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Performance of Fuel-Rich Propellants for Ramjet Applications

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ABSTRACT

A hydroxy terminated block copolymer-based fuel-rich propellant has been studied for gun and missile applications. The copolymer has shown certain advantages over hydroxy terminated polybutadiene. Zirconium was found as a promising metal fuel.

1. INTRODUCTION

In air-augmented propulsion systems, atmospheric air is used as oxidiser. The propellant is highly fuel-rich and carries very little or no oxygen. Such ramjet systems deliver high specific impulse (I_{sp}) and are used advantageously during the long, sustained missile flight as gas generator. In ducted ramjet (DRJ) system, ducts are used to feed air from outside into the secondary chamber, wherein combustion products from a primary chamber are fed for further combustion/oxidation. In certain applications, where air feed rate varies depending on the system acceleration or altitude, modulation of fuel feed rate to secondary chamber is necessary for efficient performance. In such variable flow ducted ramjet (VFDR), higher pressure index (n) for the fuel-rich propellant (FRP) is an additional design requirement. However, in all such applications, satisfactory ignition, sustained combustion, efficient expulsion, negligible residue in primary chamber are prerequisites in realising the predicted performance. In DRJ application, self sustaining pyrolysis of FRP in primary chamber needs certain amount of oxidiser.

Air-breathing propulsion is also promising in solid fuel ramjet (SFRJ) mode, wherein outside air is made to pass over combusting solid fuel in the same chamber. Thus, in SFRJ mode, incorporation of oxidiser in the fuel may not be necessary as pyrolysis of fuel is effected by the ram air. However, flame stabilisation and efficient combustion are dependent on the propulsion hardware design and the dynamics of fluid flow. SFRJ propulsion is being studied both for gun and rocket applications and several research publications are available on the combustion and energetics of various fuels and the design aspects of SFRJ motor[1,2]. However, the mechanical properties of the fuel grain become critical especially in gun applications, where the grain experiences high acceleration (20,000-800,000 g). Hydroxy terminated poly butadiene (HTPB) is an ideal fuel for both DRJ and SFRJ applications, because of its high heating value and ease of processability. However, HTPB grain is reported[3] to mechanically fail, when used in guns operating at high acceleration. Results of various studies conducted on FRP formulations containing various fuel additives and their characteristics are reported in literature[4-7]. Results of our study on hydroxy terminated block copolymer (HTBCP) and nitric ester-based formulations have been reported elsewhere[8].

In view of the distinct merits of HTBCP-based FRP systems, particularly their combustion characteristics, we have conducted systematic experiments to generate information on the mechanical properties and energetics of various formulations. This paper reports the details of a few formulations suitable for SFRJ and DRJ applications. The study also includes the effect of plasticiser, crosslinker, curing agents and fillers. Static evaluation of FRP grains was conducted in a rocket motor to evaluate ballistics in terms of performance and burn rates.

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2. EXPERIMENTAL DETAILS

HTPB having hydroxyl value 40-45 mg *KOH*, molecular weight 2700-2900, functionality 2.0-2.2 received from NOCIL, Bombay and HTBCP having hydroxyl value 18-23 mg *KOH*, molecular weight 7000-9000, functionality 2-2.2 prepared in the Laboratory following the reported[9] procedure were used in all the formulations. Explosive plasticiser (EP) of Ordnance Factory origin was used after modifying it by incorporating stabilisers and desensitisers. Nitrate ester polymer used was in the form of dense spheroidal nitrocellulose (SNC)[10]. A polyisocyanate compound (PP-20)[11] was prepared and used as a curing agent. All other ingredients procured from trade were used after drying in an oven to moisture level of less than 0.1 per cent. Propellant grains were prepared[8] by mixing the ingredients in the form of slurry in a planetary mixer of 5 litre capacity at 55 °C and then cast and cured at 60-65°C in aluminium moulds. Sample pieces conforming to ASTM D-412 specification were cut from cured propellant grains and mechanical properties were determined using INSTRON 1185. Calorific and calorimetric values (Cal-Val) were calculated using reported values for the ingredients (Table 1). Thermochemical data were calculated using NASA-SP-273 program[12]. HTPB-based FRP formulation details, suitable for SFRJ application, are given in Table 2.

Table 1. Important properties of ingredients

Ingredient	Density (g/cc)	Oxygen balance (%)	Calorimetric value (cal/g)	Calorific value (cal/g)
HTPB	0.92	-325	-3300	10400
HTPB binder	0.90	-294	-2033	8766
HTBCP	0.92	-275	-1800	8500
NC	1.60	- 24	+ 833	2164
NG	1.59	+3.5	+1785	- 200
DEP	1.12	-194	-1765	8350
DOA	0.93	-264	-2003	8766
TDI	1.21	-175	-1512	5700
PP-20	1.00	-150	-1500	5680
Carbamite	1.11	-256	-2381	7200
Carbon black	2.25	-267	-3300	7830
Pyrogallol	-	-191	-1710	8300
Mg powder	1.74	- 65	-	5910
Zr powder	6.44	- 35	-	2881
AP	1.95	+ 34	+1605	- 500
RDX	1.82	- 22	+1350	500

Note: Data available from literature have been taken and in a few cases data have been assumed based on similar compounds.

3. RESULTS & DISCUSSION

The effect of formulation changes on the mechanical properties are given in Table 3. Incorporation of fine carbon as filler increased both tensile strength (T.S.) and elongation (% E) by 10 and 50 per cent respectively. Significant increase in elongation (150 per cent) was obtained when toluene diisocyanate (TDI) was replaced with a mixed polyisocyanate PP-20 , inspite of the fact that the plasticiser content was reduced substantially (Composition-3). Curing and crosslinking agents increased both T.S. and Young's modulus (Y) to a high level (22.5 kg/cm^2 and 56 kg/cm^2) and reduced elongation values in formulation 4 & 5. With zirconium (*Zr*) powder as a filler, marginally lower % E was obtained, although T.S. remained unaffected when compared with carbon.

Table 2. Formulation details of HTPB based fuel grains for SFRJ

Compn No.	Po/Pl	*NCO/OH*	Curing agent	Filler	Cross linker
1	60/40	1.0	TDI	-	-
2	50/40	1.0	TDI	*C*/10	-
3	75/5	1.0	PP-20	*C*/20	-
4	75/5	1.2	PP-20	*C*/20	2
5	75/5	1.2	PP-20	*Zr*/20	2

Polymer (Po) : HTPB, Plasticiser (Pl): Dioctyl phthalate
Curing agent : Toluene diisocyanate (TDI)
: PP-20 - a mixed polyisocyanate compound
Cross linker : Pyrogallol
Fillers : *C*-carbon black, *Zr*-zirconium powder

Table 3. Mechanical properties of HTPB formulations

Compn. No.	Tensile strength (kg/cm^2)	Elongation (%)	Modulus (kg/cm^2)
1	3.8	57	2.5
2	4.2	87	3.5
3	4.6	235	3.7
4	22.5	59	56.0
5	22.5	44	89.0

The energetics of these HTPB formulations are gien in Tables 4 and 5. Incorporation of carbon as filler increased density (0.05 to 0.10 g/cc). Calorific value and I$_{sp}$ were found to be highest for pure hydrocarbon fuel (1150 s at 11 A/F ratio) and decreased with the inclusion of fillers. However, with zirconium as filler, the reduction was compensated and more or less same values were observed for density-impulse(d.I_{sp}).

Table 4. Energetics of HTPB formulations

Compn. No.	Density (g/cc)	Oxygen balance (%)	Calorimetric value (cal/g)	Calorific value (cal/g)	Stoichio-metric A/F ratio	I_{sp} (s)
1	0.90	-294	-2720	9528	11	1150
2	0.95	-289	-2720	9284	11	1140
3	1.00	-286	-2971	9172	11	1120
4	1.00	-277	-2870	8966	10	1090
5	1.10	-240	-2350	8187	9	950

Table 5. Results of thermochemical calculations of HTPB formulations in secondary chamber

Compn. No.	Chamber Temp (K)	C(m/s)	I_{sp} (s) (at A/F 12)	d.I_{sp} (s.g/cc)
4	2476	1295	1094	1094
5	2539	1310	955	1050

Table 6 Results of thermochemical calculations of HTBCP and HTPB formulations

Compn. No.	Po/Oxidiser	Chamber Temp (K) Primary	Chamber Temp (K) Secondary	I_{sp}(s) at(A/F)	d.I_{sp} (s.g/cc)
6	HTPB/AP(60/40)	1178	2023	839(10)	1007
7	HTBCP/EP(50/50)	1263	2055	771(9)	848
8	HTPB/AP(70/30)	1131	2210	917(12)	1009
9	HTBCP/EP(80/20)	1181	2213	855(10)	855
10	HTBCP/EP/*Zr* (60/20/20)	1621	2229	721(9)	937

EP : Energetic Plasticiser
AP : Ammonium Perchlorate

Table 6 lists the results of thermochemical calculations of a few comparable FRP based on HTPB and HTBCP fuel binders. Unfilled HTBCP formulation gave I_{sp} of 771 s as compared to 839 s for 40 per cent AP loaded HTPB composition. However, primary chamber temperature for HTBCP-based formulation was higher by 85 K, whereas the secondary chamber temperature was comparable to HTPB formulation, indicating thereby more efficient combustion for HTBCP formulations in the primary chamber. Similarly, for another set of formulations secondary chamber I_{sp} for HTBCP-based composition was less by 62 s, whereas secondary chamber temperature is again comparable to HTPB formulation.

In the case of zirconium-based compositions, the primary and secondary chamber temperature increased to 1621 and 2229 K respectively and density-impulse values were found to be higher and closer to HTPB-based formulations. Recently, zirconium is drawing more attention of researchers as a filler. In addition to boron, in view of its high density and pyrophoric nature[13,14], although its heating value is much lower than boron. During the course of the present investigation, no adverse effect on mechanical properties was observed either in HTPB or HTBCP-based zirconium containing formulations. Some of the other attractive features of zirconium are higher Cal-Val and ease of ignition. Thus, HTBCP-*Zr* based systems cured with PP-20, though produced marginally lower energetics, appears promising in gun and missile applications because of their superior combustion and physical characteristics.

Table 7. Formulation details of HTBCP grains for DRJ

Compn. No.	Po/EP/NP	PNC	*NCO/OH*	Filler	Cross linker
11	75/20/-	5	1.0	-	-
12	70/25/5	-	1.0	-	-
13	50/40/5	5	1.0	-	-
14	50/40/5	5	1.2	-	-
15	50/20/15	5	1.0	*C*-10	-
16	50/20/5	5	1.2	*Zr*-20	-
17	70/- /5	5	1.2	AP-20	-
18	70/- /5	5	1.2	AP-20	1

Polymer (Po):HTBCP, Energetic Plasticiser (EP): Nitroglycerine, Nitric ester polymer (PNC) : Spheroidal Nitrocellulose (SNC) Non-energetic Plasticiser (NP) : Diethylphthalate (DEP) Fillers:Carbon (*C*), Zirconium (*Zr*), Ammonium Perchlorate(AP) Curing Agent:PP-20 Crosslinker:Pyrogallol

Table 8. Energetics of HTBCP formulations

Compn. No.	Density (g/cc)	Oxygen Balance (%)	Calorimetric value (cal/g)	Calorific value (cal/g)	Stoichio-metric ratio	Isp at (A/F) (s)
11	1.1	-203	-1000	6334	8	855 (10)
12	1.1	-198	- 757	6276	7	-
13	1.2	-147	- 312	4743	6	730 (7)
14	1.2	-147	- 334	4760	6	730 (7)
15	1.2	-192	-1125	5576	7	-
16	.1.3	-152	- 659	4798	6	780 (7)
17	1.1	-192	-1324	6313	7	-
18	1.1	-192	-1328	6331	7	-

The formulation details of filled and unfilled HTBCP-based compositions studied for possible use in DRJ mode are given in Table 7 and the calculated results of important propellant parameters are given in Table 8. Inclusion of energetic plasticiser increased density and Cal-Val and reduced calorific value. As observed earlier, incorporation of zirconium raised calorimetric value and oxygen balance as compared to carbon filled formulations. For the same level of oxygen balance, compositions containing ammonium perchlorate (AP) or explosive plasticiser (EP) gave comparable calorific values whereas Cal-Val was found to be less negative with EP formulations. Oxygen balance and I_{sp} varied from -147 to -203 per cent and 730 to 855 s respectively depending on the fuel content in these formulations.

Table 9 Mechanical Properties of HTBCP formulations

Compn. No.	Tensile strength (kg/cm^2)	Elongation (%)	Modulus (kg/cm^2)
11	3.7	97	8
12	4.8	191	8
13	4.0	73	10
14	10.5	32	66
15	4.1	341	6
16	11.8	108	44
17	13.5	108	39
18	12.4	31	96

Table 9 is a compilation of results of mechanical properties of various HTBCP formulations. Based on our earlier findings on curing of HTBCP binder and propellant[9], a long chain polyisocyanate prepolymer (PP-20) having functional groups more than three is used in the present study. It is seen that when used in HTPB based system, significant increase in T.S. values are obtained with PP-20. Increase in curing agent content further increased T.S. with a reduction in % E in all the compositions. Generally, aliphatic isocyanates improve % E and aromatic isocyanates produce rigid three dimensional network with higher strength. In the present study, the polyisocyanate used has higher functionality than the diisocyanates and has a comparatively long chain length. This provides more reaction sites giving improved mechanical properties to the matrix. Improvement in T.S. and modulus are also obtained when additional sites for crosslinking are provided by increasing *NCO:OH* ratio by way of increasing the curing agent content in the composition. Incorporation of 1 per cent crosslinker brought down the % E to 30 per cent of the original value and increased the modulus to 96 kg/cm^2. Crosslinker like pyrogallol used in this formulation further reacts to increase crosslink density and the polymer forms a rigid three dimensional structure. In the case of long chain polycaprolactone propellants, reported[15] increase both in T.S. and % E values were attributed to the internal crystal structure of polycaprolactone molecular chain between isocyanate curing sites. Polymer binder HTBCP used in the present study contains blocks of polycaprolactone in its polymer chain and improvement in mechanical properties may be partly attributed to these blocks. Incorporation of minor amounts of SNC improved both T.S. and % E in HTBCP-based compositions, whereas increase in EP content with a corresponding reduction in polymer affected both these properties adversely. Highest elongation and lowest modulus value of 341 per cent and 6 kg/cm^2 respectively were obtained when fine carbon black was used as filler along with increased plasticiser percentage

This significant effect on the % E values with the incorporation of carbon black in HTBCP formulations has been reported earlier[8]. Fine carbon black acts as an excellent filler and improves the % E values. The effect of various plasticisers on the polymer properties are specific for any system and large increase in % E is obtained by selecting suitable plasticisers. Similar effect of plasticiser on the mechanical properties of cured binder is observed when nitroglycerine (NG) and diethyl phthalate (DEP) were used either alone or in combination, as seen from the increase in % E. However, plasticising effect of DEP appears to be better as compared to NG as seen from the large increase in the % E value when DEP is used in HTBCP system

In all these FRP formulations, HTBCP forms a backbone structure to provide the necessary mechanical properties. HTBCP has a long linear chain and forms a highly elastic polymer matrix as compared to HTPB matrix. In addition, nitrocellulose, which forms a high strength, rigid polymer is highly compatible with HTBCP because of the ester links in the caprolactone blocks of HTBCP molecular chain. Combination of

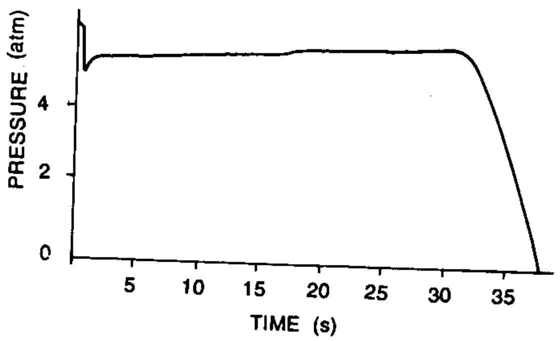

Figure 1. Pressure-time profile of test firing of composition No. 13.

HTBCP and nitrocellulose can thus be advantageously used to get flexibility in the mechanical properties of cured matrix.

Table 10. Results of static test in primary mode

Propellant parameters		
Composition No.	:	13
Density(g/cc)	:	1.2
Oxygen balance(%)	:	-147
Calorimetric value (cal/g)	:	-312
Calorific value(cal/g)	:	4743
I_{sp} at 7-8 A/F (s)	:	700-750
Grain details	:	70 mm O.D. cylindrical
Test firing data		
P_{max} (kg/cm^2)	:	104
P_{av} (kg/cm^2)	:	6
Burning time (s)	:	34
Ignition delay (s)	:	0.01
Pressure area (s.kg/cm^2)	:	209
Charactreristic velocity (m/s)	:	886
Throat dia (mm)	:	2.5
Burning rate (mm/s) at P_{av}	:	0.7
Residue (%)	:	4

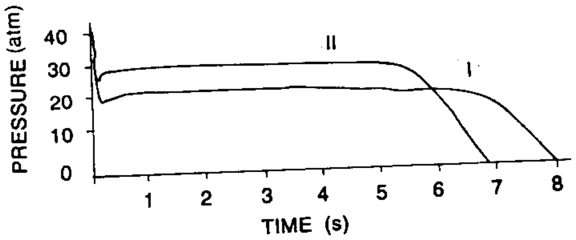

Figure 2. Pressure-time profile of test firings (I & II) of composition No. 13 (modified).

Composition No. 13 was chosen for further evaluation for its possible use in VFDR application. Table 10 and Fig. 1 show the results obtained from static evaluation of a cylindrical grain (70 mm OD) in primary mode. The burning rate of 0.7 mm/s was obtained at 4 kg/cm^2 pressure. Ignition pressure was found to be high which was reduced in later firings by adjusting the ignition mode, quantity of the igniter charge and its composition. Pressure-time profile was smooth, indicating sustained combustion. Residue inside the motor at the end of the test was found to be less than 4 per cent of the total weight of the propellant. Table 11 and Fig. 2 indicate the results of static test of a modified composition. The burn rates of 1.25 and 1.6 mm/s at 18 and 29 kg/cm^2 pressures respectively were obtained. Pressure index *n* was around 0.5 (18-29 kg/cm^2). Ignition and combustion were smooth. Residue obtained after completion of the test inside the motor was found to be around 2-3 per cent. Higher *n* value of FRP grain is a design requirement for ease of fuel feed rate modulation in VFDR application. Manipulation of pressure index is expected to be easier with pressure dependent gas phase reactions dominating the decomposition of FRP grains. From this point of view, HTBCP containing energetic plasticiser may have an advantage over the conventional AP and HTPB-based grain. Incorporation of organic oxidisers are also reported[4,16] in some of the FRP formulations. In the present study, one of the HTBCP formulation modified for higher *n* (combination of organic and inorganic oxidisers) gave encouraging results both in combustion efficiency and pressure index. Further study at different pressure ranges is necessary before recommending such compositions for specific mission use.

Table 11. Results of static test in primary mode for VFDR application

Propellant parameters			
Composition No.	:	13 (modified)	
Density(g/cm^3)	:	1.2	
Oxygen balance (%)	:	-130	
Calorimetric value (cal/g)	:	-120	
Calorific value (cal/g)	:	4250	
I_{sp} at 6-7 A/F (s)	:	650-700	
Grain details	:	110 mm O.D. tubular	
Test firing data		I	II
P_{max} (kg/cm^2)	:	43	50
P_{av} (kg/cm^2)	:	18	29
Burning time (s)	:	7.6	6.4
Ignition delay (s)	:	0.04	0.03
Pressure area (s.kg/cm^2)	:	139	187
Charactreristic velocity(m/s)	:	911	957
Throat dia (mm)	:	9.1	8.1
Burning rate (mm/s)at P_{av}	:	1.25	1.6
Residue (%)	:	3	2
Pressure index coefficient	:	0.51	0.03

4. CONCLUSION

Fuel grains and fuel-rich propellants based on HTBCP copolymer show certain advantages over HTPB grains both for SFRJ and DRJ applications. Zirconium-based HTPB fuel grains show promising results both for mechanical properties and energy parameters. HTBCP-based formulations produce higher pressure index, one of the important requirement for VFDR application.

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