# BALLISTIC AND MECHANICAL PROPERTIES OF HTPB BASED COMPOSITE PROPELLANTS

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#### Summary

This paper reports the results of the effect of solids loading on ballistic and mechanical properties of hydroxy terminated polybutadiene composite propellants. Burning rates were doubled with solids loading (Ammonium perchlorate and aluminium powder) increase from 80 to 88%. Pressure index ( $\eta$ ) values were lower (0.3) with 80-85% solids. Burning rates obtained by a static test evaluation method were higher by 3-5% than with the strand burner method. Delivered specific impulse of 246 and 249 s were obtained with compositions having 87 and 88% solids loadings. Tensile strength ( $\sigma$ ) was increased from 0.78 MPa to 1.38 MPa with the use of 0.3 parts MAT bonding agent.

#### 1. Introduction

In view of higher energy  $(I_{sp} 230-260 \text{ s})$ , composite propellants have been extensively used for rocket/missile applications and space missions. A higher specific impulse  $(I_{sp})$  of composite propellants is obtained by incorporating a maximum possible amount of solids (oxidizer/metallic fuel) in the binder matrix. Present day applications demand propellants of superior mechanical properties in addition to higher energy content. Due to these contradictory requirements hydroxy terminated polybutadiene (HTPB) based propellants are replacing polybutadiene-acrylic acid-acrylonitrile (PBAN) and carboxy terminated polybutadiene (CTPB) based composite propellants. HTPB is capable of taking up solids upto 90% and imparts superior mechanical properties without compromising on high storage life [1].

A number of studies have been carried out in the past on the formulation, processing, improvement of mechanical properties and ballistic evaluation of HTPB based composite propellants [2–7]. However, detailed information on their ballistic and mechanical properties is not reported in the open literature. This paper reports the results on the ballistic and mechanical properties of HTPB based composite propellants having 80–88% solids loading (ammonium perchlorate (AP) as oxidizer and aluminium powder as metallic fuel).

The experimental results of burn rates at various pressures have been used to test the applicability and validity of Vieille's law, the Summerfield equation and the recently proposed Rastogi equation [8] on dependence of burn rates of composite propellants on pressure.

### 2. Experimental

All the studies were carried out using HTPB (R-45 M) received from ARCO, U.S.A., having viscosity 4000-6000 cP, molecular weight 2200-2600 and functionality of 2.2-2.4; AP from M/s WIMCO, Bombay of 99% purity; emolein from M/s Emery U.S.A. and aluminium powder from M/s MEPCO, Madurai. Their purity was checked before use. Toluene di-isocyanate (TDI) recieved from M/s Bayer Fabriken Incorporation, W. Germany was used as a curing agent. Tris-2-methyl-1-aziridinyl phosphine oxide (MAPO) based bonding agent (condensation product of dicarboxylic acids namely, adipic acid and tartaric acid with MAPO) was used to bolster mechanical properties. Lecithin was used as a processing aid. The binder contained 80 parts HTPB and 20 parts emolein (plasticiser), 0.01 parts Ferric acetyl acetonate (Polymerisation catalyst) and 0.3 parts lecithin (processing aid) by weight. Aluminium content was kept constant (17%) in all the formulations. The coarse AP of 200  $\mu$ m was ground with the help of Jet-O-Mizer fluid mill to produce fine AP (10  $\mu$ m). Bimodal AP (50% coarse and fine) was used in all the formulations. Propellants were made by mixing the ingredients in a 25 l capacity planetary mixer. Mixing and casting were carried out under vacuum of 2-3 mmHg (2.7 mbar). Aluminium casting fixtures of of 110 mm ID and 600 mm length were used for casting tubular grains of 70 mm ID. Propellant charges were cured at  $70^{\circ}$ C for 8 days. Cured propellants were cut into pieces of 200 mm length, 106 mm OD and 70 mm ID. Mechanical properties were evaluated by using an Instron ma-



Fig. 1. Typical pressure-time and thrust-time curves.

chine at ambient conditions  $(25^{\circ}C)$ . Cross head speed of 50 mm/min, recorder speed of 100 mm/min and gauge length 35 mm were maintained in all the experiments. Formulations were selected for cartridge loading application.

Burning rates were determined using strand burner equipment in the pressure range 3.43–10.29 MPa and in rocket motor using grains of 200 mm length, 106 mm OD, 70 mm ID and about 2 kg weight. Nitrogen was used as inert gas for pressurisation of bomb. The variation of burn rates was of the order of  $\pm 0.1$ mm/s. Propellant grains were inhibited with an epoxy resin filled with antimony trioxide and loaded in the ballistic evaluation motor (BEM) and fired to evaluate the ballistic properties. Typical P-t (pressure-time) and F-t(thrust-time) profiles are given in Fig. 1. Burning rates and  $I_{sp}$  were calculated form P-t and F-t profiles.

## 3. Results and discussion

The results of burning rates (strand burner method) with varying solids loading (80-88%) at various pressures in the pressure range 3.43-10.29 MPa are given in Table 1. As expected burning rates increased in the entire pressure range studied with increasing solids loading. Burning rates were almost doubled at various pressures, when solids loading was increased from 80 to 88%. In general, burn rate increase was of the order of 10-25% with one percent increase of oxidizer at the cost of binder cum fuel. While pressure index ( $\eta$ ) values were lower (0.32-0.35) with 80-85% solids loading, the same were marginally higher (0.40-0.44) with 86-88% solids loading. Higher ' $\eta$ ' values with more energetic composites (Calorimetric Value 1646-1565 cal/g) can be expected, in view of higher burning rates with hotter compositions. The results of burning rates of HTPB based composite propellants obtained by static evaluation in a rocket motor using inhibited propellant grains of 2.2 kg weight are

Sr. no.	Composition			Solids loading %	Cal-val value cal/g	Burning rates in mm/s at pressure (MPa)					Burning rate law over pressure range 3.43-10.29 MPa	
	AP %	Al %	Binder %			3.34	4.90	6.86	8.82	10.29	η	а
1	63	17	20	80	1272	4.4	5.0	5.6	6.2	6.5	0.35	0.28
2	66	17	17	83	1407	5.3	6.6	7.2	7.7	8.2	0.39	0.33
3	68	17	15	85	1494	6.0	6.7	7.5	8.2	8.6	0.32	0.40
4	69	17	14	86	1546	6.4	7.4	8.4	9.4	10.0	0.40	0.39
5	70	17	13	87	1615	6.8	8.0	9.2	10.2	11.0	0.44	0.39
6	71	17	12	88	1665	8.1	9.3	10.5	11.7	12.6	0.40	0.49

Results of Calorimetric values and burning rates of HTPB based composite propellants (strand burner method)

given in Table 2. It can be seen that burning rates obtained in static firing were higher by 3-5% than those obtained with a strand burner. This is expected as propellant burns in the atmosphere of its own combustion products in the former case and in the inert atmosphere (nitrogen) in the latter case.

The practical data of burn rates of HTPB based composite propellants were used to verify the applicability and validity of three combustion models namely. Vieille's law  $(r=aP_c^{\eta})$ , Summerfield model  $(p/r=a+bp^{2/3})$  and Rastogi's equation  $[(r/p)^2=(a/p)-b]$ , where r= burning rate,  $P_c=$  chamber pressure,  $\eta=$  pressure index of burning rate law, a and b are constants) for burning ratepressure relationship of composite propellants. As shown in Figs. 2-4, linear burning rate data of the present study obey all the three laws proposed to explain burning rate-pressure variation for composite propellants. This implies

Sr. No.	Composition			Solids loading	Burning rates in mm/s at pressures (MPa)					Burning rate law over pressure range 4.90–9.80 MPa		
	AP %	Al %	Binder %		4.90	5.88	6.86	7.84	8.82	9.80	η a	а
1	63	17	20 •	. 80	5.2	5.5	5.8	6.1	6.4	6.6	0.34	0.30
.2	66	17	17	83	6.4	6.8	7.3	7.6	8.0	8.4	0.39	0.34
3	68	17	15	85	6.6	7.1	7.5	7.9	8.3	8.6	0.38	0.36
4	69	17	14	86	7.8	8.3	8.8	9.2	9.6	10.0	0.36	0.44
5	70	17	13	87	7.9	8.6	9.3	10.0	10.5	11.3	0.51	0.35
6	71	17	12	88	9.3	10.2	11.0	11.7	12.5	13.0	0.48	0.43

Results of burning rates of HTPB based composite propellants (static test method)





Fig. 3. Burning rate-pressure relationship of HTPB based composite propellants (Summerfield equation). Static test method. Solids loading: -80%,  $\odot 83\%$ ,  $\triangle 85\%$ ,  $\odot 86\%$ ,  $\blacktriangle 87\%$ ,  $\blacksquare 88\%$ .

that burning rate behaviour of HTPB based composite propellants can be explained by above relationships.

A number of experimental and theoretical studies have been conducted on the combustion of AP based composite propellants [9-11]. The basic objective of these studies is to deduce information about the combustion mechanism to predict the burning rate characteristics. The decomposition gases generated from AP particles and binder yield diffusional flamelets in the gas phase. Thus, heat feed back from the gas phase to the burning surface is largely dependent not only on the chemical reaction of the gas phase but also on the diffusional process of the decomposed gases. There have been limited studies on the impact of binders on the burning rate of composite propellants and it has been reported that binders have an important effect on the burning rate [12]. Even in case of catalysed propellants, it has been established experimentally that catalysts affect the rate of decomposition on binder [13]. Recently, while studying the mechanism of burning rate catalysts in HTPB-AP based propellant combustion, Fong et al. have concluded that binder thermal degradation is rate limiting at low pressures (2-7 MPa) and at higher pressures (8-14 mPa)MPa) burning rate is increasingly controlled by gas diffusion processes [14].

In addition to burn rates data at various pressures, the information on two important parameters namely,  $I_{\rm sp}$  and characteristic velocity ( $C^*$ ) were also generated using the values obtained from pressure-time and thrust-time profiles. The results are given in Table 3.  $I_{\rm sp}$  increased from 237 s to 246 s with increasing solids loading (83% to 87%). With 88% solids loading,  $I_{\rm sp}$  could not



Fig. 4. Burning rate-pressure relationship of HTPB based composite propellants (Rastogi's equation). Static test method. Solids loading: — 80%, ⊙ 83%, △ 85%, ⊡ 86%, ▲ 87%, ■ 88%.

Sr. No.	Compo	sition		Solids loading	$I_{ m sp}$	<i>C</i> * m/s
	AP %	Al %	Binder %	%	S	
1	63	17	20	80	227	1464
					(predicted)	
2	66	17	17	83	237	1536
3	68	17	15	85	239	1548
4	69	17	14	86	244	1577
5	70	17	13	87	246	1590
6	71	17	12	88	249	1610
					(predicted)	

Results of  $I_{\rm sp}$  and  $C^*$  of HTPB based composite propellants

be calculated as thrust was not recorded. However, increase in  $C^*$  by about 20 m/s suggests that  $I_{sp}$  may be of the order of 249 s.

The results on the effect of solids loading on mechanical properties of HTPB based composite propellants are given in Table 4. There was not much change in tensile strength ( $\sigma$ ) when solids loading was increased from 80–83%. However, 87–88% solids with binder content of 12–13% gave  $\sigma$  in the range of 0.98–1.07 MPa. Interestingly,  $\sigma$  increased with increasing solids loading and a maximum  $\sigma$  of 1.12 MPa was obtained with 87% solids loading. These results suggest that by proper size selection of oxidizer, keeping the same percentage and size of Al and by maintaining strict quality control, AP can be made to act as a reinforcing agent. This is contrary to the general observation that AP acts as a poor reinforcing agent.

In view of higher mechanical properties ( $\sigma$ ) requirements, further experiments were carried out using bonding agent. MAT, an adduct of MAPO (tris-2-methyl-1-aziridinyl phosphine oxide) and dicarboxylic acids (tartaric and adipic acids), was used as bonding agent. Results of mechanical properties of HTPB based composite propellants with MAT are given in Table 5. 0.3 parts

### TABLE 4

Sr. No.	Comp	osition		Solids loading %	Mechanical properties				
	AP %	Al %	Binder %		σ Mpa	% Elongation	Young's Modulus MPa		
1	63	17	20	80	0.60	3.0	23.5		
<b>2</b>	66	17	17	83	0.66	2.5	28.6		
3	68	17	15	85	0.75	2.5	35.0		
4	69	17	14	86	1.02	3.0	37.8		
5	70	17	13	87	1.12	3.5	31.7		
6	71	17	12	88	1.03	2.5	34.1		

Effect of solids loading on the mechanical properties of HTPB based composite propellants

Effect of bonding agent on the mechanical properties of HTPB based composite propellants

Sr. No.	Comp	osition			σ MPa	Mechanical Properties		
	$^{ m AP}_{\%}$	Al %	Binder %	MAT (parts)		% Elongation	Youngs modulus MPa	
1	68	17	15	0.3	1.26	3.5	35.5	
<b>2</b>	68	17	15	0.3	1.42	5.5	27.9	
3	68	17	15	0.5	1.29	5.0	27.0	

bonding agent increased  $\sigma$  from 0.78 MPa to 1.07–1.37 MPa. Percentage elongation was increased from 2.5% to 5% level. Increase in concentration of bonding agent to 0.5 parts gave  $\sigma$  and percentage elongation more or less similar to those obtained with 0.3 parts MAT. In the case of bonding agents, improvement in  $\sigma$  is expected as a strong chemical bond is formed between binder (HTPB) and filler (AP) through the bonding agent. Compounds used as bonding agents either react chemically with the oxidizer or get absorbed physically on the oxidizer surface and react with the binder to form a chemical bond. Hori et al. [15] have suggested that in case of HTPB and AP based composite propellant, hydrogen bonding is responsible for adhesion of bonding agents to AP and the role of bonding agents consists in the concentration increase of polar groups. Thus, hydrogen bonds strenghten the bond between AP and binder.

### 4. Conclusions

1. Burn rate increase of 10-20% was obtained with increase of each percentage of oxidizer. Hotter propellants (Cal-Val 1660 cal/g) gave higher ' $\eta$ ' values than cooler compositions (Cal-Val 1400 cal/g). Delivered  $I_{\rm sp}$  of 249 s can be obtained with 88% solids loading.

2. Burning rate data obey Vieille's law, Summerfield and Rastogi's equations for burning rate-pressure relationship.

3. 0.3 parts MAT bonding agent (adduct of MAPO and dicarboxylic acids) was effective in increasing  $\sigma$  by 75%. Percentage elongation was also significantly improved.

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