistically modified by FO. (c) DSC thermogram of butacene- and HTPB-based propellants ballistically modified by CC.



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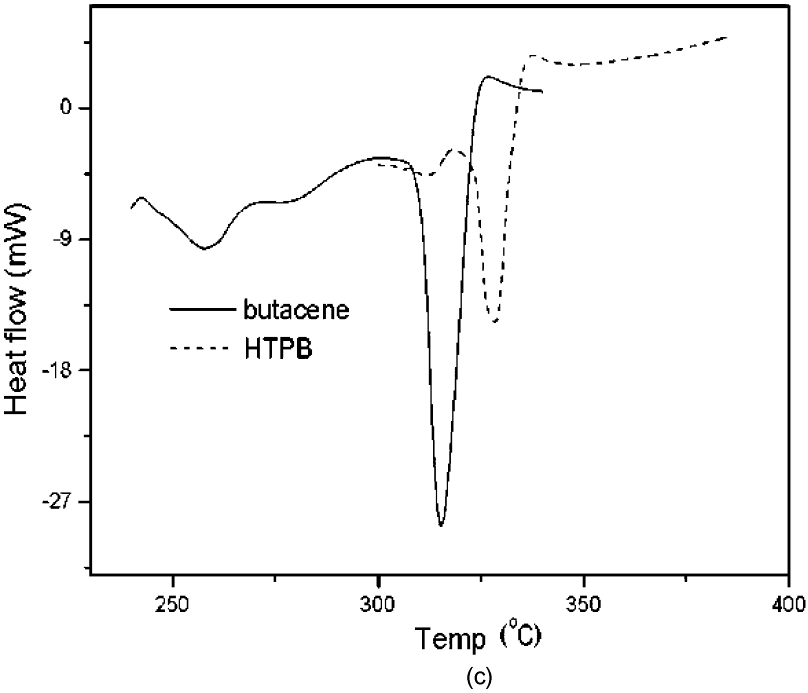


(c)

Figure 5. (Continued).

DSC of HTPB and butacene also revealed that the grafting of ferrocene on HTPB (in butacene) changes the energy release pattern despite a similar weight loss pattern, as revealed in TG of both. (Figures 6a and 6b). Addition of BM to butacene-based propellant did not result in further lowering of decomposition temperature, unlike in the case of HTPB propellants.

DSC data generated at different heating rates gave activation energies of 188 and 251 kJ/mol for first- and second-stage decomposition of AP-HTPB propellant, in comparison to that of 117 and 176 kJ/mol for AP-butacene based propellant. Addition of FO/CC did not change appreciably the activation energy values of AP-butacene propellants (Table 3), while for AP-HTPB propellant the values were lowered drastically. These results suggest that butacene catalyzed both stages of decomposition and is effective in a condensed/near-surface gas phase.

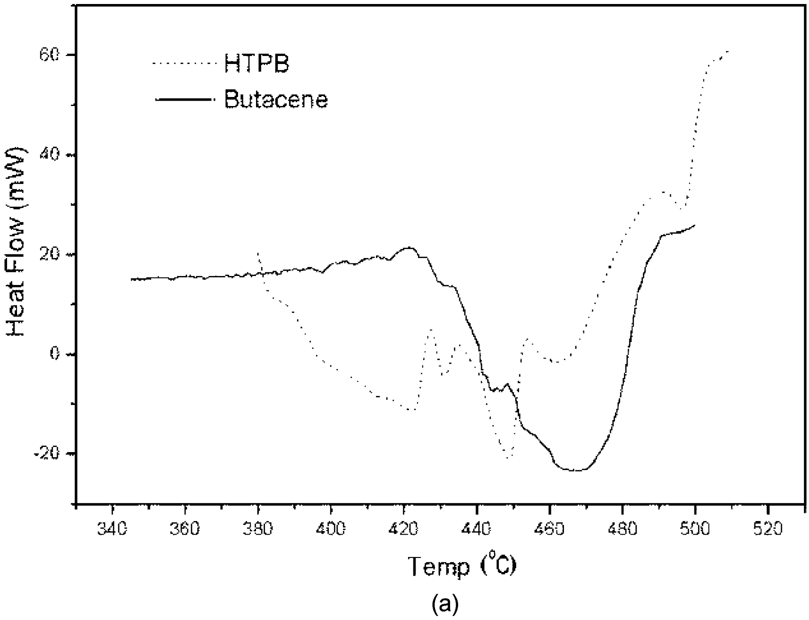


Figure 6. (a) DSC thermogram of HTPB and butacene in zero air. (b) TG thermogram of HTPB and butacene.

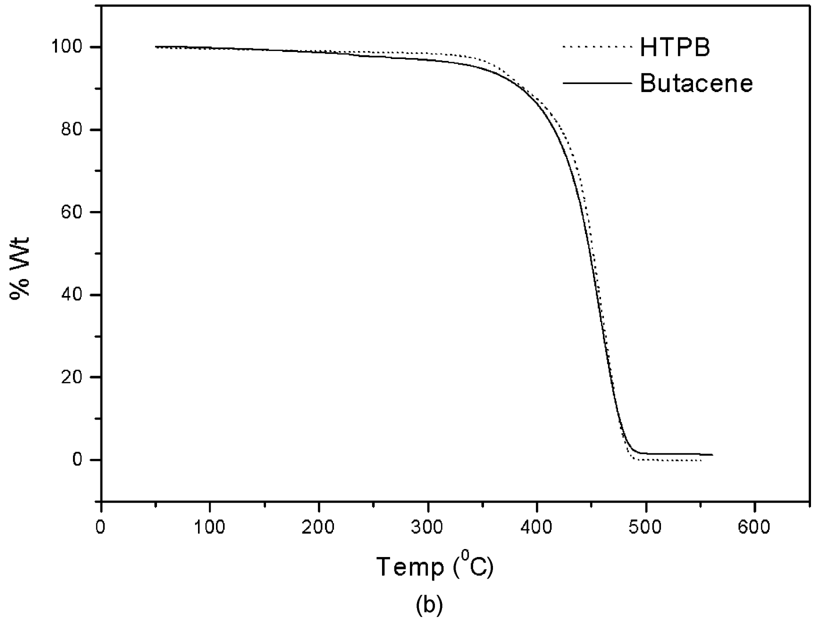


Figure 6. (Continued).

The TGA data presented in Table 4 and Figures 7a, 7b, and 7c, like the DSC results, brought out that the decomposition pattern corresponds to that of AP alone, suggesting that AP plays an important role in decomposition of the propellants. The TG pattern for butacene- and HTPB-based composite propellants revealed that propellant decomposition occurs in two stages, leaving behind 6–10% residual matter. The first stage decomposition for butacene-based propellant occurs in the temperature range 162–235°C with 23% weight loss against 15% loss in weight for HTPB-based system in the range 196–281°C. Further decomposition of butacene-based propellant amounting to weight loss of about 70% occurred in the temperature range 235–339°C, while that for HTPB-based propellant occurred in the temperature range 281–360°C. FO- and CC-containing HTPB- and butacene-based propellants exhibited a more or less similar weight loss pattern. Complete decom-

Table 3
Decomposition temperature and activation energy of HTPB-butacene–based propellant compositions

HTPB/ butacene	BM (p)	Peak temperature (°C) ats canning rate (°C/min)					E_a (KJ/mol)	
		5	10	15	20	25	1st stage	2nd stage
HTPB	–	311	324	329	331	338	188	251
		361	371	375	381	382		
HTPB	CC (3)	299	313	315	322	326	159	171
		316	329	333	340	343		
HTPB	FO (3)	266	277	283	289	292	146	159
		308	321	326	332	336		
Butacene	–	244	250	258	261	267	117	176
		312	323	329	334	338		
Butacene	CC (3)	247	258	264	269	272	142	163
		304	315	323	328	330		
Butacene	FO (3)	250	255	261	264	268	159	176
		310	314	320	324	328		

Basic composition: Binder 22%, AP(4 µm) 78%

Binder composition: HTPB/butacene: DOA (45:55), TDI(NCO:OH, 1:1).

position for ballistically modified HTPB propellants also occurred in the temperature region below 340°C.

Conclusion

Butacene-binder based AP-composite propellants offer superior burning rates with lower pressure exponent (n) values compared to HTPB-based systems. Burning rate enhancement was more prominent up to 25% replacement of HTPB by butacene. Thermal analysis data in the case of a butacene binder bring out the shift in temperature of exotherms associated with AP/AP binder decomposition, suggesting catalytic activity in

Table 4

Thermogravimetric analysis of HTPB-butacene–based propellant compositions

HTPB:butacene	Weight loss 1st stage	2nd stage
1:0	23%	71%
3:1	15	68
1:1	19	73
1:3	12	70
0:1	13	75

Basic composition: Binder 22%, AP(4 μm) 78%.

Binder composition: HTPB/butacene: DOA (45:55), TDI(NCO:OH, 1:1)

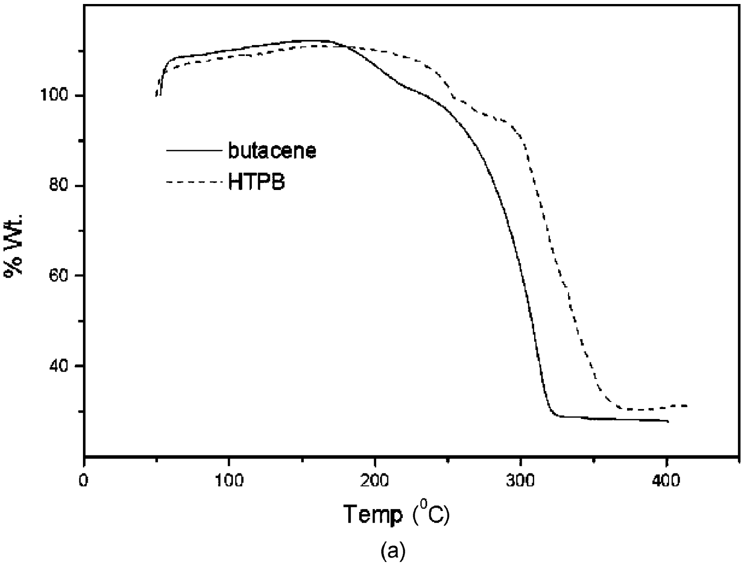
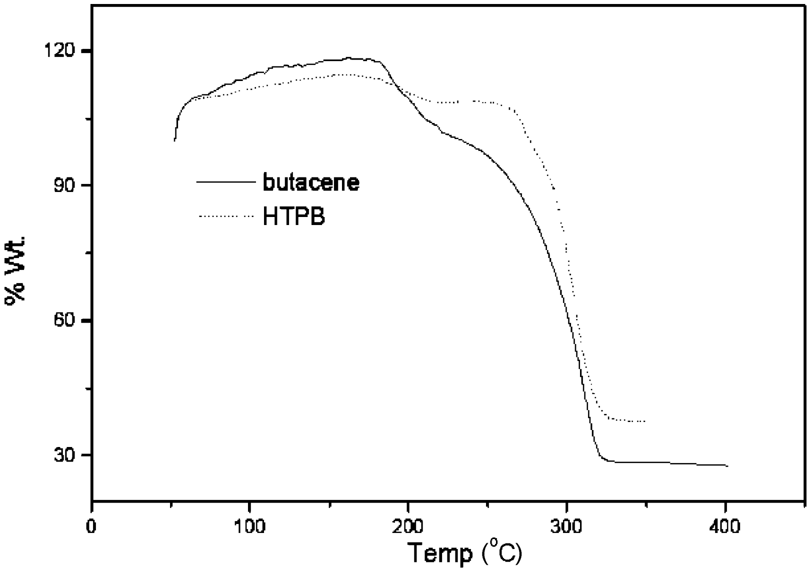


Figure 7. (a) TG thermogram of butacene- and HTPB-based propellants. (b) TG thermogram of butacene- and HTPB-based propellants ballistically modified by FO. (c) TG thermogram of butacene- and HTPB-based propellants ballistically modified by CC.



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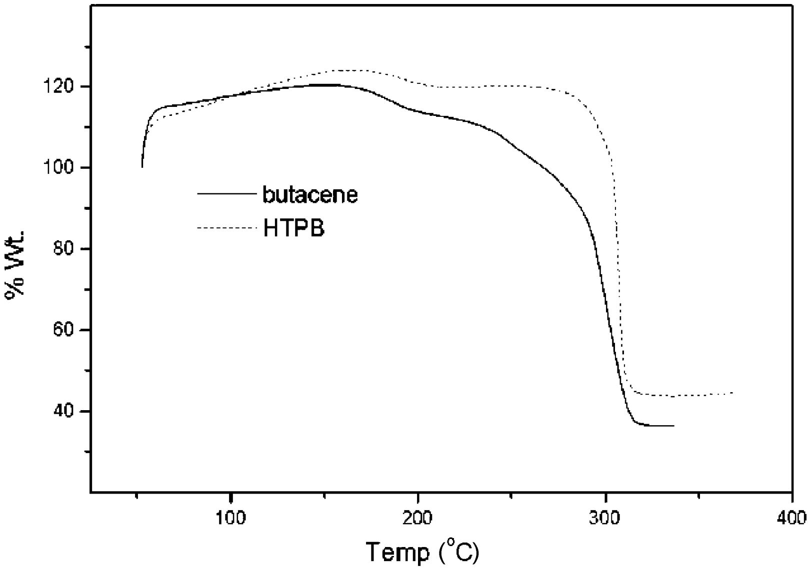

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Figure 7. (Continued).

the condensed/near-surface gas phase. The site of action of major ballistic modification in butacene-based propellants appears to be the gas phase.

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