

Synthesis and Characterization of Iron Carbonyl-Modified Hydroxyl-Terminated Polybutadiene: A Catalyst-Bound Propellant Binder for Burn-Rate Augmentation

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ABSTRACT: Iron was coordinately linked to the hydroxyl-terminated polybutadiene (HTPB) backbone using iron carbonyl via a ligand displacement reaction. The modified HTPB thus obtained was reddish brown in color and was characterized by GPC, FTIR, NMR, thermal, and propellant studies. No significant changes in the rheology, molecular weight, and molecular weight distribution were seen in the modified resin when the bonded Fe content was >0.8.0 wt %. However, the hydroxyl value of the resin decreased by 3–7 irrespective of the weight percent of the bonded Fe, and this was more likely due to the Fe-catalyzed oxidation of the —CH₂OH moiety, mostly to the —CHO group. Apparently, this has not affected the cure characteristics of the binder, as demon-

strated by the good mechanical properties of the gum stock and the propellant. The catalytic efficiency of the bonded Fe on the burn rate of the propellant was more efficient than was the free Fe added to the propellant. The aging characteristics of the resin for the bound iron content of ≤0.8 wt % was apparently good, as its viscosity and molecular weight did not undergo any drastic changes even after 18 months' storage under ambient conditions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2813–2823, 2003

Key words: polybutadiene; iron pentacarbonyl; ligand displacement; composite solid propellant; burn rate catalyst; oxidative degradation

INTRODUCTION

The burn rate (BR) of a composite solid propellant (CSP) is usually increased by the physical addition of transition metal-based BR catalysts, such as iron oxide, copper chromite, and ferrocenic derivatives, to the propellant mix.^{1–4} But this method of increasing the BR by the commonly and conventionally chosen transition metal oxides (TMOs) makes it difficult to realize a workable propellant when the BR requirement is very high. This is due mainly to the poor processing, aging, and mechanical characteristics of the propellant at the high TMO loading levels necessary to achieve such a high BR. Moreover, TMOs also have inherent disadvantages such as agglomeration, inhomogeneities in their distribution and particle size, and diminishing BR enhancement and settling with catalyst loadings. Besides, they are poorly defined compositionally and morphologically, and their efficiencies vary from batch to batch from a single manufacturer. Use of binder-soluble ferrocenic derivatives as BR catalysts also have inherent drawbacks, such as their

migration under storage and evaporation/sublimation loss during propellant processing, leading to poor aging and reproducible propellant properties.

However, the above-addressed problems can be eliminated by linking the catalyst chemically to the binder instead of adding it to the propellant mix. Moreover, this technique will also facilitate a quantitative comparison of the relative catalytic efficiencies of the different BR catalysts in mechanistic terms,¹ which is inherently ambiguous in TMO catalysts. But, unfortunately, only sporadic efforts have been made by a few propellant investigators to link the catalyst to the binder backbone^{5–13} either directly or as a pendant group with an organic carrier to achieve efficient high BRs with reproducible propellant properties. Hence, in this direction, an attempt was made here to link iron as —Fe(CO)₃ to a hydroxyl-terminated polybutadiene (HTPB) backbone, coordinately using either iron pentacarbonyl [IPC, Fe(CO)₅] or tri-iron dodecacarbonyl [FDC, Fe₃(CO)₁₂]. It was reported¹⁴ that, by this method, about 10–12 wt % of Fe can be easily linked to polydienes such as polybutadiene and polyisoprene. This roughly corresponds to the involvement of 20% of their double bonds in the complexation. However, using excess IPC, nearly 80% of the double bonds in these polydienes can be made to coordinate with Fe. The Fe-linked HTPB thus prepared was characterized for its binder-propellant properties.

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EXPERIMENTAL

Materials

The HTPB (specific gravity: 0.9) used here is a free-radically prepared one with a number-average molecular weight (M_n) and polydispersity (GPC) around 4000–5500 and 2–2.5, respectively. 1,4-Dioxane (AR) and *n*-hexane were dried and distilled over CaH_2 just before use. Xylene (AR, low S content) was first dried over anhydrous CaCl_2 , then over CaH_2 , and distilled. Dimethoxyethane (DME) and benzene were dried over Na under refluxing conditions. 4-*tert*-Butylcatechol (TBC), methanol, trimethylolpropane (TMP), toluene diisocyanate (TDI), 1,4-butanediol (1,4-BD), glacial acetic acid (AR), dibutyl tin dilaurate (DBTDL), dichloromethane (DCM, AR), IPC (98%, Fluka; specific gravity: 1.46), and tri-iron dodecacarbonyl (FDC, Aldrich), silica gels for column and thin-layer chromatography (TLC), ferric oxide, and Al powders of average particle sizes of 2 and 15 μ , etc., were used as received. Ammonium perchlorate (AP, coarse and fine)¹³ was dried at 80°C under a vacuum just before use.

Complexation of iron carbonyl and HTPB

Using IPC [$\text{Fe}(\text{CO})_5$]

In a typical experiment, about 200 g of HTPB was dissolved in 1.3 L of sulfur-free dry xylene taken in a three-necked 2-L flask fitted with a mechanical stirrer, condenser, and nitrogen inlet. To this, 60 mL of dry 1,4-dioxane or DME, 67 g IPC, and 0.1 g of TBC (inhibitor) were added. The solution was refluxed at 129°C with continuous stirring over an oil bath (137°C) for 7 h. After the reaction, xylene, 1,4-dioxane/or DME, and unreacted IPC were recovered by distilling under a vacuum in a rotary evaporator at 70°C and recycled. The dark brown viscous resin, dissolved in 500 mL DCM, was washed with a mixture of glacial acetic acid, methanol, and water (2:1:1 by volume) repeatedly to remove the free Fe impurities and dried. The dried solution was then passed through a silica gel column and distilled under a vacuum in a flash evaporator at 60°C to get a brownish yellow or dark reddish brown resin, free from impurities. The purity of the resin was monitored by TLC. It is to be noted here that IPC is insoluble in HTPB, and, hence, the color of the resin is attributed to the bonded iron carbonyl.

It was seen that refluxing a xylene solution of IPC without HTPB gave an insoluble brown residue (iron oxides/hydrated iron oxides). A blank experiment (at 137°C, for 8 h) was also done without iron carbonyl to determine the thermal effect on the hydroxyl value of HTPB.

Using FDC [$\text{Fe}_3(\text{CO})_{12}$]

Here, refluxing a benzene or *n*-hexane solution of HTPB and FDC in the presence of dioxane or DME for 4–12 h resulted in complexation. The initial solution, which was green in color, turned dark and then to dark red after 1 h. After the reaction, the solvents were removed under a vacuum and the crude resin was purified using a similar procedure employed in the HTPB–IPC reaction.

Thermal studies

Differential scanning calorimetry (DSC) and thermogravimetric (TG) studies were performed on 4–8 mg samples using a Mettler TA 3000 (Switzerland) with a DSC 20 thermal analyzer and a DuPont 951 TGA, respectively, in nitrogen and air at a heating rate of 10°C/min.

Molecular weight (MW)

MW measurement was made by GPC (Waters ALC/GPC 244 with an R401 differential refractometer and 440-V UV detector) using ultra-Styrigel columns of 10⁴, 10³, 500, and 100 Å with THF as the eluent at 75°C. The columns were calibrated using polystyrene (MW 6000) standards of narrow polydispersity.

Spectral studies

FTIR spectra of the polymer (neat) and its cured gum stock were recorded on a Perkin–Elmer Spectrum GX FTIR spectrometer. ¹H (300 MHz)- and ¹³C (75 MHz)- NMR spectra were recorded on a Bruker 300 spectrometer in CDCl_3 using TMS as the internal reference standard. The Fe present in $\text{HTPB-}\{\text{Fe}(\text{CO})_3\}_x$ was estimated by atomic absorption spectroscopy on a Spectra AA 250 Plus atomic absorption spectrometer (Australia) from the oxide residue obtained after controlled pyrolytic combustion of $\text{HTPB-}\{\text{Fe}(\text{CO})_3\}_x$. The validity of this method was checked by estimating the iron content in HTPB containing a known amount of IPC, adopting the above method.

Viscosity measurements

Viscosity measurements were made using a Brookfield (Model DV-11+) viscometer at 30°C.

Propellant studies

Nonaluminized and aluminized propellant strands (cured at 30°C for 5 days) were made both from HTPB and $\text{HTPB-}\{\text{Fe}(\text{CO})_3\}_x$ as binders for 84.5% AP loading using TDI/TMP or TDI/ambilink, that is, a 2:1 mol ratio of 1,4-BD and TMP as curatives and DBTDL as a catalyst, keeping the R (= $[\text{NCO}]/$

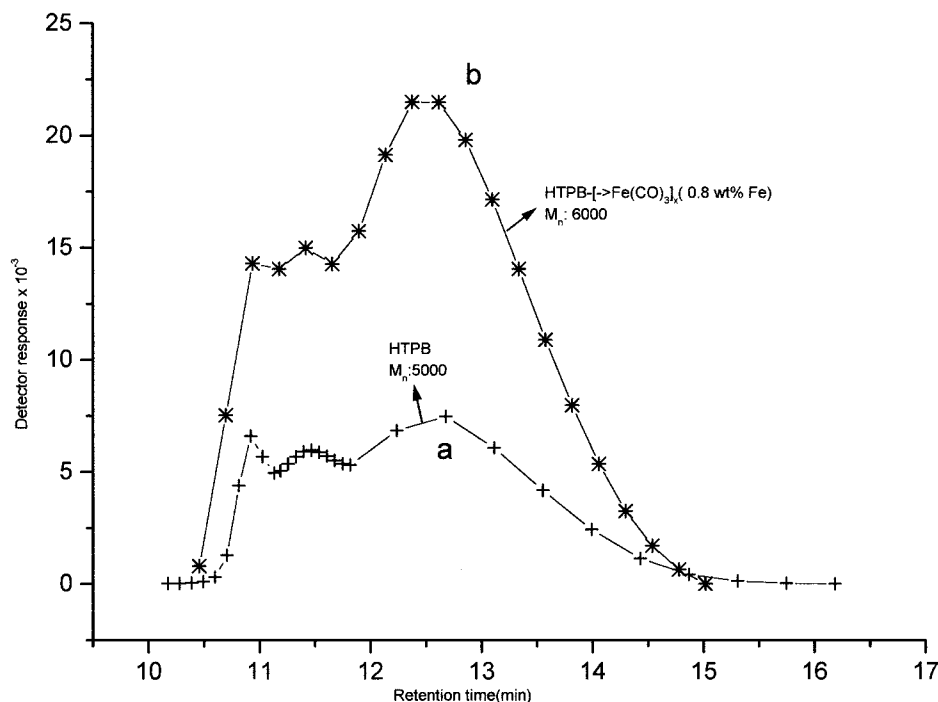


Figure 1 GPC traces of (a) pristine HTPB and (b) HTPB-[-Fe(CO)₃]_x (0.8 wt % Fe).

[OH]) value around 0.8–0.9. Propellant mixings, of 0.8–2.0-kg size, in a horizontal mixer at 45°C were also done on typical compositions for $R = 0.8–0.95$ using TDI/ambilink as curatives, then cast as cartons and cured at 60°C for 5 days. Propellant strands (6 × 6 × 80 mm) and dumbbell specimens were cut from the cured cartons to evaluate the BR (at 3.9 MPa) and mechanical properties. The linear BRs of the propellant strands were determined under water in a strand burner pressurized with N₂ at 3.9 MPa as described elsewhere.¹⁵

Glass transition temperature (T_g)

The T_g of the cured gum stock was determined by thermomechanical analysis (TMA) in expansion on a Perkin-Elmer 7 series thermal analysis system.

Mechanical properties

Mechanical properties of the cured gum stock and propellants were determined using a Instron universal testing machine under a crosshead speed of 500 mm/s on dumbbell specimens after conditioning the samples at 26°C.

RESULTS AND DISCUSSION

Mechanistic aspects of complexation between IPC and HTPB

IPC has a remarkable ability to react with compounds containing C=C bonds such as olefins^{16–23} and poly-

mers containing a significant number of olefin bonds,^{14,24–26} resulting in either a stable or unstable π complex via a CO (ligand) displacement reaction with or without double-bond migration. Since HTPB is a polyene with isolated double bonds, it also forms such a complex, namely, tetrahaptoiron-tricarbonyl complexes.^{14,23–26} Since the rate-determining step²⁷ in this reaction, namely, the dissociation of IPC to Fe(CO)₄ and CO, requires about 184.5 kJ/mol of energy,²⁸ complexation was done at temperatures²⁹ >100°C in xylene. To minimize the degradation of the polymer chain under these conditions, complexation was effected in the presence of polar nonacidic solvents (5–10%) such as 1,4-dioxane and DME. But the reaction invariably resulted in a variable small reduction in the OH value depending on the bound Fe content, and this was most likely due to the Fe-catalyzed^{30–32} oxidation of —CH₂OH to the —CHO group. This oxidation, subsequently, may generate a structure such as C=C—C=O via double-bond migration in the presence of iron carbonyls as reported¹⁶ in simple olefinic ketones/aldehydes. Since the reduced average OH value of HTPB-[-Fe(CO)₃]_x was within the range of the functionality distributions comprising nonfunctional, monofunctional, difunctional, and trifunctional chains reported³³ for HTPB, the reduction in the OH value did not affect the cure characteristics of HTPB-[-Fe(CO)₃]_x.

GPC

The GPC traces of HTPB and iron carbonyl-linked HTPB shown in Figure 1 did not reveal any significant

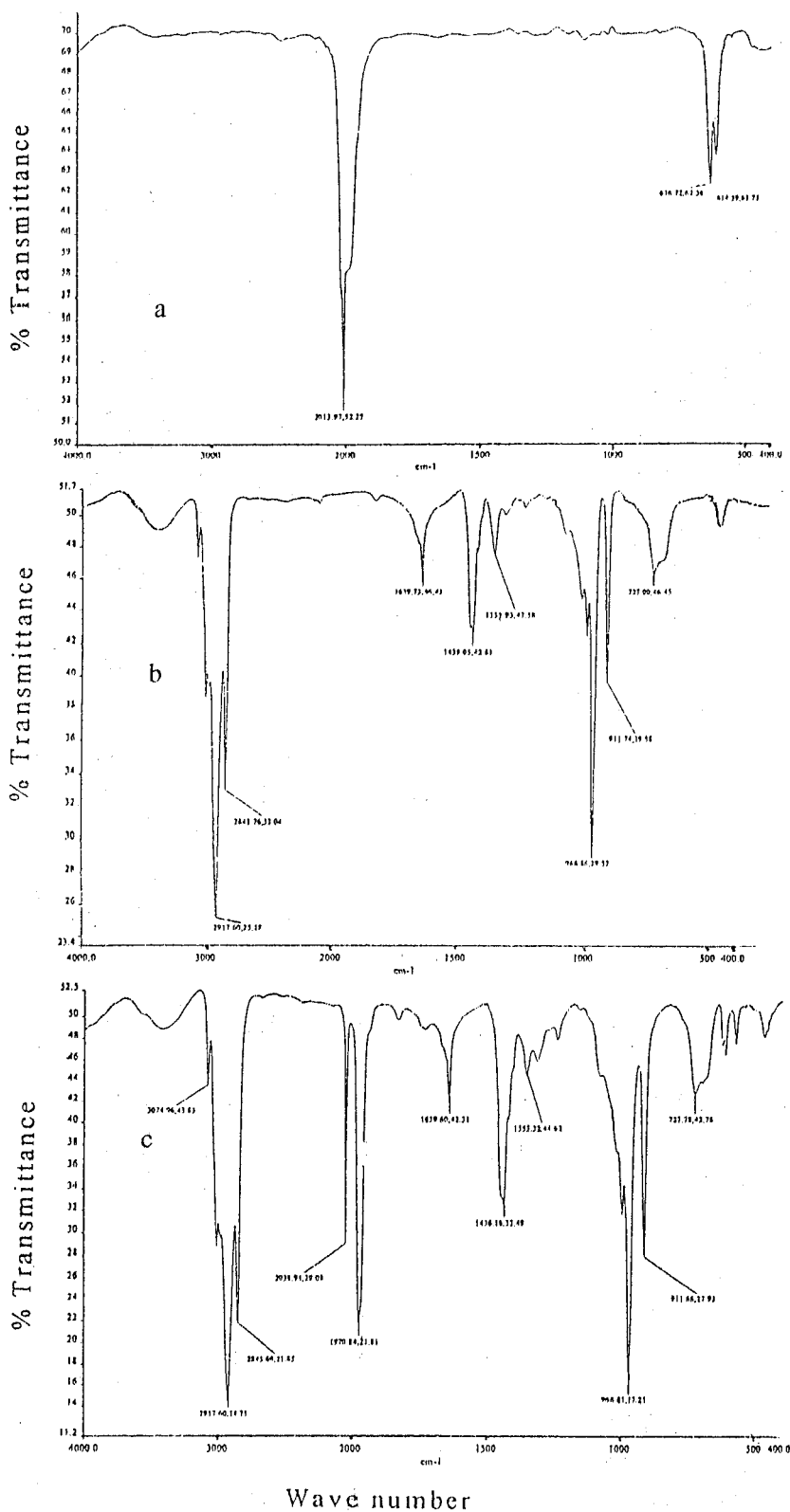


Figure 2 FTIR spectra of (a) IPC, (b) pristine HTPB, and (c) HTPB- $\text{Fe}(\text{CO})_3$.

difference either in their MW or molecular weight distribution (MWD). This indicates that complexation of iron carbonyl with HTPB under the reaction conditions has not resulted in any undesirable side reactions

such as drastic chain degradation or crosslinking. Hence, it is anticipated that the physical (rheological) properties of HTPB may not be affected significantly by the complexation reaction.

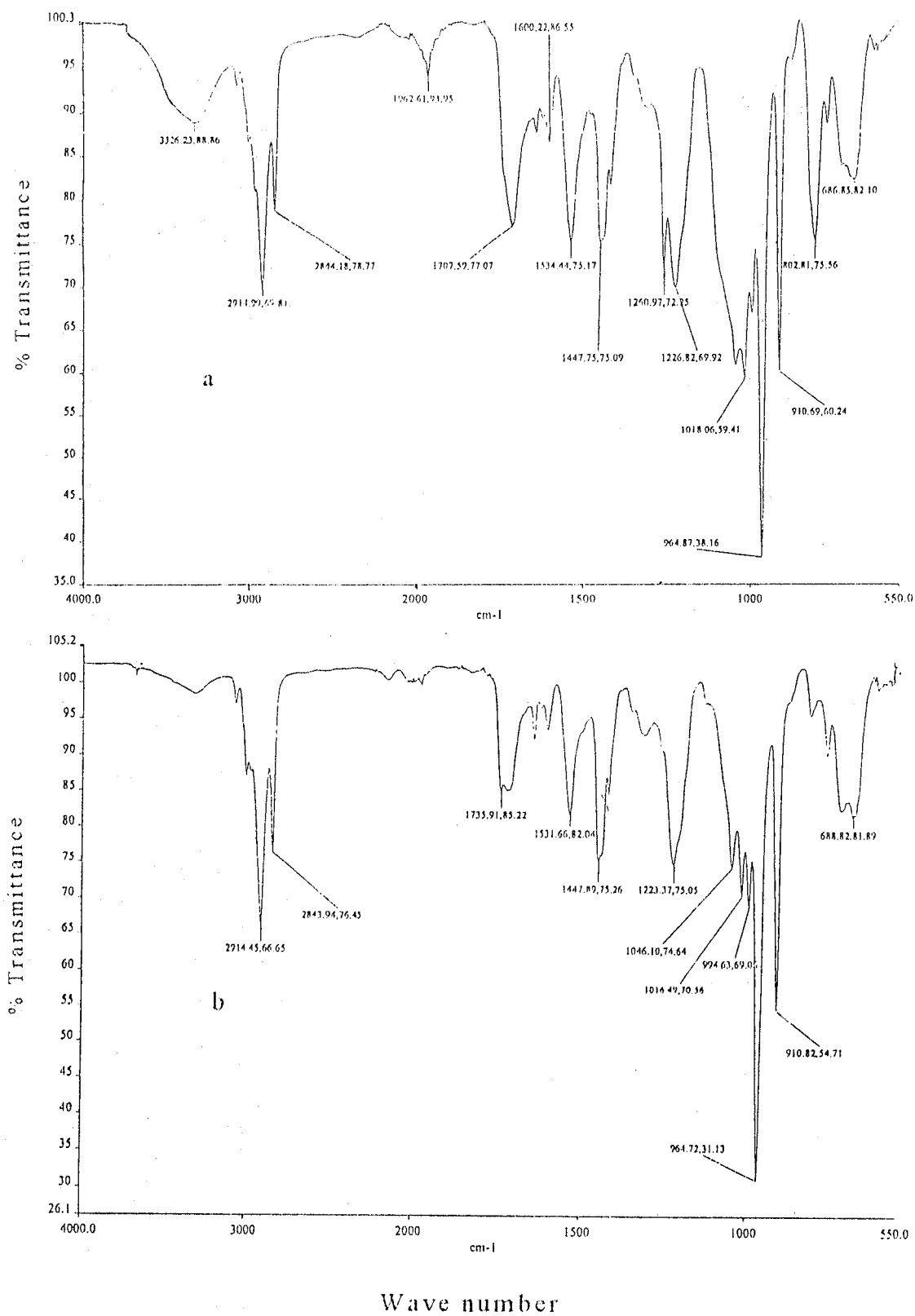


Figure 3 FTIR of spectra of typical polyurethane gum stocks from (a) HTPB-[Fe(CO)₃]_x and (b) pristine HTPB.

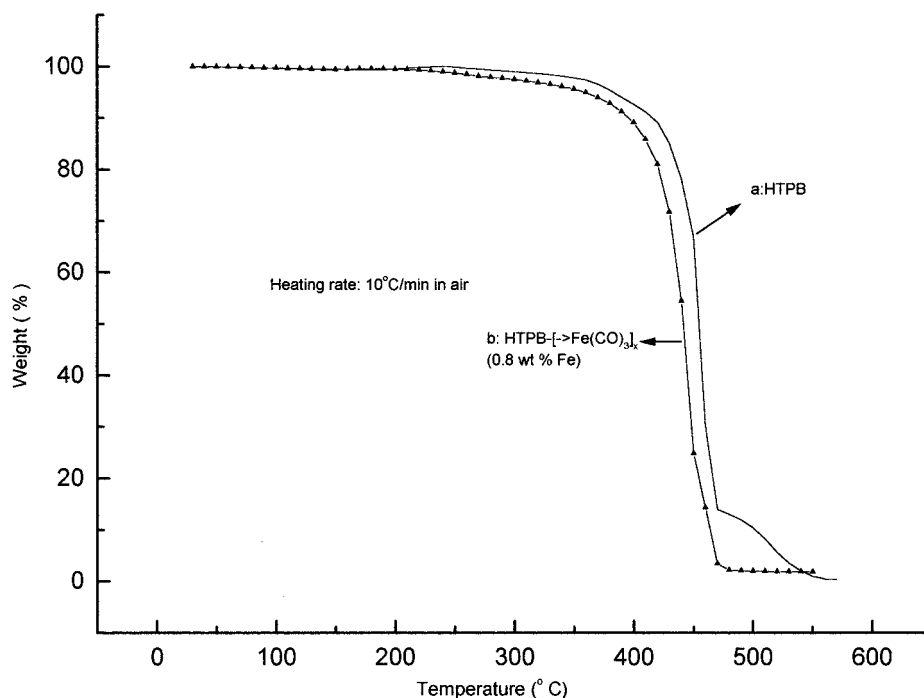


Figure 4 TG traces of (a) pristine HTPB and (b) HTPB- $[-\text{Fe}(\text{CO})_3]_x$ (0.8 wt % Fe).

Spectral studies

FTIR

The FTIR spectra of iron carbonyl-reacted HTPB exhibited a pair of carbonyl stretching frequencies at 2039 and 1971 cm^{-1} [Fig. 2(c)], characteristic of tricarbonyl (conjugated diene) iron complexes,^{14,18} apart

from the usual absorption frequencies of HTPB [Fig. 2(b)], irrespective of the type of iron carbonyl used. The weak absorption around 1700 cm^{-1} [Fig. 2(c)] is most likely due¹³ to the $>\text{C}=\text{O}$ group, as in $\text{C}=\text{C}-\text{C}=\text{O}$, and the most likely mechanism of its formation was mentioned earlier. The characteristic frequency

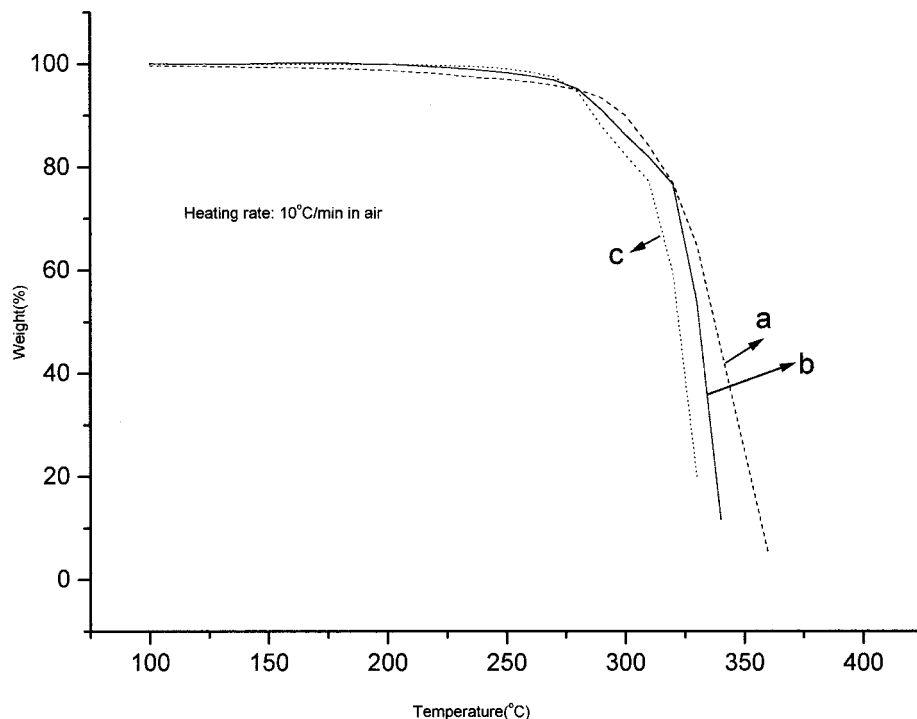


Figure 5 TG traces of nonaluminized propellants from (a) pristine HTPB, (b) HTPB containing free $\text{Fe}(\text{CO})_5$, and (c) HTPB- $[-\text{Fe}(\text{CO})_3]_x$.

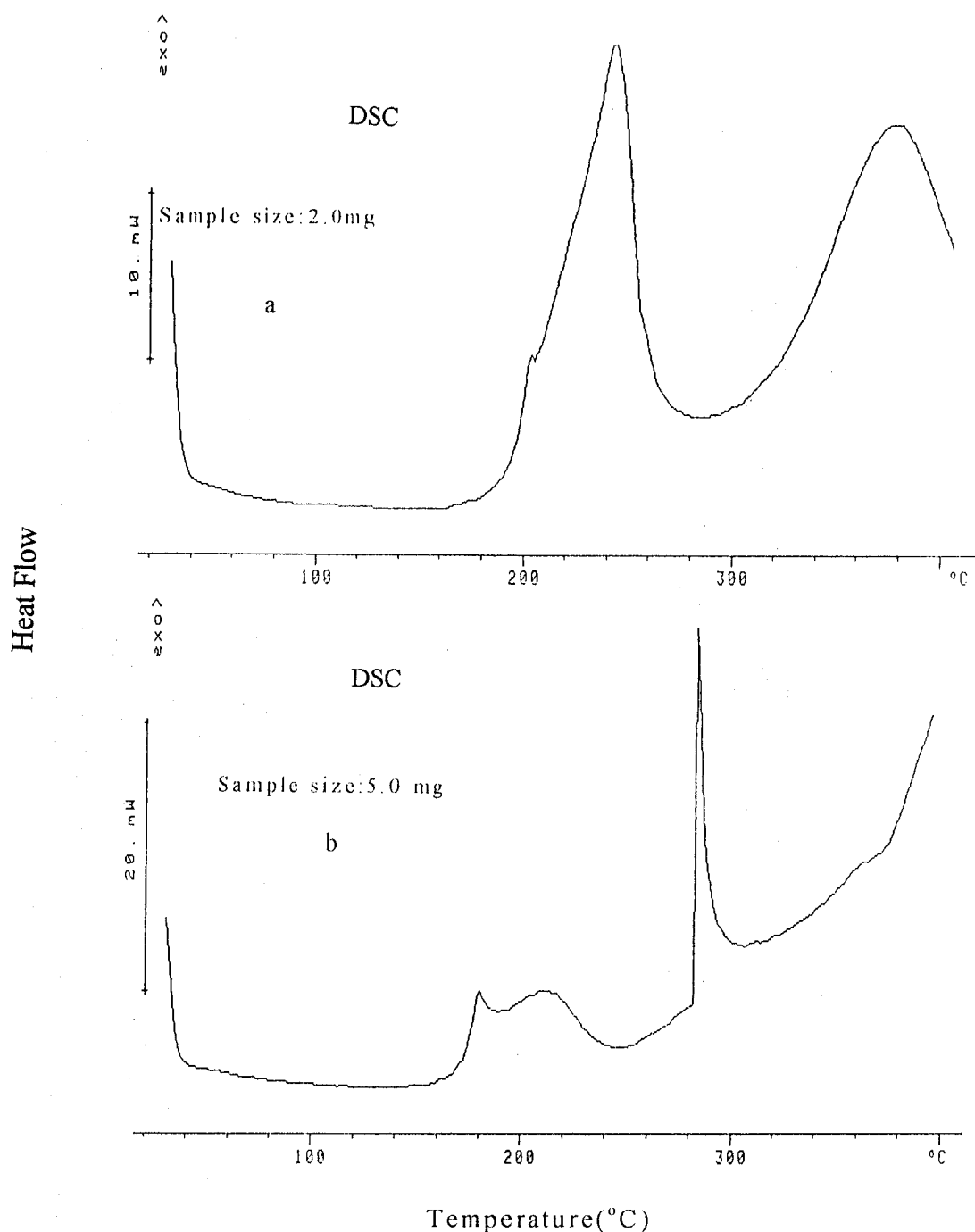


Figure 6 DSC traces of (a) pristine HTPB and (b) HTPB- $\text{Fe}(\text{CO})_3$ (0.8 wt % Fe).

around 2000 cm^{-1} attributed to the $-\text{Fe}(\text{CO})_3$ moiety HTPB- $\text{Fe}(\text{CO})_3$ remains unchanged in the cured gum stock [Fig. 3(a)], implying good stability of HTPB- $\text{Fe}(\text{CO})_3$ under the curing conditions (60°C , 5 days).

NMR

Due to the very low average concentration of $-\text{Fe}(\text{CO})_3$ in HTPB- $\text{Fe}(\text{CO})_3$ per repeat unit of HTPB, no new ^1H - and ^{13}C -NMR signals, originating from the HTPB

backbone part that is coordinately linked with the iron carbonyl, were seen. However, a weak resonance signal around 211 ppm, attributed to the carbonyl³⁴ carbon in the HTPB- $\text{Fe}(\text{CO})_3$ moiety linked to HTPB, was observed in the ^{13}C -NMR.

Thermal studies: TG

TG traces of HTPB and HTPB- $\text{Fe}(\text{CO})_3$ and their corresponding propellants recorded in air are shown in Figures 4 and 5, respectively. The onset and major

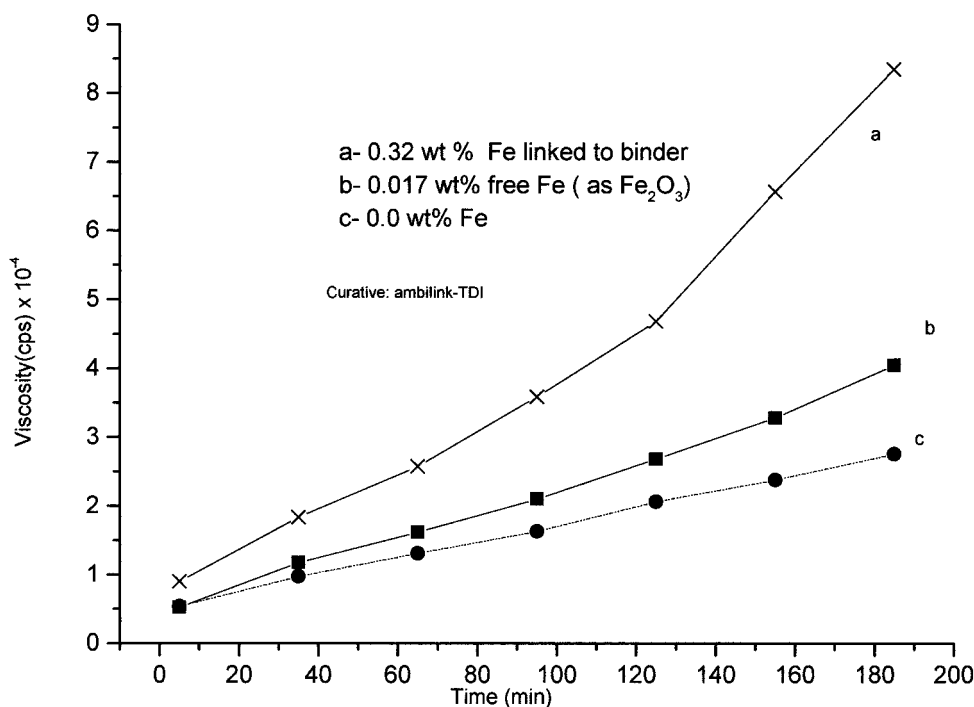


Figure 7 Viscosity buildup at 30°C in typical polyurethane gum stocks from (a) HTPB- $\text{Fe}(\text{CO})_3$, (b) iron oxide-added HTPB, and (c) pristine HTPB.

degradation temperatures of Fe-linked HTPB [Fig. 4(b)] were lower than those of pure HTPB. The weight loss in the temperature region 180–220°C for the HTPB- $\text{Fe}(\text{CO})_3$ [Fig. 4(b)] is attributed¹⁴ to the loss of the carbonyl group, as well as due to the first-step exothermic degradation reported¹³ for pure HTPB. But unlike the distinct two-step weight losses observed for HTPB, the TG trace of HTPB- $\text{Fe}(\text{CO})_3$ [Fig. 4(b)] displayed a nearly single-step weight loss after 220°C, with a comparatively faster weight loss rate near the major degradation region. Moreover, both the onset and major degradation temperatures for HTPB- $\text{Fe}(\text{CO})_3$ (r) propellant [Fig. 5(c)] are lower than those of the propellants based on HTPB (p) and [HTPB + IPC] (q), and these decreased in the order $p > q > r$. This indicated the better catalytic efficiency of the bound Fe on the oxidative degradation of HTPB than that of the free Fe as reported^{3,13} elsewhere. The temperature (viz., 200°C) of the initial broad exotherm in the DSC trace [Fig. 6(a)] of HTPB assigned to oxygen insertion¹³ shifted to a lower temperature [Fig. 6(b)], perhaps due to the Fe-catalyzed peroxidation.¹³ Hence, it is obvious that the Fe in HTPB- $\text{Fe}(\text{CO})_3$ catalysis involves dual reactions, namely, the incorporation of weak peroxy links in HTPB and its thermooxidative degradation as reported¹³ in poly(vinyl ferrocene)-grafted HTPB (HTPB-g-PVF). But the DSC trace of HTPB- $\text{Fe}(\text{CO})_3$ also displayed an extrasharp exotherm [Fig. 6(b)] around 300°C not witnessed¹³ in the DSC traces of pure IPC, pristine HTPB, and HTPB-g-PVF. This may be more likely attributed to the accompanying oxidative reac-

tions of Fe, carbonyl, etc., after decarbonylation. This exotherm became very weak and broad in the DSC run under a nitrogen atmosphere. The second sharp exotherm was followed by the usual broad exotherms attributed^{13,35,36} to major oxidative degradations of HTPB involving chain unzipping. The catalytic action of Fe on the thermooxidative degradation of HTPB is ascribed to the various faster electron-transfer reactions between HTPB and the bound Fe, as reported in the literature^{30–32,37–40} for simple organic compounds. Even though Fe in HTPB- $\text{Fe}(\text{CO})_3$ is expected to have a zero-valence state, it appears that some of the Fe is also in the oxidized state, as the resin showed the characteristic color reaction¹³ with the phenolic derivative added as a stabilizer.

Viscosity buildup in typical gum-stock compositions

The viscosity versus time plots for HTPB and HTPB- $\text{Fe}(\text{CO})_3$ with the TDI/ambulink curative are displayed in Figure 7. They clearly reveal that iron present either as free Fe_2O_3 or as a binder-linked iron carbonyl enhances the viscosity buildup rate, but it appears to be more in the latter. This could be due to the well-known⁴¹ catalytic effect of Fe on the urethane-forming reaction involving isocyanate and hydroxyl groups. However, the faster viscosity buildup in HTPB- $\text{Fe}(\text{CO})_3$ has not affected the processability or castability of the propellant.

TABLE I
Typical Synthetic Conditions and Properties for Iron Carbonyl-linked HTPB Binder

Recipe/or binder	Fe wt % in the binder	OH value: mg KOH/g		Viscosity (cp, 30°C)		Fe wt % in the propellant ^a	BR (mm/s) (3.9 MPa)
		Before reaction	After reaction	Before reaction	After reaction		
IPC _{wt} /HTPB _{wt} : 1/3; 4% (vol) dioxane; xylene; reflexed ^b under N ₂ , 7 h	0.80 ^c	42.4	37.0 ^b	6000	9000 ^d	0.116	10.6 9.3 (2.9MPa) 11.6 (4.87 MPa) 12.5 ^e
IPC _{wt} /HTPB _{wt} : 1/1; 2% (vol) dioxane; xylene; reflexed under N ₂ , 5 h	1.25	42.4	32.0	6000	nd	0.175	16.3 ^e
HTPB	—	40.4	—	5750	—	0.116 (free IPC)	8.7
HTPB→[Fe(CO) ₃] _x	0.34	42.4	37.0	6000	nd	0.049	8.7
	0.28	42.4	38.0	6000	nd	0.040	8.4
	0.29	40.4	37.3	5750	nd	0.029	8.0
HTPB	—	40.4	—	5750	nd	(i) 0.116 (free Fe ₂ O ₃)	(i) 8.0 6.3 (2.9MPa) 8.8(4.87MPa)
						(ii) 0.033 (free Fe ₂ O ₃)	(ii) 7.3
IPC _{wt} /HTPB _{wt} : 1/5; 4% (vol) dioxane; xylene; reflexed under N ₂ , 7 h	0.35	42.3	38.0	6100	7900	0.05	8.6
IPC _{wt} /HTPB _{wt} : 1/5; 4% (vol) dioxane; xylene; reflexed under N ₂ , 8 h	0.28	40.4	36.6	5750	6500	0.04	8.2
FDC _{wt} /HTPB _{wt} : 1/15, 4% (vol) DME; benzene, reflexed 7.5 h under N ₂	0.63	42.3	37.6	6100	7200	—	—
FDC _{wt} /HTPB _{wt} : 1/15, 4% (vol) DME; <i>n</i> -hexane, reflexed, 4.5 h, under N ₂	0.4	42.3	36.4	6100	6650	—	—

^a Propellant composition (wt %): binder (14.5) and AP (84.6) in nonaluminized and binder (14.5), AP (68.6), and A1 (15.5) in aluminized propellants; weight ratio of coarse and fine AP = 2:1.

^b OH value of HTPB in a blank experiment (at 133°C) without Fe(CO)₅ for 8 h was 42.3; IPC_{wt}/HTPB_{wt} = weight ratio of IPC and HTPB; HTPB_{wt} = 100–250 g; nd, not determined.

^c Weight percents of bound Fe in HTPB for the reaction times of 3 and 5 h were 0.35 and 0.56, respectively.

^d Viscosity, MW, and OH value of the resin and BR of the propellant based on this resin remained unchanged even after 18 months' storage under ambient conditions

^e For nonaluminized propellant.

Propellant BR studies

The BR values determined for the nonaluminized HTPB and HTPB- $\text{Fe}(\text{CO})_3$ propellant strands with different BR catalysts are given in Tables I and II. The BR increases with increase of the Fe content in

HTPB- $\text{Fe}(\text{CO})_3$ but not proportionately. For the same weight percent of Fe, the BR values of the propellant for different Fe-carrying catalysts decreased in the following order: bonded Fe (as iron carbonyl) > free IPC > Fe₂O₃ (Table I), that is, the increase in BR

TABLE II
Mechanical Properties of Gum Stock and Propellant with Typical Compositions

Binder	Fe wt % in the binder	OH value mg KOH/g	Tensile strength (KSC)	Elongation (%) & T_g (°C)	Modulus (KSC)	Shore A hardness	R value	BR at 3.9 MPa (mm/s)
HTPB (gum stock)	0.00	40.3	10.0	200 and -76	—	—	0.82	—
HTPB- \rightarrow [Fe(CO) $_3$] $_x$ (gum stock)	0.25	37.7	7.5	300 and -74	—	—	0.82	—
HTPB- \rightarrow [Fe(CO) $_3$] $_x$	0.33	37.0	7.8	39 and -	35	67	0.82	8.6
HTPB- \rightarrow [Fe(CO) $_3$] $_x$	0.35	38.0	10.7	19 and -	82	78	0.95	8.9

Composition (wt %): binder (10.25), AP (67.86) (ratio of coarse and fine AP is 2:1; see ref. 13 for the particle-size distributions in coarse and fine AP), Al (18); plasticizer, dioctyladipate; curative, Ambilink/TDI; stabilizer, Nonax; propellant (0.8 kg) mixed at 45°C, cast as cartons and cured at 60°C for 5 days.

is less pronounced when IPC is physically mixed with the propellant. For instance, a typical BR around 8 mm/s at 3.9 MPa was achieved when the bound Fe content in the propellant was in the range 0.026–0.029 wt % (Table I). This is much lower than the weight percent of free iron (either as Fe $_2$ O $_3$ or IPC) added to the propellant to achieve the same (Table I). The improved catalytic efficiency of bound Fe on BR augmentation is probably due more to the enhanced degradation of the binder^{3,13} as well as the propellant in the condensed phase (binder/AP) (Figs. 5 and 6). The decrease in the major degradation temperature of the propellant [Fig.6(c)] also indicates that the Fe may catalyze the binder/AP interface rather than AP alone. The increase of BR in the HTPB- \rightarrow [Fe(CO) $_3$] $_x$ -based propellant is also attributed to the superior catalytic efficiency of *in situ* formed superfine iron oxide on AP decomposition,^{1,2,42} compared to the conventional iron oxide catalyst used in the propellant. This observed BR augmentation in the HTPB- \rightarrow [Fe(CO) $_3$] $_x$ propellant discloses that the catalytically active sites are also likely to be present in the binder as reported^{3,13} in ferrocenic derivative-linked HTPB. In this context, it is worth mentioning the literature report⁴³ that if AP is catalytically decomposed very much faster than the binder as reported at higher weight percentages of the TMO catalyst then one may either observe a decrease or no change in the BR with catalyst loadings. But it may be possible to witness an enhancement in the BR even at higher catalyst loadings provided that the binder is made to degrade much faster than AP to facilitate steady-state combustion. This could be realized, to some extent, by binding the catalyst to the binder.

Mechanical properties

Mechanical properties of typical propellant and gum-stock compositions are given in Table II and these values are roughly within the desirable range required for a good workable propellant when $R = 0.82$. But $R = 0.95$ gives a propellant with poor elongation, higher modulus, and hardness. By adjusting the value of R between 0.8 and 0.86, the mechanical properties can be fine-tuned

to the desired level.⁴⁴ Incorporation of Fe as iron carbonyl has not altered the T_g of the gum stock (Table II).

CONCLUSIONS

The reaction of iron carbonyls with HTPB offers an effective and efficient way of linking Fe chemically to the HTPB backbone to the required levels. The catalytic efficiency of the coordinately linked Fe on the BR of the CSP was superior to that of free iron added as IPC or Fe $_2$ O $_3$. The modified binder-cum-BR catalyst can be used either alone or can be blended with pure HTPB depending upon the BR and mechanical property requirement of the CSP. Bonding of Fe to the extent of 0.8 wt % does not significantly alter the rheology, MW, and MWD of the resin. The reduction in the hydroxyl value of the modified resin has been attributed to the iron carbonyl-catalyzed reaction of the OH group. But this is not detrimental to the cure characteristics of the binder as it gives a propellant with good mechanical properties. The modified resin with an iron content of ≤ 0.8 wt % seems to have good aging properties as the MW, viscosity, —Fe(CO) $_3$ moiety, and physical appearance of the resin with 0.8 wt % Fe remained unaltered even after 18 months' storage under ambient conditions. The greater increase of BR in the HTPB- \rightarrow [Fe(CO) $_3$] $_x$ -based propellant compared to that of the HTPB/free IPC or Fe $_2$ O $_3$ propellant containing the same weight percent of Fe is attributed to the enhanced degradation of the binder as well as the propellant (binder/AP) in the condensed phase. If the bound Fe catalyzed the decomposition of AP alone in the condensed phase, then a greater BR enhancement may not be observed. Detailed investigations on the propellant formulation and aging behavior of the binder as well as the propellant are being continued.

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