

Burning-Rate Enhancement of a High-Energy Rocket Composite Solid Propellant Based on Ferrocene-Grafted Hydroxyl-Terminated Polybutadiene Binder

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ABSTRACT: Four different samples of ferrocene-grafted hydroxyl-terminated polybutadiene (Fc-HTPB), containing 0.20, 0.52, 0.90, and 1.50 wt % iron, were synthesized by the Friedel–Crafts alkylation of ferrocene with hydroxyl-terminated polybutadiene (HTPB) in the presence of AlCl₃ as a (Lewis acid) catalyst. The effects of the reaction conditions on the extent of ferrocene substitution were investigated. The Fc-HTPBs were characterized by IR, ultraviolet–visible, ¹H-NMR, and ¹³C-NMR spectra. The iron content and number of hydroxyl groups were estimated, and the properties, including thermal degradation, viscosity, and propellant burning rates (BRs), were also studied. The thermogravimetric data indicated two major weight loss stages around 395 and 500°C. These two weight losses were due to the depolymerization and

decomposition of the cyclized product, respectively, with increasing temperature. The Fc-HTPB was cured with toluene diisocyanate and isophorone diisocyanate separately with butanediol–trimethylolpropane crosslinker to study their mechanical properties. Better mechanical properties were obtained for the gumstock of Fc-HTPB polyurethanes with higher NCO/OH ratios. The BRs of the ammonium perchlorate (AP)-based propellant compositions having these Fc-HTPBs (without dilution) as a binder were much higher (8.66 mm/s) than those achieved with the HTPB/AP propellant (5.4 mm/s). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2517–2524, 2011

Key words: antioxidants; catalysts; composites; gel permeation chromatography (GPC); polybutadiene

INTRODUCTION

Most state-of-the-art composite solid propellants (CSPs) are composed of a combination of chemical ingredients, namely, hydroxyl-terminated polybutadiene (HTPB; prepolymer), a diisocyanate (curative), plasticizer, antioxidants, a burning-rate (BR) modifier, a catalyst, and an ammonium perchlorate (AP) oxidizer.^{1–7} The cured polymer, in addition to being a fuel, acted as a binder for the particulate AP to achieve good mechanical properties. Among various types of catalysts, transition-metal oxides, ferrocene, and ferrocene derivatives^{8–10} have been widely used to enhance the BRs of CSPs. A large number of polymeric ferrocene derivatives produced from different precursor monomers are also found in the literature.^{11,12} Most of

the known ferrocene-containing combustion moderators, however, display unwanted properties of migration, which is travel out of the rubberlike binder matrix of the propellant into the surrounding insulation material; this leads to uneven combustion and worsens the resistance to aging and the formation of highly sensitive boundary layers.^{13,14} Furthermore, it affects the pourability of the propellant slurry to a significant degree and the poor mechanical and ballistic properties of the finished propellant. A binuclear ferrocene derivative, for example, catocene or butacene,^{15,16} is the main impediment for their use as BR modifiers in rocket applications. Herein, we report the synthesis of ferrocene-grafted hydroxyl-terminated polybutadienes (Fc-HTPBs) by Friedel–Crafts alkylation as potentially useful additives for composite rocket propellants. The significant advantage of this study was that the ferrocene group was covalently linked to the HTPB backbone, and it could not migrate from the backbone. Another advantage was that the crystallization of catalyst did not occur at low temperature. Therefore, these binder-based propellants were expected to have good aging and ballistic (BR) properties. Fc-HTPB was characterized by IR, NMR, and ultraviolet–visible (UV–vis) spectroscopy; iron content; viscosity; OH value; and molecular weight [gel permeation chromatography

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TABLE I
Synthetic Data for Fc-HTPB

HTPB (g)	Ferrocene (g)	AlCl ₃ (g)	Yield (%)	Iron (%)
100	10 g, 1.43 mol equiv to HTPB	3 g, 0.57 mol equiv to HTPB	80	0.20
100	16 g, 2.28 mol equiv to HTPB	5 g, 1.35 mol equiv to HTPB	75	0.52
100	20 g, 2.76 mol equiv to HTPB	7 g, 1.35 mol equiv to HTPB	75	0.90
100	40 g, 5.52 mol equiv to HTPB	10 g, 1.93 mol equiv to HTPB	72	1.50

(GPC)]. The thermal properties of Fc-HTPB were studied by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) analysis. The aging, mechanical properties of gumstock, and BR of the Fc-HTPB-based propellant were also evaluated and analyzed.

EXPERIMENTAL

Material

HTPB, made by the free-radical polymerization of butadiene gas with H₂O₂ as an initiator and with a process developed by Vikram Sarabhai Space Centre, India, was used. Ferrocene (98%) and aluminum chloride (99.99%, Aldrich, India) were used as received, whereas dichloroethane was dried over calcium chloride, distilled over phosphorous pentoxide, and stored over molecular sieves. All of the other materials were used as received. The reactions were performed under a nitrogen atmosphere.

Physical measurements

The iron content of Fc-HTPB was analyzed with a PerkinElmer 2380 atomic absorption spectrophotometer (Perkin-Elmer Corp., Norwalk, CT). The atomic absorption spectroscopy (AAS) samples were prepared by the treatment of a weighed quantity of Fc-HTPB with diluted nitric acid (50%, to prevent autoignition) and their subsequent heating with fuming nitric acid until the polymers completely decomposed and mineralized. The mineralized solutions were made up to a known volume and used for AAS analysis. The inherent viscosities were determined at 25°C in dichloroethane with an Ubbelohde viscometer (India). The hydroxyl content of HTPB was determined by acetylation with excess acetic anhydride followed by back-titration with standard alcoholic KOH, and this was used to calculate the equivalent weight of HTPB. IR spectra were recorded on a Hitachi 270-50 spectrophotometer (Japan) in the range 400–4000 cm⁻¹. Electronic spectral studies were carried out in dichloroethane on a Hitachi 320 double-beam spectrophotometer in the range 200–800 nm. ¹H-NMR and ¹³C-NMR spectra were recorded in CDCl₃ solvent with a JEOL GSX-400 Fourier transform NMR spectrometer (Japan Electron Optics Laboratory Co., Ltd.,

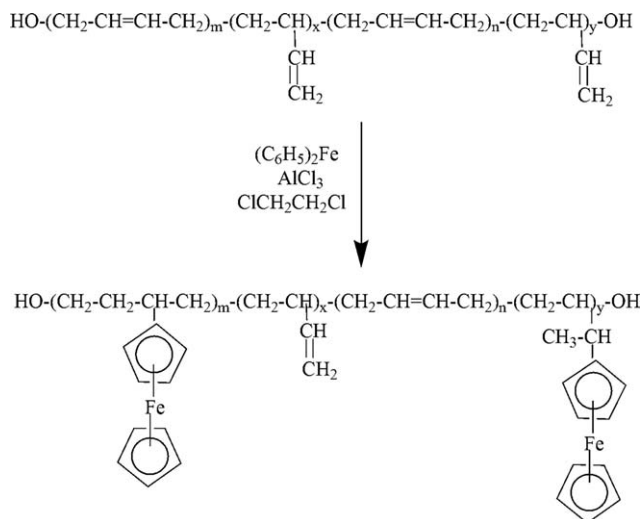
Japan). The molecular weight of the polymer was determined by GPC with tetrahydrofuran as the mobile phase (flow rate = 1 mL/min) with monodisperse polystyrene as a standard and a refractive-index detector (Shodex R1SE-61, Showa Denko, Tokyo). The thermal stability of the polymer was determined with a Seiko thermogravimetric analyzer (TGA/DTG; model SSC-5200, Chiba, Japan) under nitrogen at a heating rate of 20°C/min.

The mechanical properties, including as tensile strength, percentage elongation, and stress at 100%, of the cured Fc-HTPB polyurethane samples were evaluated with an Instron 1121 universal testing machine (Instron 1121, UK). Test specimens were made from slabs by cutting 3–5 mm thick dumbbells of ASTM specification D 412-68 type and tested at a crosshead speed of 500 mm/min at 25°C. The dumbbells were conditioned in CaCl₂ desiccators for 24 h before testing. The average mechanical properties were evaluated from the stress versus strain graphs of five dumbbells. The tensile strength is represented in kilograms per square centimeter (ksc).

Synthesis of Fc-HTPB

Ferrocene was dissolved in 1,2-dichloroethane (1 L) under a nitrogen atmosphere in a 3-L, three-necked flask. To this solution, a suspension of aluminum chloride in 300 mL of dichloroethane was added, and the mixture was stirred for 30 min at room temperature. To this clear reddish brown solution, a solution of HTPB (100 g, dried in a vacuum oven at over 60°C before use) in 500 mL of dichloroethane was added. The HTPB was dried before use in a vacuum oven at over 60°C. After 24 h of stirring, the reaction mixture was poured into excess methanol containing antioxidant, diphenylamine (0.5%) and a reducing agent, and ascorbic acid (0.5%) to precipitate the polymer. The product was reprecipitated several times into methanol to remove the unreacted ferrocene. The product was redissolved in dichloroethane and stored in the presence of an antioxidant. The amount of grafted ferrocene in polymer backbone was determined from AAS.

Four batches of Fc-HTPB¹⁷ were synthesized with various concentrations of ferrocene and aluminum



Scheme 1 Mechanism of the synthetic pathway.

chloride catalyst, as shown in Table I. The mechanism of the synthetic pathway is shown in Scheme 1.

Synthesis of the Fc-HTPB-based polyurethane

Fc-HTPB was homogeneously mixed with ambilink, such as butanediol and trimethylolpropane. The diisocyanate [isophorone diisocyanate (IPDI) or toluene diisocyanate (TDI)] was then added, and we mechanically agitated the contents of the kettle for 10 min. All of these operations were carried out as quickly as possible to avoid quick gelation. The viscous reaction mixture obtained was degassed under a reduced pressure of 5–6 Torr for 30 min to eliminate air bubbles and cast on a mold and cured in an air oven at 60°C for a period of 48 h. After curing, the 3–5 mm thick dumbbells of ASTM specification were cut from the sample mold to evaluate the me-

chanical properties. The formation of Fc-HTPB polyurethane is shown schematically in Scheme 2.

Formation of the Fc-HTPB-based solid propellants

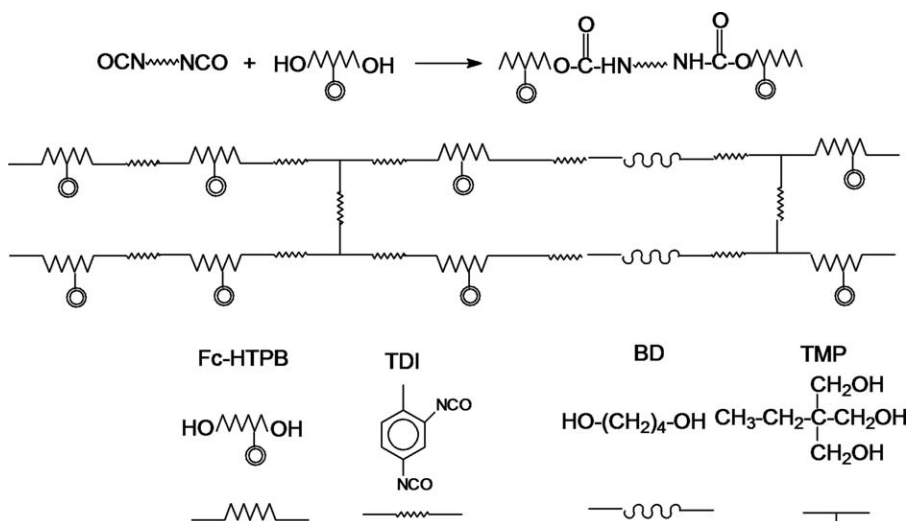
The CSPs were formulated¹⁸ on the basis of Fc-HTPB as a binder and AP as a solid oxidizer. A propellant composition with a solid loading of 86% and 18% Al was used. The triol crosslinker Butanediol–Trimethylolpropane (BD–TMP) content was kept at 0.12% along with 3% plasticizer (dioctyl adipate) and an NCO/OH equivalent ratio equal to 0.83. Calculated amounts of the prepolymers, BD–TMP, AP, and TDI were mixed (1 kg size) in a thermostatically controlled, double-bladed sigma kneader at 60°C, as per the standard procedure. The slurry was cast in polyethylene cartons *in vacuo* and cured at 60°C for 120 h.

The BRs of the solid propellants were determined in a nitrogen pressurized strand burner by an acoustic emission technique. BR was evaluated from the acoustic output given by the sample during burning. The signals were picked up by an acoustic emission sensor (Vikram Sarabhai Space Centre, India), from which the BRs could be accurately derived.

RESULTS AND DISCUSSION

Characterization of Fc-HTPB

The iron content, viscosity, and OH value of the different Fc-HTPB batches are given in Table II. Figure 1 shows the effects of the viscosity and OH values with respect to the concentration of iron in the Fc-HTPBs. AAS analysis revealed that the concentration levels of iron in the Fc-HTPBs were 0.20, 0.52, 0.90, and 1.50 wt %. As shown in Table II, it was clear that the grafting of ferrocene increased as the iron content of the samples increased. This



Scheme 2 Formation of Fc-HTPB polyurethane.

TABLE II
Physical Characteristic Data of Fc-HTPB

Sample	Iron content (%)	Viscosity (dL/g)	OH value
HTPB	0.0	0.74	44.1
Fc-HTPB	0.20	1.25	21.4
Fc-HTPB	0.52	1.72	30.7
Fc-HTPB	0.90	2.22	32.4
Fc-HTPB	1.50	2.85	34.0

clearly confirmed the presence of ferrocene with respect to the amount of grafting. The viscosity increased with increasing iron content because of the greater extent of ferrocene grafting in the polymer. As shown in Figure 1, the OH values increased with iron content. At higher ferrocene contents, the number of OH groups also increased. This may have been due to the larger number of ferrocene molecules linked per unit of polymer. Obviously, the OH value was high in polymers containing more ferrocene. To determine the storage and shelf life of the Fc-HTPB samples, the specific viscosity of Fc-HTPB (0.20 wt % Fe) was measured at room temperature at regular time intervals (30 days) over 6 months, and the data are tabulated in Table III. In this study, we observed that the viscosity of Fc-HTPB increased (from 1.26 to 2.25) compared with HTPB. This was due to an increase in the molecular weight of Fc-HTPB, as estimated by GPC. The polymer chains underwent even more aggregation and formed larger structures, characterized by significantly higher intrinsic viscosities, as the concentration of Fc increased. Another reason may have been a decrease to some extent of OH groups by AlCl_3 attack, which led to the interlinking of the polymer chains. Hence, the viscosity buildup of the Fc-HTPB was greater than that in HTPB.

The IR spectrum (Fig. 2) of the Fc-HTPBs exhibited the characteristic features of bands at 735, 1440, 1640, and 2930 cm^{-1} , which belonged to polybutadiene¹⁹

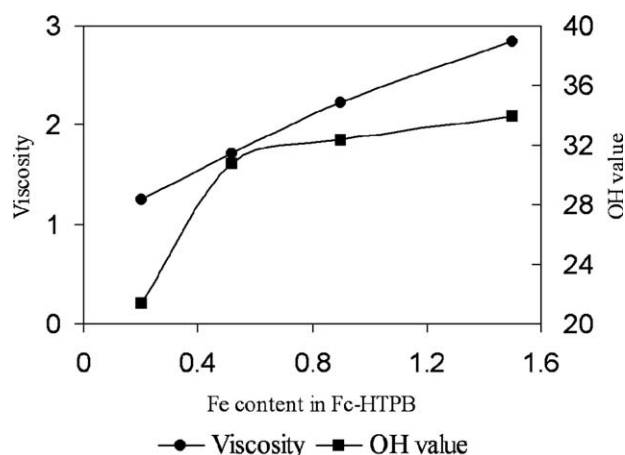


Figure 1 Plot of the iron content versus the viscosity and OH value.

TABLE III
Viscosity Data for Aged HTPB and Fc-HTPB

Sample	1st month	2nd month	3rd month	4th month	5th month	6th month
HTPB	0.74	0.78	0.76	0.80	0.81	0.81
Fc-HTPB (0.20% Fe)	1.25	1.46	1.58	1.76	2.02	2.25
HTPB: Fc-HTPB (1:1)	1.17	1.35	1.48	1.67	1.83	2.03

segments, whereas the presence of a ferrocene moiety^{20–22} was evident from the peaks at 820, 1000, 1100, and 3074 cm^{-1} . The broad peak at 3425 cm^{-1} indicated the presence of OH groups. The UV-vis spectra of Fc-HTPB are shown in Figure 3. The UV-vis spectrum of Fc-HTPB showed two bands at 450 and 345 nm due to the presence of a ferrocene moiety in the HTPB. The intensity of the bands increased with the increasing weight percentage of iron [0.20, Fig. 3(a); 0.52, Fig. 3(b); and 0.90, Fig. 3(c)]. The ¹H-NMR spectrum (Fig. 4) of the ferrocene-substituted HTPB (0.20 wt % Fe) showed a broad multiplet at 5.50 due to the vinylic proton ($-\text{CH}=\text{CH}-$) in the compound, and the multiplet at $\delta = 5.13$ was due to the methylene proton, which was attached to a hydroxyl group ($-\text{CH}_2-$)—OH). A broad singlet at $\delta = 3.52$ was due to the ferrocene moiety, a broad singlet at $\delta = 2.91$ was due to the methine proton attached to the ferrocene nucleus ($-\text{CH}-\text{Fc}$), and a broad singlet at $\delta = 2.12$ was due to the methylene proton ($-\text{CH}_2-\text{CH}_2-$) in the polymer. The ¹³C-NMR spectrum exhibited a peak at $\delta = 76-77$ ppm due to the presence of the ferrocene moiety in the Fc-HTPB.

GPC data of the Fc-HTPBs are given in Table IV. Gel permeation chromatograms of HTPB and Fc-HTPB showed that the shapes of the chromatograms were not modified; only increases in the molecular weights were observed, which corresponded to the addition of ferrocene units in the polymer backbone. As shown in Table IV, the iron content increased, and the retention time decreased, which clearly indicated an increase in the molecular weight by the grafting of the ferrocene moiety onto HTPB. This was in accordance with the number-average and average molecular weight of a polymer. Generally, the molecular weight of a polymer depends on the retention time. As the retention time increases, the molecular weight decreases. These results show that the chemical modifications were statistical, without side reactions, and especially without crosslinking.^{23,24}

Thermal properties of Fc-HTPB

The thermal behavior^{25,26} of HTPB and Fc-HTPB were investigated by TGA carried out in nitrogen and in air. Figure 5(a,b) shows the thermograms of HTPB and Fc-HTPB, respectively. There were two weight loss stages in free HTPB. In the first stage, there was a

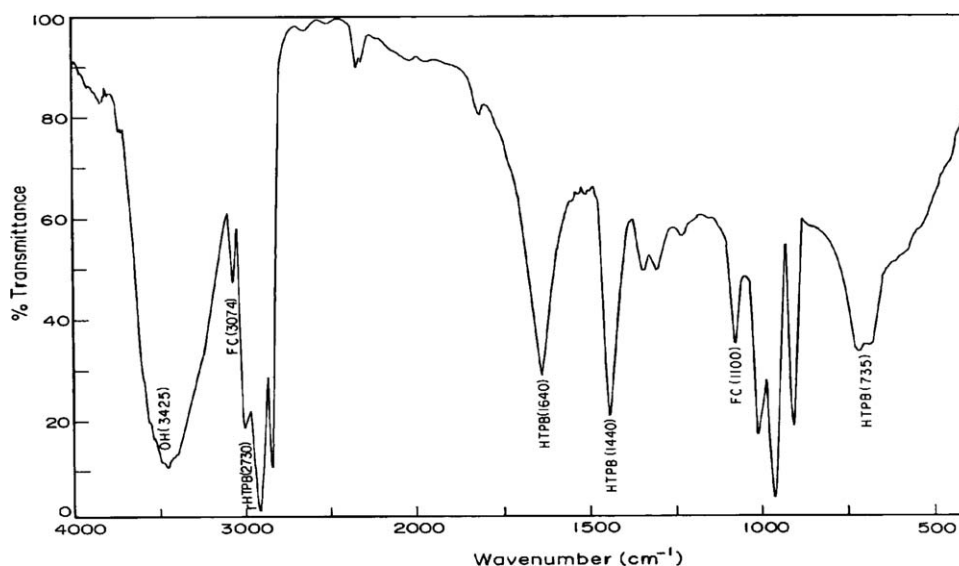


Figure 2 IR spectrum of Fc-HTPB.

5% weight loss up to 370°C, and in the second stage was separated into three small stages, in which the maximum rates of weight loss occurred around 415, 425, and 470°C, respectively. HTPB left about 1% residue at 500°C. The thermogram of 0.90 wt % Fc-HTPB left about 2.4% residue at 500°C. The DTG trace indicated two major weight loss stages. For the first stage, the maximum rate of weight loss occurred around 375°C. The first stage was primarily depolymerization, cyclization, and crosslinking accompanied by the par-

tial decomposition of the cyclized product. The second stage involved the decomposition of the cyclized product with increasing temperature, whereas depolymerization and cyclization reactions gradually disappeared.^{29,30} When compared to HTPB with 0.90 wt % Fc-HTPB, a considerable change in the degradation pattern was observed, and the onset of thermal decomposition shifted from a lower temperature to a higher temperature. These indicated considerable interaction taking place on the polymer backbone because of the incorporation of the ferrocene moiety. Thus, we observed that Fc-HTPB had more thermal stability than HTPB.

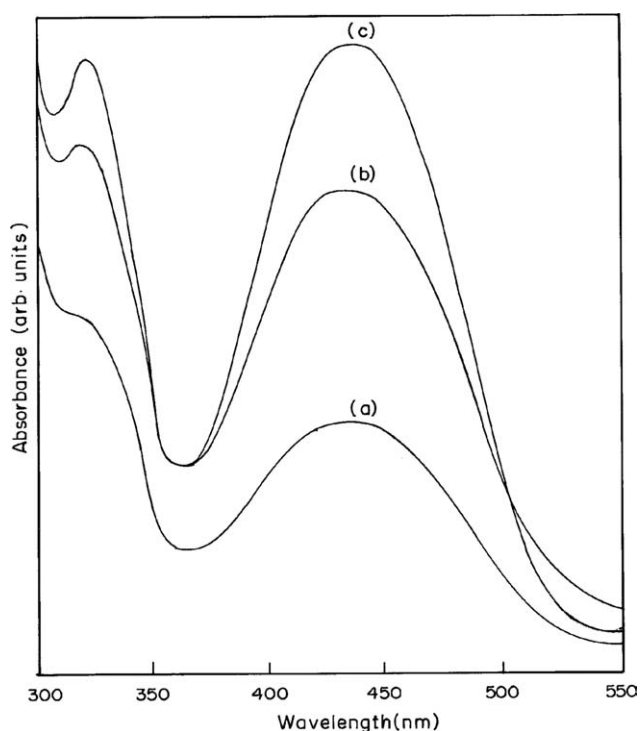


Figure 3 UV-vis spectrum of Fc-HTPB. Iron content in Fc-HTPB: (a) 0.2, (b) 0.9, and (c) 1.5%.

Mechanical properties of Fc-HTPB

Effect of the NCO/OH ratio

The mechanical characterization of Fc-HTPB polyurethanes, which were cured with IPDI and TDI at

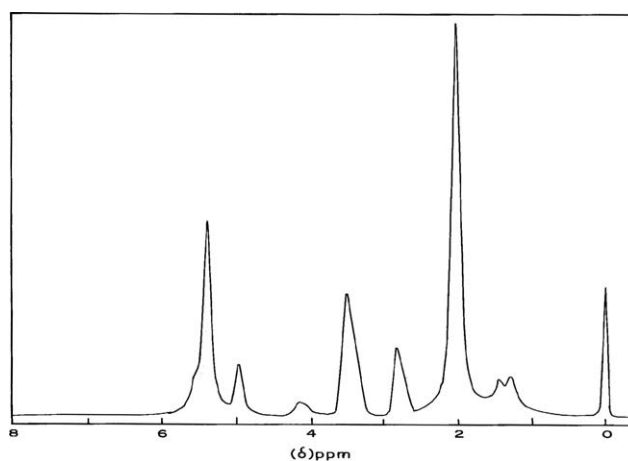


Figure 4 ¹H-NMR spectrum Fc-HTPB.

TABLE IV
GPC Data

Sample	M_n	M_w	Retention time (min)	M_w/M_n
HTPB	4379	10290	28.3	2.35
Fc-HTPB (0.20%)	5230	10977	28.1	2.27
Fc-HTPB (0.90%)	6789	31368	27.6	3.80
Fc-HTPB (1.50%)	8237	32001	26.8	3.90

M_n = number-average molecular weight; M_w = weight-average molecular weight.

different NCO/OH ratios ranging from 0.75 to 1.5 and BD/TMP (2.4%) as ambilink, were determined, and the values are given in Table V. The results show that a higher NCO/OH ratio resulted in samples having greater tensile strengths, hardnesses, and lower elongation percentages for IPDI and TDI as curing agents. This resulted in highly crosslinked products at higher NCO/OH ratios.^{31,32} At lower NCO/OH ratios, chain growth was retarded because of excess hydroxyl groups. Another possibility was the occurrence of side reactions with traces of moisture present in the atmosphere. The choice between IPDI and TDI as a curing agent had little impact on the mechanical properties.³³ The mechanical properties, including tensile strength, elongation, and hardness, remained more or less the same in both cases. Better processability was obtained when IPDI was used as a curing agent. The trend in the percentage elongation was different for a 0.90 wt % iron content Fc-HTPB when compared to the other iron content. This obvious improvement in the mechanical properties below 0.90 wt % iron content may have been due to the different network nature. The polymer chains below 0.90 wt % iron content had a broad distribution in length between the crosslink points and were restricted because of the decreasing number of ferrocene moieties.

Effect of ambilink

The mechanical properties of Fc-HTPB (0.20 wt % Fe) with two different concentrations of BD-TMP

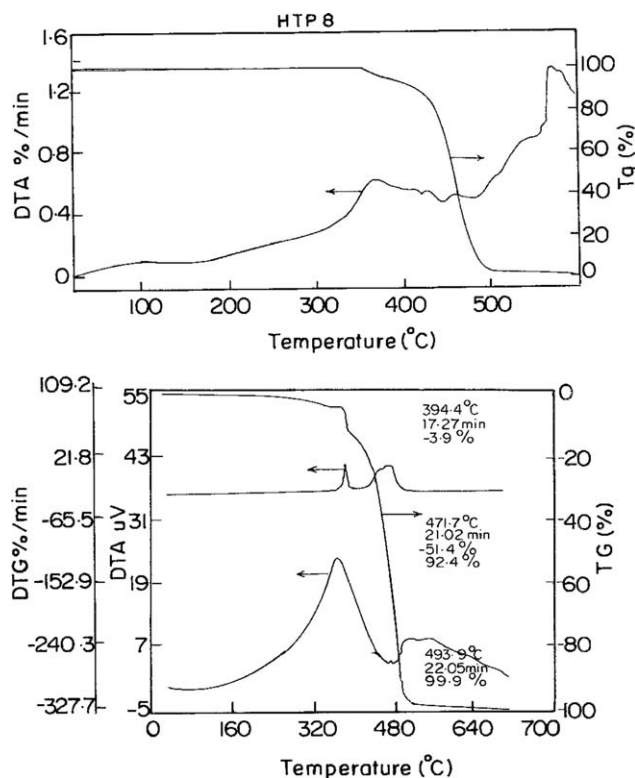


Figure 5 Thermograms of (a) HTPB and (b) Fc-HTPB (0.9 wt % Fe) at a 20°C/min heating rate. DTA, Differential thermal analysis; TG, Thermogravimetry.

(1:2 ratios) are given in Table VI. With increasing total BD-TMP concentration from 1.2 to 1.8%, the effect of the BD-TMP ratio on the mechanical properties showed a more pronounced effect. These results show that an increase in the percentage of ambilink from 1.2 to 1.8 enhanced the properties, including the tensile strength and hardness, whereas the percentage elongation decreased. This variation in properties could be explained by the formation of a three-dimensional structure with a crosslinker. An increase in the crosslink density resulted in a harder and more rigid sample with an ability to withstand larger breaking loads. The higher tensile strength and lower elongation with higher percentage of BD-TMP

TABLE V
Mechanical Characterization

Mechanical properties		Tensile strength (ksc)				Elongation (%)				
		0.20	0.52	0.90	1.50	0.20	0.52	0.90	1.50	
Curing agent	NCO/OH ratio	–	–	–	–	–	–	–	–	
	IPDI	0.75	3.4	3.7	4.2	3.1	540	500	94	964
		1.00	9.5	9.8	9.8	10.1	320	250	93	524
		1.25	14.3	14.5	14.9	13.3	242	225	242	283
		1.50	19.5	20	18.0	19.0	154	148	154	114
TDI	0.75	3.1	3.6	4.0	6.4	1084	1050	1084	595	
	1.00	9.0	9.4	9.9	7.0	294	275	234	98	
	1.25	15.3	15.6	16.0	16.4	185	175	232	135	
	1.50	18.6	19.2	19.7	18.2	148	135	101	235	

TABLE VI
Effect of the Variation of Ambilink on Fc-HTPB
(0.20 wt % iron)

Mechanical properties	TDI		IPDI
	1.2% BD-TMP	1.2% BD-TMP	1.8% BD-TMP
Tensile strength (ksc)	11.7	9.5	13.3
Elongation (%)	118	112	36
Modulus (ksc)	10.4	8.5	–
Hardness (Shore A)	55	45	60

showed an increase in the extent of crosslinking. A comparison of the mechanical properties of the samples cured with IPDI and TDI revealed that both curing agents had tensile strength, hardness, and elongation values in the same range.

CSPs

The mechanical properties, viscosity, and BR of AP-based Fc-HTPB propellants (0.20 wt % Fe), which were cured with TDI, are given in Table VII. The solid loading was 86% with 18% Al along with 0.12% crosslinker (BD-TMP) and the curing agent TDI (60°C) for 5 days. We evaluated the mechanical properties of the Fc-HTPB propellant (1 : 1 dilution) by increasing the NCO/OH ratio from 0.88 to 0.94 and comparing them with those of the normal HTPB alone. These results show that an increase in the NCO/OH ratio increased the tensile strength and hardness, whereas the percentage elongation decreased compared to normal HTPB.

Catalytic effect on the BRs of the Fc-HTPB CSPs

The BRs and mechanical properties of the AP-Fc-HTPB-based propellants with different NCO/OH ratios were analyzed, and the data are given in Table VIII. Figure 6 shows a comparative analysis of the BR and percentage BR of the cured Fc-HTPBs with respect to different weight percentages

TABLE VIII
Mechanical Properties and BR of the Fc-HTPB (0.2 wt %
iron)-Based Solid Propellants

Parameter	Fc-HTPB		
	Fc-HTPB:HTPB (1:1 dilution)	(without dilution)	Fc-HTPB:HTPB (1:1 dilution)
Fe content in the resin (%)	0.45	0.90	0.75
Fe content in the propellant (%)	0.045	0.09	0.075
Tensile strength (ksc)	9.1	11.3	7.6
Elongation (%)	26	23	23
Modulus (ksc)	63	91	55
Hardness (Shore A)	79	85	78
Viscosity (Ps) at 40°C			
0 h	9,920	12,800	16,000
1 h	10,880	14,080	16,320
2 h	13,440	15,680	16,640
3 h	15,040	16,960	17,920
Burn rate at 40 ksc (mm/s)	7.84 ± 0.09	8.66 ± 0.15	8.34 ± 0.13
Enhanced (%)	50	67	60

of iron in the Fc-HTPBs. The BRs of the Fc-HTPB propellants increased with increasing NCO/OH ratio, and higher BRs were observed compared to those based on HTPB. The strand-burner results revealed that the incorporation of ferrocene into the HTPB backbone increased BR. The Fc-HTPB (without dilution) showed a BR of 7.5 mm/s at 40 ksc. Compared to the base propellant HTPB BR (5.4 mm/s at 40 ksc), the Fc-HTPB (experiment 1) showed a 38% higher BR. Although the 1 : 1 diluted Fc-HTPB + HTPB showed a nearly 26% higher BR than the normal HTPB, the BR study indicated that the variation in the NCO/OH ratio had little impact on BR.

The ferrocene-grafted HTPB with 0.45% iron content and 1 : 1 dilution showed a nearly 50% higher BR than the base propellant HTPB. It gave good processability, mechanical properties, and required BR. The Fc-HTPB with 0.90% iron showed a nearly 67% higher BR than the base propellant. The Fc-HTPB with 1.5% iron and 1 : 1 dilution showed a

TABLE VII
Mechanical Properties of the Fc-HTPB (0.2 wt % iron)-Based Propellants with Different NCO/OH Ratios

Experiment	1	2	3	4	
Parameters	Fc-HTPB without dilution	Fc-HTPB + HTPB 1:1 blend	Fc-HTPB + HTPB 1:1 blend	Fc-HTPB + HTPB 1:1 blend	HTPB (normal uncatalyzed)
NCO/OH ratio	1.18	0.94	0.88	0.83	
Tensile strength (ksc)	8.1	11.9	10.4	8.6	6.8
Elongation (%)	7.0	15	21	29	39
Modulus (ksc)	134	173	129	60	54
Hardness (Shore A)	90	90	82	80	70
Burn rate (mm/s) 40 ksc	7.5	6.85	6.72	6.8	5.4
Enhanced BR (%)	38	26	24	25	–

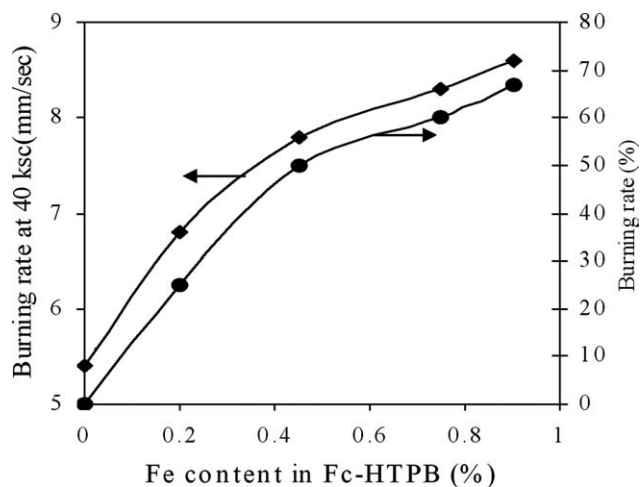


Figure 6 Plot of the iron content in Fc-HTPB versus BR and percentage of enhanced BR.

nearly 60% higher BR than the base propellant HTPB. iron in Fc-HTPB was found to be more efficient than conventional BR catalysts, such as ferric oxide³⁴ and copper chromite. A conventional catalyst, such as 0.5% Fe₂O₃ (0.35% Fe) gave a BR enhancement of 25%, and 0.5% copper chromite (0.36% Cu + Cr) gave an enhancement of 52%, only even at higher levels of metal content than Fc-HTPB (0.90% Fe). This result indicates that BR increased with increasing iron content.

CONCLUSIONS

Fc-HTPBs with different concentrations of iron were synthesized by Friedel–Crafts alkylation, as potentially useful additives for composite rocket propellants. The tensile strength and hardness values of the cured Fc-HTPBs increased with increasing crosslink density, whereas the percentage elongation decreased. A comparative study of IPDI and TDI as a curing agent in the Fc-HTPB system showed that both of these yield elastomers had nearly the same mechanical properties. Better processability was obtained when IPDI was used as a curing agent. The BRs of the Fc-HTPB-based propellants depended significantly on the binder composition. A higher BR was achieved for Fc-HTPB with out dilution. When the iron content was increased beyond 1.50%, even with 1 : 1 dilution with HTPB, the propellant slurry showed a high viscosity. Increasing the iron content above 2% resulted in greater crosslinking; as a result, the polymer became more viscous, and solidification

took place on standing, and the solid was insoluble in all of the solvents.

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